Response to Reviewers

"Surprisingly Robust Photochemistry in Subarctic Particles During Winter: Evidence from Photooxidants" by Laura Heinlein 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 the reviewer's comments) due to changes in the manuscript.

Comment by Frank Leresche received on March 11th, 2025

The study investigates the photochemistry happening in atmospheric liquid water in Fairbanks, Alaska in winter. The authors evaluated the indirect photochemistry happening in the condensed phase under rain/fog conditions and under more concentrated aerosol liquid water conditions. I do appreciate the works that the authors have put in the manuscript and would support its publication. My expertise is in photochemistry and ozone chemistry in the condensed phase. I will focus my review on these topics and let other referees address the gas phase side of the manuscript.

Main comment

Aqueous-phase hydroxyl radical production. I think that the authors should mention the potential for ozone to generate hydroxyl radical in the condensed phase. Hydroxyl radicals can be generated in the condensed phase by ozone from mostly two reactions:

1) ozone reaction with superoxide:

$O_3 + O_2^{\bullet -} \rightarrow O_3^{\bullet -} + O_2$ $k=1.6E^{9}\ M^{-1}\ s^{-1}$

$O3^{\bullet -} \rightarrow O_2 + O^{\bullet -}$

Assuming that all the hydrogen peroxide formed during irradiation comes from superoxide dismutation, the authors should be able to estimate the superoxide steady-state concentration and the hydroxyl radical production rate from this reaction. This chemistry is discussed in details in Ma et al.[1] and Guo et al.[2]

Response: We thank the reviewer for the thoughtful and encouraging comments. During winter pollution episodes in Fairbanks, AK, high NOx concentrations lead to ozone titration, with gas-phase O_3 concentrations less than 1 ppb. As such, we assumed that O_3 would not play an important role in $^{\bullet}OH$ formation during pollution episodes. Furthermore, our calculations indicate that HOOH is the dominant condensed-phase $^{\bullet}OH$ source, as described by Sunday et al. (2024). . Nonetheless, below we examine the potential role of O_3 in $^{\bullet}OH$ production.

If we assume all HOOH formation is from uncatalyzed dismutation of superoxide/hydroperoxyl radical, we can rearrange the equation for HOOH production to calculate the superoxide concentration with

$$[\mathrm{HO_2/O_2^-}] = \frac{2\,P_{\mathrm{H2O2}}}{k_{HO_2+HO_2}}$$

We use the $k_{\mathrm{HO2+HO2}}$ of 8.3×10^{5} M^{-1} s^{-1} measured at pH 1 (Bielski et al., 1985) because the majority of our experimental solution work was performed at this pH and because the pK_a of HO_2 is 4.60 (Zafiriou, 1990) and therefore HO_2/O_2^- is dominantly in the HO_2 form at pH 1. The resultant range of [HO_2] is (3-20)×10^{-14} M. Next, we use the pKa of HO_2 to calculate that O_2^- concentrations will be between (0.7-6)×10^{-17} M. Using condensed-phase O_3 concentrations for ALPACA calculated in this work (Table S19) and the $k_{\mathrm{O3+O2-}}$ of 1.6×10^{9} M^{-1} s^{-1} reported by Guo et al. (2023), we estimate an upper bound for •OH production from the reaction of ozone and superoxide between (0.05-3)×10^{-12} M s^{-1}, which accounts for, at most, 0.3% of our observed •OH production. Accordingly, the ozone reaction with superoxide should be an insignificant source of hydroxyl radical in our study. We have added this information to the manuscript on lines 479-482.

2) Ozone reaction with DOC. It is known that ozone reaction with Dissolved organic matter (DOM) produces hydroxyl radical with a yield between 10-20% and that the reaction is dominated by DOM phenolic moities.[3; 4] *Using the ozone concentration of 3E*$^{-9}$ *M for the 2/4 sample and the carbon concentration of 22M for the same sample, the 2/4 sample phenolic moieties concentration can be estimated to be ≈0.54M using the relationship presented in Onnby et al.*[4] *(note that this relationship was developed for DOM and that a value for atmospheric PM would be more appropriate). Using the apparent phenol,* O_3 *second-order rate constant at pH 5 (1.4E*^{4}*) one can calculate a reaction rate constant of 2.3E*$^{-5}$ *M s*$^{-1}$ *and using a hydroxyl radical yield of 15% a hydroxyl radical production rate of 3.4E*$^{-6}$ *M s*$^{-1}$*. This is relatively higher than the hydroxyl radical production transfer rate presented on Table S6 for the same sample (1.9E*$^{-7}$ *M s*$^{-1}$*).*

It should be noted that both pathways 1 and 2 are pH dependent and faster at higher pH due to superoxide pKa and to the apparent phenol, O_3 *second-order rate constant being pH dependent.*

Response: We thank the reviewer for this important comment identifying that reactions between ozone and phenolic moieties in DOC may be a source of hydroxyl radical. First, we estimate the concentration of phenolic moieties using the average ratio of phenolic moieties to total DOC concentration reported by Önnby et al. (2018), 2.2 mmol phenol g-C^{-1}. We agree with the reviewer's comment that a measurement of the ratio of phenolic moieties in atmospheric organic carbon would be more accurate, however because such a measurement has not been made, we used the estimate from surface waters. As the reviewer notes, the reaction between ozone and phenol is pH dependent, with apparent reaction rate constants ranging from 10^{3} to 10^{8} M^{-1} s^{-1} between pH 2 and pH 9 (Önnby et al., 2018). Using the lower bound rate constant of 10^{3} M^{-1} s^{-1} for pH 2, and the average of •OH yields reported at pH 2 by Önnby et al. (2018) of 9.8%, we calculated •OH production rates between (0.01-2)×10^{-7} M s^{-1}. As the reviewer notes, the highest of these production rates is on the order of •OH from mass transport reported in Table S6. However, mass transport is a minor source of •OH in ALW, and therefore the reaction between ozone and phenolic moieties in DOC accounts for at most 1% of the total •OH production in particles. We have added this information to the manuscript on lines 479-482.

