Reviewer Responses of

Formation and Loss of Light Absorbance by Phenolic Aqueous SOA by •OH and an Organic Triplet Excited State

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Reviewer comments are shown in italics.

Our responses are shown, in plain text, following each reviewer comment.

Referee #1

Main:

- *It seems that the yields of aqSOA (mass yield? Molar yield?) was used for the calculation of MAC (eq. 1). My question is, how was the mass of aqSOA obtained? By measuring total organic carbon then minus the remaining precursor phenol? Of just using the original phenols to minus the remaining phenol? If the former, it might involve some assumptions of how much oxygen atoms (on average) are incorporated into the aqSOA products. If the latter, it might underestimate the aqSOA mass, thereby affecting MAC estimation. Please clarify the potential uncertainty in this estimation.*

The mass yields of phenolic aqSOA were determined previously (Arciva et al., 2022; Ma et al., 2021), using high-resolution aerosol mass spectrometry (AMS) as described by Sun et al. (2010). To briefly summarize, the masses of phenolic aqSOA were determined using AMS to quantify the total organic mass using sulfate as an internal standard. Organic masses of aqSOA were corrected by subtracting any background organic concentration. In this method, only low-volatility compounds are detected, so the parent phenols and volatile products do not contribute to the mass yield measurement.

- *5: Are the R_abs notations in the upper and lower panels the same thing? If so, the natural log of the upper might not give the numerical values of the lower. Or is there a*

difference in the unit (min vs. s)? This is also why that putting units in the y axis titles might be helpful.

Yes, the R_{abs} in the upper and lower panels of Figure 5 are the same. The units for the top panel are 10^{-4} mol photon g^{-1} s^{-1}, but this was described only in the caption. We have moved the units so that they are now on the y-axis of the top panel so that they're more visible.

- *By saying reaction with ^3C* (as opposed to reaction with OH radicals), do the authors mean only direct reactions with ^3C*, or it includes secondary reactions with potentially formed oxidants other than ^3C*?*

We added Section S1 to examine the potential significance of the most likely secondary oxidants - $^{\bullet}OH$ and singlet molecular oxygen ($^1O_2{}^*$) - as oxidants in the $^3C^*$ solutions. Based on this new section, these two oxidants each represent less than 1% of the oxidation of our six phenols, while triplet excited states are the dominant oxidant.

Technical:

- *6/7: are the lifetimes in these two figures referring to the same thing? If so, please use consistent notation. Besides, "Lifetime of R_abs" reads a bit wired. R_abs is the rate of photon absorption, which does not have a lifetime. It is the process of light absorption that has the lifetime, right?*

Yes, those lifetimes refer to the same process, which is the lifetime of light absorbing aqSOA or brown carbon (BrC). We have clarified this in the Methods section and by changing the axis labels to 'Lifetime of BrC' for Figures 6 and 7.

- *P5/L125: is the Ox in the subscript denoting OH radicals and ^3C*? It might be confused with odd oxygen (Ox = NO_2 + O_3). What about [O] or another notation, and specifying it?*

Yes, in this case Ox referred to $^{\bullet}OH$ radicals and $^3C^*$. We have clarified this by removing 'Ox' and replacing with 'either $^{\bullet}OH$ or $^3C^*$'.

- *Some of the figures/tables in SI are actually quite important, and I suggest the authors to put a few that come with extensive discussion back to the main text. For example, Fig. S10 is quite informative.*

We appreciate the compliment. It is sometimes difficult to decide whether a given figure belongs in the main text or supplement, but we are satisfied with the current setup. We decided to keep Figure S11 (previously S10) in the supplement because Figure 7 provides essentially the same information of the two endpoints (ALW and cloud/fog drops) with the addition of the lifetime across a wide range of liquid water contents.

Referee #2

General comments:

In this work, the formation and loss of light-absorbing SOA from phenol reaction with OH and organic triplet excited states were investigated. The mass absorption coefficients, rates of sunlight absorption and lifetimes of the formed light-absorbing SOA were discussed in the manuscript. My comments are listed below that I kindly ask the authors to address.