Small comments/corrections

L.65, I think that the authors should also mention long-lived phenoxyl radicals as they play an important role in surface waters for the phototransformation of phenols.[5]

Response: We agree that long-lived photooxidants such as phenoxy radicals may play an important role in particles, particularly in Fairbanks where biomass burning emits abundant phenols. We have added a comment about phenoxy radicals and other long-lived photooxidants to line 94.

L.80 "In addition, Kapur et al. (2024) reports •OH in dark samples from the ALPACA campaign using EPR, noting their environmental persistence in the dark at low concentrations." Production of Hydroxyl radical in the dark is known for DOM, see Page et al.[6] I would suggest switching persistence for production.

Response: Thank you for this suggestion. We have made the suggested correction on line 80.

L. 180 (equation 1). It is known that the non-linearized form of the equation is slightly better for fitting the data.

Response: Thank you for this comment. In response to this comment, we have analyzed the probe decay data with a linearized and non-linearized fit to determine if the nonlinearized form would provide more accurate data. Our analysis show that for our data, there is a minimal difference between the R^2 values for the linearized and non-linearized fitting: the average R^2 for linearized data is 0.99(±0.01) and for the nonlinearized data it is 0.98(±0.02). The percent difference in k'_P calculated using the linearized and nonlinearized fitting is typically less than 0.1% for our data, with only three fits with a difference between the linearized and nonlinearized data greater than 1%. In addition, we think that using the linearized fit will have a minimal impact on the downstream accuracy because the error associated with the fitting from equation 1 is minimal compared to the cumulative error on the calculated photooxidant concentrations in our laboratory experiments. The error in our triplet concentration measurements range from 45 to 72%, and these high errors are due to the errors in rate constant measurements used to calculate the steady-state oxidant concentrations at low pH, which have error between 19 and 47%. The error from our linear fitting in equation (1) is typically less than 9% (with only one experiment with an error on k'_P greater than 10%). After this analysis, we have continued to use the linear fitting to determine k'_P in this work.

L. 413 "Altogether, we attribute the wide range of Φ^{1O2*} values to minor differences in BrC sources or small changes in the degree of chemical aging". Ozone exposure is also known to increase DOM Φ^{1O2*} dramatically.[7]

Response: We thank the reviewer for this comment and have updated the sentence on line 435 to include example oxidants involved in chemical aging, like ozone.

L. 460. "the average predicted lifetime of $^3C*$ is 0.9(±0.6) nanoseconds". This number is getting close to the lifetime of the singlet excited state. Boyle et al. fitted the decrease in DOM fluorescence using a 3 component exponential, the faster exponential had lifetime below 150ps while the medium exponential was between 0.3-1.3 ns and the longer exponential 2-5.5 ns.[8] this suggest that singlet excited state may also play a role at ALW concentrations.

Response: We thank the reviewer for making an interesting point about the potential role of singlet excited states of brown carbon ($^1C*$) in aerosol liquid water. The role of singlet excited states in aerosols has not been studied. We have added a comment about the overlap of $^1C*$ and $^3C*$ lifetimes and thus the potential role of $^1C*$ on lines 503-505.

References

1. *Ma J, Nie J, Zhou H, Wang H, Lian L, Yan S, Song W. 2020. Kinetic consideration of photochemical formation and decay of superoxide radical in dissolved organic matter solutions. Environ Sci Technol. 54(6):3199-3208.*
2. *Guo Y, Yu G, von Gunten U, Wang Y. 2023. Evaluation of the role of superoxide radical as chain carrier for the formation of hydroxyl radical during ozonation. Water Research. 242.*
3. *Sonntag C, Gunten U. 2012. Chemistry of ozone in water and wastewater treatment: From basic principles to applications.*
4. *Onnby L, Salhi E, McKay G, Rosario-Ortiz FL, von Gunten U. 2018. Ozone and chlorine reactions with dissolved organic matter - assessment of oxidant-reactive moieties by optical measurements and the electron donating capacities. Water Research. (144):64-75.*
5. *Remke SC, Burgin TH, Ludvikova L, Heger D, Wenger OS, von Gunten U, Canonica S. 2022. Photochemical oxidation of phenols and anilines mediated by phenoxyl radicals in aqueous solution. Water Research. 213.*
6. *Page SE, Sander M, Arnold WA, McNeill K. 2012. Hydroxyl radical formation upon oxidation of reduced humic acids by oxygen in the dark. Environ Sci Technol. 46(3):1590-1597.*
7. *Leresche F, McKay G, Kurtz T, von Gunten U, Canonica S, Rosario-Ortiz FL. 2019. Effects of ozone on the photochemical and photophysical properties of dissolved organic matter. Environmental Science & Technology. 53(10):5622-5632.*
8. *Boyle ES, Guerriero N, Thiallet A, Del Vecchio R, Blough NV. 2009. Optical properties of humic substances and CDOM: Relation to structure. Environ Sci Technol. 43(7):2262-2268.*

Comment by Nadine Borduas-Dedekind on March 21st, 2025

Note on reviewers: Nadine Borduas-Dedekind at UBC worked with two graduate students, Keighan Gemmell and Claudia Sardena to compile this review.

Overview:

In this article, the authors quantify the concentrations of three photo-produced oxidants from $PM_{2.5}$ *filters in Fairbanks, Alaska. These filters were extracted in the lab and then illuminated with a xenon lamp to measure the production of OH radicals, triplet excited state BrC, and singlet oxygen. The measurements were then used to model their concentration as a function of aerosol liquid water content. The authors found that laboratory-irradiation of wintertime extracts can generate substantial amounts of these oxidants. They conclude, like in their title, that once modeled they are surprised at how many oxidants could be produced.*

This manuscript is nicely suitable for ACP and makes an important contribution to the field by working with field-collected samples, in the laboratory and using these measurements to predict concentrations. There is a large quantify of data presented (which at times had us confused and other times impressed, *see comments below), and the presentation could also be improved for clarity and conciseness, but overall, congratulations to the authors.*

General comments:

L220-225 & 271: We wondered how the presence of H_2SO_4 could impact the lifetime of the excited state oxidants? A major sink of excited state oxidants, specifically singlet oxygen, is the deactivation with the solvent. Is the deactivation of these oxidants the same in H_2O and $H_2SO_4(aq)$? What might be the additional role of ionic strength of the solution on singlet oxygen lifetime?

Response: We thank the reviewers for their thorough, collaborative comments. We agree with the reviewers on the need to understand the impact of sulfuric acid and ionic strength on the lifetime of $^1O_2$*.

To our knowledge, there has not been a measurement of $^1O_2$* lifetimes in sulfuric acid. In our work, the H^+ concentration in our pH 1.3 solutions is around 0.05 M. The molar concentration of water in aqueous solution is greater than 50 M. As the molarity of water is more than 100-times greater than the concentration of H^+, the only way for H^+ (or H_3O^+) to be a significant sink would be if the quenching rate constant of $^1O_2$* by H^+ (or H_3O^+ or SO_4^{2-}) was more than 10-times faster than the deactivation rate constant of $^1O_2$* by H_2O (2.8×10^5 s^{-1}).

In this work, we also expect the impact of ionic strength on the deactivation rate constant of $^1O_2$* by water to be negligible. Aggarwal et al. (2007) explores the impact of ionic strength on $^1O_2$* quenching by water in solution of NaCl with ionic strengths up to 7 M and found no impact on $^1O_2$* quenching. In our pH 1 extracts, where the pH due to H_2SO_4 was 1.3, the ionic strength due to sulfuric acid is 0.1 M. The combined ionic strength of all other ions measured in our PM extracts (reported for these samples in the SI of Sunday et al. (2025)) was on average 0.003(±0.002) M, resulting in a low overall ionic strength of 0.1 M. Based on the lack of change in $^1O_2$* quenching by water in high ionic strength solutions and the low ionic strength of our PM extracts, we expect no significant impact by ionic strength.

Dark OH radical chemistry: line 80-81, the authors cite (Kapur et al., 2025) about the dark OH source. When estimating OH radical concentrations in ambient PM, how would these concentrations be affected by the dark OH source? Was this dark source taken into account? If so how? (We didn't see these calculations in Table S18.)

Response: We thank the reviewer for the comment and agree with the reviewer's stated need to account for dark $^\bullet$OH formation. For each PM extract with each probe, we performed dark control experiments to test for dark loss of probes. We found no dark loss of any probe in any of our PM extracts and conclude that dark $^\bullet$OH generation Kapur et al. (2024) is negligible compared to photochemically generated $^\bullet$OH. We have experimental decay plots for each of the dark control experiments in Figure S2. Note that for syringol and furfuryl alcohol, the dark control experiments were performed for 4-5 hours, while the illumination experiments lasted on the order of minutes.

Liang et al. 2024 showed that triplets oxidize SO2 (not accounted for in this study's model as per line 561) and could be further mentioned in the introduction on line 92.

Response: We thank the reviewer for this comment. We have added information in our introduction on line 92 about photosensitized sulfate formation on particle surfaces reported by Liang et al. (2024).

It might be worth adding some clarity over the filter description. Lines 120-123 explains that these filters are 24h, but Table S1 suggests different times, including the footnotes. If different numbers of filters were mixed together, then their mass would be different, and we're wondering how to interpret this inconsistency. Why did they authors extract different number of filters for their extracts? Also, Table S1 footnote mentions different collection times and that the timing was corrected, but we were confused at how this value was corrected. We think this information could benefit from additional clarity in the main text and on Figure 2. How did mixing the filters together affect the interpretation of the results (how to compare such different masses)?

Response: We thank the reviewer for identifying this lack of clarity. We used filter composites because we had limited filter area and our experiments require large volumes of PM extracts with high concentrations of PM-solutes. The filters at both sites were collected for roughly 23.5 hours, which we rounded up to 24-hours in lines 120-123 (specific filter collection times are listed in Moon et al. (2024) and Edwards et al. (2024)). As each individual filter sample represents a 24-hour day, we created multi-day composites by combining several 24-hour filter samples, with the entire composite period listed in Table S1. We have added a footnote to Table S1 to clarify this point.

For each composite, we used an equal number of filter squares from each individual filter to ensure the composites equally represented every individual day within a given composite. Each square was individually extracted into 1 mL of solvent, resulting in a final solution that was the sum of 1 mL solvents from each extracted filter square. For example, the 1/31 composite includes five days with five individual filters. To prepare the 1/31 composite, we cut eight 1x1 cm filter squares from each 24-hour filter, extracted each filter square into pH 1 H_2SO_4, and after extraction, we combined all forty of the individual 1 mL extracts into one 40 mL extract, equally representing all five days in the composite. In other words, we controlled the ratio of filter area from each individual filter to the total area of filter extracted to create a composite. We therefore don't expect there to be a mass bias due to our extraction procedure. Instead, the 1/31 composite has the highest PM-mass and highest DOC concentrations because the filters in this composite were collected during the pollution event. We have added a sentence in line 132-133 of the manuscript to help clarify this point.

For one House site composite, we used a filter sample collected for 45.5 hours. The original subscript 'b' in Table S1 listed a 43.5-hour sample used from House site composite 1/21, which has been corrected to be a 45.5-hour sample collected from 1/14 12:40 to 1/16 10:16 associated with the 1/15 House site composite. We prepared the 1/15 extract in the same way as described above, resulting in a PM extract with higher solute concentrations due to longer sampling times. We corrected the 1/15 sample for the higher solute concentrations using the trends observed in our dilution experiment: $^{\bullet}OH$ concentrations are not dependent on solute concentrations, but $^3C^*$ and $^1O_2^*$ concentrations are. As such, we did not adjust the $^{\bullet}OH$ concentration, but we did adjust the $^3C^*$ and $^1O_2^*$ concentrations by the ratio of the volume of solute used for the extraction to the volume that would have been used for the extraction is the 45.5 hour filter has been two 23.5 hour filters. Specifically, because the 1/15 composite was a 4-day composite but was only extracted into the volume of solvent equivalent to 3-day composite, the extract should be 4/3x more dilute. As such, the $^3C^*$ and $^1O_2^*$ concentrations, DOC, metals, and ion concentrations were multiplied by 0.75 to reflect this. We have added a footnote on each SI table with data pertaining to the 1/15 composite impacted by this correction.