Major:

1. *As SA can undergo direct photodegradation, the blank experiments should be performed for SA in the absence of aqueous oxidant, and this data should be provided in the left panel of Figure 1.*

Three of the phenols we studied undergo direct photodegradation: SA, FA, and SyrAcid. We previously published the direct photodegradation data so don't show it again in the current manuscript. However, we added a plot in the supplement (Figure S3) to show the expected contribution of direct photodegradation to ArOH loss; this is 27-35%, 6-15%, and 22-27% for SA, FA, and SyrAcid, respectively.

1. *Throughout the manuscript, the authors compared the optical properties of aqSOA produced from phenols reaction with OH and $^3C^*$, respectively. However, the reaction of phenols with $^3C^*$ can lead to the formation of H_2O_2 (Anastasio Cort et al. Sci. Technol. 1997, 31, 218−232), which is a source of OH in phenol + $^3C^*$ reaction. So in the phenol + $^3C^*$ reaction solution, OH also reacts with phenols forming light-absorbing SOA. Did the author exclude the contribution of OH to the formation and loss of light-absorbing SOA when refer to the 'phenol + $^3C^*$ reaction'? Please clarify this.*

This is a good point. We added Section S1 to examine the contribution of secondary $^•OH$ in the $^3C^*$ reactions. Based on our calculations, hydroxyl radical is a negligible oxidant in our triplet experiments because the amount of H_2O_2 formed is small. The reviewer's comment also made us consider the potential role of singlet molecular oxygen ($^1O_2^*$) in the triplet experiments. But our Section S1 estimates suggest that $^1O_2^*$ was a minor oxidant as well.

Minor:

- *Line 60: Atmospheric aqueous oxidants also contain reactive nitrogen species. In addition, replace 'triplet excited states of brown carbon ($^3C^*$)' with 'organic triplet excited states ($^3C^*$)'.*

We agree that nitrate radical is probably an important sink for phenols during nighttime, but our focus is on photochemically generated oxidants. We added the phrase "during the daytime" to the sentence to clarify this. We have modified the triplet state phrase as suggested.

- *Please add error bar to the left panel of Figure 1, Figure 5 and Figure 6.*

We have added error bars to the figures.

- *Line 301: Revise the sentence to 'Triplets-mediated reaction efficiently forms oligomers, while OH-mediated reaction tends to form hydroxylated products that eventually fragment.'*

We have revised the sentence.

Referee #3

This manuscript focuses on the evolution of light absorption by aqSOA formed from reactions of highly substituted phenols with $^\bullet OH$ and $^3C^*$ during continued illumination. The mass absorption coefficient (MAC), rate of sunlight absorption by aqSOA throughout the reactions, and lifetimes of absorbance were calculated. Continued illumination of $^\bullet OH$-derived phenolic aqSOA led to faster photobleaching than $^3C^*$-derived phenolic aqSOA. The discussion is logically structured, but the manuscript lacks background information on related references that this study seems to build upon. For example, the introduction mentioned the scarcity of information on how phenol-derived brown carbon is photobleached with continued reaction, but this has been studied by Jiang et al. (2023), along with experiments involving additional $^\bullet OH$ and $^3C^*$, and corresponding kinetic and chemical analyses. In addition, a more detailed literature search should be performed as more recently published studies discuss aqSOA formation by $^3C^*$ chemistry and their impact on aqSOA light absorption.

1. *How do the results here compare with those in Jiang et al. (2023)? They reported faster decay of 3C*-aqSOA compared to $^\bullet OH$-aqSOA, which they attributed to the higher light absorptivity of the former contributing to faster direct photodegradation.*

Measurements of the rate of decay of $^3C^*$-aqSOA and $^\bullet OH$-aqSOA have been reported previously by Jiang et al. (2023) but these differ from our results due to differences in $^3C^*$ and $^\bullet OH$ concentrations. Compared to their photoaging exps of GA (with no additional added oxidant), the rate of decay of $^3C^*$-aqSOA in Jiang et al. (2023) is higher than our value because their $[^3C^*]$ is higher by a factor of ~ 4. In contrast, for $^\bullet OH$ -aqSOA, our decay value is higher than that of Jiang et al. (2023) because our $[^\bullet OH]$ is higher by a factor of ~ 3. However, despite these differences in oxidant concentrations, the observed trends for aqSOA are similar. That is, initial photooxidation forms light absorbing aqSOA, but extended aging results in differences in $^\bullet OH$ and $^3C^*$ aqSOA. In addition, we also see that $^\bullet OH$ -aqSOA photobleaches rapidly while $^3C^*$-aqSOA photobleaches more slowly and remains more resistant to degradation. We have added this comparison to our discussion. We also note that light absorption by aqSOA (and its loss during continued oxidation) have not been previously reported for the other five phenols we study here.