Specific comments:

Lines 302-303 & 318: "Moreover, BrC and HONO both have significant UV-A absorbance and are not impacted by the suppression of UV-B photons in winter sunlight…". BrC absorbs in the UV-B range, and can be impacted by the suppression of UV-B photons in the winter. We agree that there is significant BrC absorbance of UV-A light, so that BrC excitation can still occur in the winter, but wouldn't it be impacted by UV-B photons? This point is reiterated in line 318 which the authors might want to consider clarifying.

Response: We thank the author for this comment. Our intended meaning was that because BrC absorbs significant UV-A photons, it is less impacted by the suppression of UV-B photons in winter sunlight. We have updated lines 307 and 324-325 to clarify that BrC is not immune to the suppression of UV-B photons, but rather than BrC is impacted less than O_3.

Line 390: "The lack of correlation might be caused by the specificity of the syringol probe, which only quantifies the oxidizing subset of the 3C population, while 1O2* is produced from the total 3C* population". We agree, and there might be additional references to consider to help support this point like: (Bodesheim, Schutz and Schmidt, Chem. Phys. Lett., 1994 ; Schweitzer et al., J. Phys. Chem. A, 2003). These authors show that low E^{o*} triplet states give higher $^1O_2$ yields. Therefore, the subset of triplets that are producing the most singlet oxygen are likely not reacting with syringol.*

Response: We thank the reviewer for the additional two references which we have added to line 407.

Figure 1: an arrow connecting BrC to OH would be important as the premise of this study is to show how BrC produces OH.

Response: We thank the reviewer for this comment. In lines 391-400 and 480-483, we discuss the various sources of $^\bullet$OH. While our calculations of $^\bullet$OH production are merely estimates, we find that the sources of $^\bullet$OH are likely related to secondary pathways after BrC light absorbance, including hydrogen peroxide formation from reactions of ^{3}C* as well as photo-Fenton chemistry. As such, we think adding an arrow from BrC to $^\bullet$OH would incorrectly suggest that BrC light absorbance leads directly to $^\bullet$OH formation. As such, we have not added an arrow between BrC and $^\bullet$OH.

Figure 3: It could be worth comparing a high pollution day with a low pollution day to indicate the spread of the absorbance of the BrC?

Response: We thank the reviewer for this comment. As base-e absorption coefficients (and MAC values) are not concentration dependent, the variability in absorbance is not dependent on the amount of pollution. While 1/31 pollution episode composite has a high MAC value, the highest MAC value is from the 2/4 composite, which has an average $PM_{2.5}$ concentration of 8.6 μg m^{-3}. To prevent Figure 4 from becoming too cluttered, we have not added the base-e absorption coefficient from a clean period sample. Instead, the comparison of rates of light absorbance in a clean and polluted periods can be seen in Figure 4, and the spread of MAC values in our composites can be seen in Figure S3.

Figures 5,6,7: What do the error bars represent? This information could be included in the figure caption to help the reader understand.

Response: We thank the reviewer for this comment. The error bars represent the error associated with each photooxidant measurement, propagated from each component of the calculation. The largest sources of error are the rate constants for the syringol probe at low pH. The $^3C^*$ measurement has the largest error because it includes the error propagated from each k'_P loss experiment for each probe, the error in each rate constant reported for each probe and photooxidant pair, the error of the screening factor, and the error from actinometry experiments. We have added a note about the error bars in the captions for Figure 5, and for $^3C^*$, we have included an explanation of the high errors associated with the $^3C^*$ measurements in the caption for Figure 5 (lines 377-380).

Figure 4: CTC has less data points plotted compared to House data points. But from Table S1 it seems like this CTC data exists. We weren't sure why some data were omitted? Could the authors clarify?

Response: We thank the reviewers for identifying this source of confusion. We used the House site samples to measure photooxidants at for each composite and used the CTC site samples to perform the dilution series experiment and explore the impact of the site of sample collection and the pH on photooxidant production. We have added a comment on line 126-128 in our methods section to clarify this point.

Figure 9: we wondered how the concept of Arctic haze might be impacting the seasonality obtained in this figure. Could the authors comment and reference Arctic haze literature?

Response: We thank the reviewer for this comment. Artic haze is a phenomenon in late winter and early spring which impacts the background air quality across the Arctic, including in Fairbanks (Law and Stohl, 2006; Simpson et al., 2024). Artic haze PM is composed of sulfate, organic matter, ammonium nitrate, black carbon, and dust, and with high gas-phase concentrations of O_3 precursors such as NOx (Law and Stohl, 2006). While Arctic haze elevates the background concentrations of these species, various studies during ALPACA suggest that Fairbanks' surface-based inversions and local emissions drive the observed high NO_2 and biomass-burning organic aerosol concentrations at ground level (Figure 9). Albertin et al. (2024) used nitrogen isotope signatures during ALPACA to identify the dominant NOx sources. They find that during pollution events, emissions are largely from vehicles and heating oil combustion, demonstrating the dominance of local emission in the Fairbanks air basin. Similarly, our discussion in lines 349-356 find that the characteristics of the BrC extracted in our PM extracts was dominated by fresh BrC, indicating that most of the BrC is not a result of long-range transport. In contrast to HONO and OA, O_3 measurements in Fairbanks do not exhibit the seasonal later-winter peak concentrations characteristic of Arctic haze, but rather exhibits a springtime increase (Law and Stohl, 2006). The sources of O_3 were not explored during the ALPACA campaign, largely because pollution episodes are dominated by high NOx and low O_3. Overall, while Arctic haze impacts the background air in Fairbanks, pollution events are driven by local emissions and regional meteorology.

Figure 9: We were also excited to see the similarity of singlet oxygen seasonality compared to what we found in Bogler et al. 2022.

Response: We agree with the reviewer's enthusiasm for the agreement between both studies.

L405-407: Could the authors help explain the uncertainty for $^3C^*$*?*

Response: We thank the reviewer for this comment. We refer the reviewer to our response to the comment above on about the uncertainty in Figure 5: the large uncertainty in all $^3C^*$ measurements, including steady-state concentration, production rates, and quantum yields, is due to the large uncertainty in the rate constant for the reaction of syringol with $^3C^*$ at low pH. We have added information about the $^3C^*$ uncertainty to the caption of Figure 5 on lines 377-380.

SI: We wondered if the authors could include their FFA and syringol decays to look at the linearity of the data? Our group would also be interested in seeing the 2NB data for comparison. (It can be a multi panel figure to help with clarity.)

Response: We thank the reviewers for the suggestion of adding the raw experimental data to our SI. Figure S2 now shows all raw data of BA, FFA, SYR, and 2NB illumination experiments, which are called on in the main text on lines 167 and 187.

SI: The SI is certainly extensive. However, we didn't find the filter mass data included. We think it would be useful to Figure 2 as a comparison of the mass collected and the ambient mass measured. This filter mass could also be added directly to Figure 2.

Response: We thank the reviewer for this comment. We included the data for the mass extracted from each filter in Table S9 in the form of the PM-mass/H_2O-mass ratio of each extract. The extracted mass of the blank filters was relatively high due to breaking up of the filters during extraction, which is likely not consistent from filter to filter. For example, the 2/7 pH 1 filter is from a clean period but has a high extracted mass, which is likely due to breakage of the filter. Due to this uncertainty, we have not included the mass extracted from each filter in Figure 2. For this particular study, where we had issues with filter fragmentation during extraction, the concentration of organic carbon in our PM extracts is a more robust measure of solution concentration. These data are shown in Figure 4 in units of ug m^{-3}. As our DOC measurements were more precise than the PM-mass/H_2O mass measurements, we used DOC concentration as our independent variable for ALWC instead of PM-mass/H_2O-mass ratio for our kinetic modeling to extrapolate $^3C^*$, $^1O_2^*$, and $^\bullet OH$ production and concentrations to ALW conditions (Figure 7).

Figure S1 would benefit from having a legend on the figure to explain the colour coding.

Response: We thank the reviewer for the suggestion and have updated the figure accordingly.

Figure S4 is likely overfitted in some panels. We might recommend not adding a linear fit. For instance, some outliers are overfitted (like panel f which incorrectly has the highest r2).

Response: We thank the reviewer for this comment and agree that some panels were overfit. We have removed the linear fit from panels that have were overfit and have removed a sentence from the main text on lines 395-396 accordingly.

Figure S8: we thought this figure was quite valuable for understanding predictions. Would the authors consider adding it to the main text?

Response: We thank the reviewer for this comment and agree that it is an important piece of predicting photooxidant concentrations in ALW. We have added the figure to the main text as Figure 7.

Small comment on the writing - it might be worth adding more headings and sub-headings to better help find the information. For example section 4.2 goes on for 3 pages. It would help us in our reading if the info was more broken down to specific results.

Response: We thank the reviewer for this comment and have added subheadings to sections 3.1, 3.2, 3.3, and 4.2.

Overall, great work on putting all this data together!
***Citation**: https://doi.org/10.5194/egusphere-2025-824-RC2*

Comment by Anonymous Referee #3 on March 28th, 2025

Heinlein et al. investigated the production of aqueous photooxidants by light absorbing PM collected in Alaska during the 2022 ALPACA field campaign. The authors reported that BrC photochemistry is significant, with daytime 3C and 1O2* concentrations in PM predicted to be up to 2×10^-12 M and 3×10^-11 M, respectively, and moderate OH radical concentrations of up to 5×10^-15 M. Using a photochemical model, the authors showed that PM photochemistry cumulatively dominates, generating 76% of daytime secondary sulfate formation largely due to in-particle hydrogen peroxide, which contributes 25-54%. Lastly, the authors reported year-round 3C* production, with the highest rates occurring in late winter when Fairbanks experiences severe pollution and in summer when wildfires generate BrC.*

Overall, the results are exciting, this paper is well-written, and the subject matter fits the scope of ACP. I have a few comments that the authors should address:

Line 114: Why was benzoic acid chosen as the OH probe in this study? Why not use benzene or terephthalate as has been previously used by the authors and other studies?

Response: We thank the reviewer for this comment. Similar to terephthalate (TPA) and benzene, benzoic acid is a chemical probe which selectively reacts with $^{\bullet}$OH (Anastasio and McGregor, 2001). Benzene wouldn't work for these experiments because of its volatility: we are removing nearly the entire volume of solution from the quartz tube over the course of each illumination experiment. TPA would have worked, but its hydroxylated product undergoes direct photodegradation in simulated sunlight, which is a complication.

Line 123: How would the collection of a different PM size range affect the results? How much BrC is expected from the missing 0.7 to 2.5 um range in the CTC PM samples? Also, do the authors expect drastically different BrC composition in the PM collected from the "House" site vs. CTC site? I suppose if the BrC composition is very different, this will impact the apparent yields and steady-state concentrations of the photooxidants.

Response: We thank the reviewer for these questions.

Robinson et al. (2023) reported the average particle size during pollution events (Figure S4 in Robinson et al. (2023)). Two particle modes dominate: the first with an average particle diameter of less than 100 nm and the second with an average particle diameter of 300-400 nm. We expect that the biomass burning particles (which are the focus of this study) are the larger particle mode, most of which is captured on the House site filters with a 0.7 µm cutoff. As such, we expect that filters with 0.7 µm particles do not neglect an entire particle mode, but rather they do not capture the fraction of biomass-burning particles with the largest diameter, which only account for the tail of the gaussian distribution of the larger particle mode. We therefore don't believe our House site results are missing a BrC source.

The impact of using a 0.7 µm size cutoff is that it decreases the overall PM-mass on the filters, which decreases the concentration of PM mass extracted into our PM extracts, making the House site PM extracts more dilute than the CTC site filter extracts, and a potential slight underestimate in DOC concentrations. This has little impact on the measured quantum yields, but likely means the House site results underestimate the rate of light absorbance and DOC concentration in aerosol liquid water. This has no impact on steady-state $^3C^*$ and $^{\bullet}OH$ concentrations in ALW, which in ALW are not dependent on DOC concentration (Figure S9), but likely leads to a small overestimate in $^1O_2^*$ concentrations in ALW because we underestimate the DOC which is the dominant $^1O_2^*$ sink in ALW. We have added a sentence about this to the caption of Figure 8 on lines 473-474.

Our initial hypothesis predicted important site differences at the House and CTC sites. We predicted the House site would be dominated by residential wood burning BrC, while the CTC site would be dominant by urban BrC source. However, our MAC values (Table S9), $^3C^*$ steady-state concentrations (Figure 5 and 8), and $^3C^*$ quantum yields (Figure 6) do not show significant site differences, but highlight the rapid $^3C^*$ production from BrC at both the House and CTC sites.

Line 136: By adjusting the PM extracts to pH 1, won't the authors be solubilizing the transition metals (e.g., Fe which solubilizes at pH ~2) during their extraction process? Won't this cause an over estimation of the concentrations of water-soluble transition metals in the extracts?

Response: We thank the reviewer for this important point. Campbell et al. (2024) reports a biomodal distribution of aerosol liquid water pH: an acidic ALW with a pH between -1 and 1, and a more neutral pH between 3 and 5. We used pH 1 solution to extract our filters to extract all the transition metals which would be soluble in the acidic aerosol liquid water. Transition metals are key components of particle photochemistry, including by complexing with BrC (Ye et al., 2018), by forming HOOH (Sunday et al., 2025), by partaking in the photo-Fenton reaction (Arakaki and Faust, 1998), and beyond. In light of this, our goal was to extract all water-soluble transition metals which may contribute to photochemistry in the strongly acidic aerosols in Fairbanks.

Line 157: What are the purposes of using a water and AM1.0 air mass filter in their photochemistry experimental setup?

Response: We thank the reviewer for this question. The AM1.0 filter is an air mass filter that mimics the atmosphere's filtering of incoming solar radiation so that that output of the ARC Xenon lamp mimics tropospheric sunlight. The water filter removes infrared photons that otherwise would heat the sample but not initiate photochemistry.

Line 175: Why set the experimental temperature to 10 C?

Response: While ambient daytime temperatures during ALPACA were between -31 and -5 °C, we cannot study solutions at these temperatures in the lab. We performed experiments at 10 °C because this is the lowest temperature that we can reliably use without having problems with water vapor condensation. The impact of temperature on ${}^3C^*$ reactivity was briefly tested by Smith et al. (2014) using the ${}^3C^*$ precursor 3,4-dimethoxybenzaldehyde. Their work, which covered the range from 5 to 20 °C, found no impact of temperature on ${}^3C^*$ production or reactivity with a few phenols.

Section 2.6.2. Why do this dilution series only for pH 1? Why not for pH 5?

Response: We thank the reviewer for this question. We had a limited sample volume because we shared the extracts we prepared as described in this manuscript with two other projects. As such, we only had sufficient filter samples to perform a single dilution series experiment. As the majority of our photooxidant measurements were in pH 1 PM extracts, we chose to perform the dilution series at pH 1. Furthermore, based on our experiment comparing photooxidant production on a single sample extracted into pH 1 and pH 5, ${}^3C^*$ production does not seem to be pH dependent, further indicating that using the dilution series from a single pH is sufficient for this work.

Figure 5: I have several comments regarding this figure

- *It looks like the x axis of panel (a) may have a different scale from those of panels (b) and (c)?*

  Response: We thank the reviewer for identifying this error. The range of the x-axis is equivalent in each panel, but the tick marks are variable. We have altered the tick marks in Figure 5a for clarity.

- *It looks like the pH may have an effect on 1O2* steady-state concentrations from panel (c) judging from the data points between 1/13 and 1/27? Can the authors comment on that?*

  Response: We thank the reviewer for this comment. While the 1/21 sample the reviewer is commenting on does show site and pH differences for ${}^1O_2^*$ concentrations, the 2/22 and 2/24 samples show no site or pH differences for ${}^1O_2^*$ concentrations. As such, we find that the data does not conclusively indicate site or pH differences in ${}^1O_2^*$ generation.

- *How did pH affect 3C* steady-state concentrations?*

  Response: Figure 5b indicates very little pH difference on ${}^3C^*$ steady state concentration. As dissolved oxygen is the main ${}^3C^*$ sink in our extracts, this indicates that pH has minimal impact on the ability of BrC in our samples to generate ${}^3C^*$.

Line 372: Which "past studies"?

Response: We thank the reviewer for this comment and have added citations into the text on lines 387-388.

Line 383: Should state that the Fe referred to here is water-soluble since water-insoluble Fe cannot drive Fenton chemistry.

Response: We thank the reviewer for this comment and have added "water" to line 395.

Figure 6: There should be some discussion on how and why pH affect the quantum yields of the photooxidants.

Response: We thank the reviewer for this comment. We have added a few sentences to lines 423-428 and 430-431 regarding the impact of pH on quantum yields.

Figure 7: I suggest adding inserts of magnified views of the traces near the x axis. Currently, it is difficult to see the data trends.

Response: We thank the reviewer for this comment. We have multiplied the PME results in Figure 8 (b) and (c) by a factor of 5 to improve clarity and have noted the change in the caption.

Section 4.2: Why was only pH 1 chosen for the modeling component? From my understanding, Campbell et al. (Sci Adv 2024) showed that there are two clusters of pH during the campaign: "high" (pH 3 to 5.5) and "low" (pH -1 to 1). How will pH affect the modeling results? Also, I assume that the authors needed to assume a ALWC value for modeling study. What ALWC was used? The campaign average of 8 ug/m3 reported by Campbell et al.?

Response: We thank the reviewer for this comment. We also ran the model at pH 5, with the results shown in Figure S9. At pH 5 during the polluted period, O_3, $^3C^*$/TMI, and NO_3 become less important sources of secondary SO_4^{2-}, while gas-phase $^\bullet OH$ becomes more important. During the clean period, the pH 5 results show that O_3 becomes less important and gas-phase $^\bullet OH$ becomes more important.

For the secondary sulfate formation model, we calculated an average ALW for each composite using high-time resolution ALW values reported by Campbell et al. (2024). The ALW values used in this work are reported in Table S20.

General comment: It is not very clear to me why two sites were used for the study. There was very little discussion on the difference in BrC composition and photooxidant production in PM collected at the "House" site vs. CTC site in the paper. I suggest more discussion on this in the revised manuscript.

Response: We thank the reviewer for this comment. As the PM filter samples collected at the two sites were of different sized particles, we cannot compare DOC, rate of light absorbance, or steady-state photooxidant concentrations in our PM extracts. Instead, we must focus our comparison on MAC values and on quantum yields, which are both similar. We have added commentary on site differences to lines 341-341, 423, 427, and 430. Overall, we can't say much about differences between the House and CTC sites because we only have four samples for which we measured photooxidants at both locations, and those four measurements were performed at either pH 1 or pH 5. We agree with the reviewer that in future work, investigations should focus on the spatial heterogeneity of BrC photooxidant generation.

***Citation**: https://doi.org/10.5194/egusphere-2025-824-RC3*

Response References

Aggarwal, L. P. F., Baptista, M. S., and Borissevitch, I. E.: Effects of NaCl upon TPPS4 triplet state characteristics and singlet oxygen formation, J Photochem Photobiol A Chem, 186, 187–193, https://doi.org/10.1016/j.jphotochem.2006.08.003, 2007.

Albertin, S., Bekki, S., Savarino, J., Brett, N., Law, K. S., Cesler-Maloney, M., Flynn, J. H., Guo, F., Barret, B., Caillon, N., D'Anna, B., Dieudonné, E., Lamothe, A., Richard, S., Temime-Roussel, B., Alexander, B., Arnold, S. R., Decesari, S., Fochesatto, G. J., Mao, J., and Simpson, W.: Unraveling Urban NOx Emission Sources in Polluted Arctic Wintertime Using NO2 Nitrogen Isotopes, Journal of Geophysical Research: Atmospheres, 129, https://doi.org/10.1029/2024JD041842, 2024.

Anastasio, C. and McGregor, K. G.: Chemistry of fog waters in California's Central Valley: 1. In situ photoformation of hydroxyl radical and singlet molecular oxygen, Atmos Environ, 35, 1079–1089, https://doi.org/10.1016/S1352-2310(00)00281-8, 2001.

Anastasio, C., Faust, B. C., and Rao, C. J.: Aromatic Carbonyl Compounds as Aqueous-Phase Photochemical Sources of Hydrogen Peroxide in Acidic Sulfate Aerosols, Fogs, and Clouds. 1. Non-Phenolic Methoxybenzaldehydes and Methoxyacetophenones with Reductants (Phenols), Environ Sci Technol, 31, 218–232, https://doi.org/https://doi.org/10.1021/es960359g, 1997.

Arakaki, T. and Faust, B. C.: Sources, sinks and mechanisms of hydroxyl radical (OH) photoproduction and consumption in authentic acidic continental cloud waters from Whiteface Mountain, New York: the role of Fe(r) (r=II, III) photochemical cycle, Journal of Geophysical Research Atmospheres, 103, 3487–3504, https://doi.org/10.1029/97JD02795, 1998.

Bielski, B. H., Babelli, D. E., Arudi, R. L., and Ross, A. B.: Reactivity of HO_2/O_2^- in Aqueous Solution, J. Phys. Chem. Ref. Data., 14, 1985.

Boyle, E. S., Guerriero, N., Thiallet, A., Del Vecchio, R., and Blough, N. V.: Optical properties of humic substances and CDOM: Relation to structure, Environ Sci Technol, 43, 2262–2268, https://doi.org/10.1021/es803264g, 2009.

Campbell, J. R., Battaglia Jr, M., Dingilian, K. K., Cesler-Maloney, M., Simpson, W. R., Robinson, E. S., DeCarlo, P. F., Temime-Roussel, B., Holen, A. L., Wu, J., Pratt, K. A., Dibb, J. E., Nenes, A., Weber, R. J., and Mao, J.: Enhanced aqueous formation and neutralization of fine atmospheric particles driven by extreme cold, Sci. Adv, 4373 pp., 2024.

Edwards, K. C., Kapur, S., Fang, T., Cesler-Maloney, M., Yang, Y., Holen, A. L., Wu, J., Robinson, E. S., DeCarlo, P. F., Pratt, K. A., Weber, R. J., Simpson, W. R., and Shiraiwa, M.: Residential Wood Burning and Vehicle Emissions as Major Sources of Environmentally Persistent Free Radicals in Fairbanks, Alaska, Environ Sci Technol, https://doi.org/10.1021/acs.est.4c01206, 2024.

Guo, Y., Yu, G., von Gunten, U., and Wang, Y.: Evaluation of the role of superoxide radical as chain carrier for the formation of hydroxyl radical during ozonation, Water Res, 242, https://doi.org/10.1016/j.watres.2023.120158, 2023.

Kapur, S., Edwards, K. C., Fang, T., Schervish, M., Lakey, P. S. J., Yang, Y., Robinson, E. S., DeCarlo, P. F., Simpson, W. R., Weber, R. J., and Shiraiwa, M.: Reactive oxygen species, environmentally persistent free radicals, and oxidative potential of outdoor and indoor particulate matter in Wintertime Fairbanks, Alaska, Aerosol Science and Technology, https://doi.org/10.1080/02786826.2024.2433656, 2024.

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, 6579–6594, https://doi.org/10.5194/acp-19-6579-2019, 2019.

Law, K. S. and Stohl, A.: Arctic Air Pollution: Origins and Impacts, 2006.

Liang, Z., Zhou, L., Chang, Y., Qin, Y., and Chan, C. K.: Biomass-burning organic aerosols as a pool of atmospheric reactive triplets to drive multiphase sulfate formation, Proc Natl Acad Sci U S A, 121, https://doi.org/10.1073/pnas.2416803121, 2024.

Ma, L., Worland, R., Jiang, W., Niedek, C., Guzman, C., Bein, K. J., Zhang, Q., and Anastasio, C.: Predicting photooxidant concentrations in aerosol liquid water based on laboratory extracts of ambient particles, Atmos Chem Phys, 23, 8805–8821, https://doi.org/10.5194/acp-23-8805-2023, 2023.

Moon, A., Jongebloed, U., Dingilian, K. K., Schauer, A. J., Chan, Y.-C., Cesler-Maloney, M., Simpson, W. R., Weber, R. J., Tsiang, L., Yazbeck, F., Zhai, S., Wedum, A., Turner, A. J., Albertin, S., Bekki, S., Savarino, J., Gribanov, K., Pratt, K. A., Costa, E. J., Anastasio, C., Sunday, M. O., Heinlein, L. M. D., Mao, J., and Alexander, B.: Primary Sulfate Is the Dominant Source of Particulate Sulfate during Winter in Fairbanks, Alaska, ES&T Air, 1, 139–149, https://doi.org/10.1021/acsestair.3c00023, 2024.

Önnby, L., Salhi, E., McKay, G., Rosario-Ortiz, F. L., and von Gunten, U.: Ozone and chlorine reactions with dissolved organic matter - Assessment of oxidant-reactive moieties by optical measurements and the electron donating capacities, Water Res, 144, 64–75, https://doi.org/10.1016/j.watres.2018.06.059, 2018.

Robinson, E. S., Cesler-Maloney, M., Tan, X., Mao, J., Simpson, W., and DeCarlo, P. F.: Wintertime spatial patterns of particulate matter in Fairbanks, AK during ALPACA 2022, Environmental Science: Atmospheres, 3, 568–580, https://doi.org/10.1039/d2ea00140c, 2023.

Simpson, W. R., Mao, J., Fochesatto, G. J., Law, K. S., DeCarlo, P. F., Schmale, J., Pratt, K. A., Arnold, S. R., Stutz, J., Dibb, J. E., Creamean, J. M., Weber, R. J., Williams, B. J., Alexander, B., Hu, L., Yokelson, R. J., Shiraiwa, M., Decesari, S., Anastasio, C., D'Anna, B., Gilliam, R. C., Nenes, A., St. Clair, J. M., Trost, B., Flynn, J. H., Savarino, J., Conner, L. D., Kettle, N., Heeringa, K. M., Albertin, S., Baccarini, A., Barret, B., Battaglia, M. A., Bekki, S., Brado, T. J., Brett, N., Brus, D., Campbell, J. R., Cesler-Maloney, M., Cooperdock, S., Cysneiros de Carvalho, K., Delbarre, H., DeMott, P. J., Dennehy, C. J. S., Dieudonné, E., Dingilian, K. K., Donateo, A., Doulgeris, K. M., Edwards, K. C., Fahey, K., Fang, T., Guo, F., Heinlein, L. M. D., Holen, A. L., Huff, D., Ijaz, A., Johnson, S., Kapur, S., Ketcherside, D. T., Levin, E., Lill, E., Moon, A. R., Onishi, T., Pappaccogli, G., Perkins, R., Pohorsky, R., Raut, J.-C., Ravetta, F., Roberts, T., Robinson, E. S., Scoto, F., Selimovic, V., Sunday, M. O., Temime-Roussel, B., Tian, X., Wu, J., and Yang, Y.: Overview of the Alaskan Layered Pollution and Chemical Analysis (ALPACA) Field Experiment, ACS ES&T Air, 1, 200–222, https://doi.org/10.1021/acsestair.3c00076, 2024.

Smith, J. D., Sio, V., Yu, L., Zhang, Q., and Anastasio, C.: Secondary organic aerosol production from aqueous reactions of atmospheric phenols with an organic triplet excited state, Environ Sci Technol, 48, 1049–1057, https://doi.org/10.1021/es4045715, 2014.

Sunday, M. O., Heinlein, L. M. D., He, J., Moon, A., Kapur, S., Fang, T., Edwards, K. C., Guo, F., Dibb, J., Flynn III, J. H., Alexander, B., Shiraiwa, M., and Anastasio, C.: Hydrogen Peroxide Photoformation in

Particulate Matter and its Contribution to S(IV) Oxidation During Winter in Fairbanks, Alaska, Atmos Chem Phys, 25, 5087–5100, https://doi.org/10.5194/egusphere-2024-3272, 2025.

Ye, C., Liu, P., Ma, Z., Xue, C., Zhang, C., Zhang, Y., Liu, J., Liu, C., Sun, X., and Mu, Y.: High H_2O_2 Concentrations Observed during Haze Periods during the Winter in Beijing: Importance of H_2O_2 Oxidation in Sulfate Formation, Environ Sci Technol Lett, 5, 757–763, https://doi.org/10.1021/acs.estlett.8b00579, 2018.

Zafiriou, O. C.: Chemistry of superoxide ion-radical in seawater. I. pK*asw (HOO) and uncatalyzed dismutation kinetics studied by pulse radiolysis*, Mar Chem, 30, 31–43, 1990.