2. *Line 23: This statement is a bit confusing as it may be interpreted as aging with additional $^\bullet OH$ and $^3C^*$.*

We have clarified this statement.

3. *How representative are the highly substituted phenols examined? This should be stated in the text, and showing their structures in one figure would be helpful.*

Highly substituted phenols have been reported in biomass burning emissions; we have clarified this by adding a sentence to line 51. We have also added a figure of all the structures in Figure S4.

4. *Why were different concentrations used for ArOH, H_2O_2, and $^3C^*$ precursor? Does this affect the major findings of this study?*

The different concentrations of reactants were chosen to give adequate decay of ArOH with reasonable reaction times. Our goal for each experiment was to react to three half-lives, i.e., the time at which approximately 12.5% of the initial phenol concentration remained in solution. Overall, the initial reactant concentrations do not affect the trends and major findings in this study.

5. *Tables S3 and S4: Previous studies have reported that the reaction of phenols with $^3C^*$ is faster than with $^{\bullet}OH$ due to higher oxidant concentration in $^3C^*$-mediated reaction (Smith et al., 2014; Yu et al., 2016; Jiang et al., 2023). Could the authors explain why this work observed the opposite, considering the higher steady-state concentration of $^3C^*$ than $^{\bullet}OH$?*

The pseudo-first-order rate constant for decay of ArOH, k'_{ArOH} (s^{-1}), is the product of the second-order rate constant for ArOH with $^{\bullet}OH$ or $^3C^*$ multiplied by the concentration of the respective oxidant. At pH 5, second-order rate constants for ArOH with $^{\bullet}OH$ are 8 to 29 times faster than the corresponding values with triplets. Additionally, $^{\bullet}OH$ concentrations in the current work are higher compared to previous work, a result of higher starting H_2O_2 concentrations. So, despite the higher steady-state concentration of $^3C^*$ compared to $^{\bullet}OH$, the pseudo-first-order decay rate constants were higher for $^{\bullet}OH$ reactions in our current work.

6. *Line 200: But doesn't the aqSOA absorbance generally decrease regardless if •OH or 3C drives the reaction*, except for TYR?*

Yes, this is correct. While there are two phenol exceptions (TYR with both oxidants and VAL with $^3C^*$), in general light absorption decreases after the first illumination time point. We have modified this sentence to reflect this.

7. *Line 259: Why would the weak absorption of parent SyrAcid lead to a greater increase in R_{abs} than for GA? For example, parent SyrAcid has a significant absorbance above 300 nm (line 178), whereas GA does not.*

The drastic increase in R_{abs} by SyrAcid-aqSOA may be explained by the contribution of longer wavelengths, especially when the R_{abs} for SyrAcid tails at ~350 nm. In comparison for GA, the case is a little different in which the R_{abs} for the starting ArOH tails at ~460 nm. Overall, this

demonstrates how the differences are drastic when we compare the weak absorption by the parent ArOH and the more light-absorbing aqSOA.

8. *Line 270: For simpler phenols, could the increase of absorbance at shorter wavelengths with reaction time be related to their slower reactions?*

The increase of absorbance at shorter wavelengths could be related to slower reactions because of the chemical nature of the phenol. For example, TYR has more available locations on the ring to undergo hydroxylation before fragmenting. In contrast, more highly substituted ArOH in this study react more rapidly due to the additional electron donating groups, which increase the reactivity with $^\bullet$OH. As a result of the additional substituents, the more substituted ArOH will likely be fragmented earlier than simple ArOH who can undergo more functionalization.

9. *Line 278: Why would continued illumination enhance the absorption for VAL-aqSOA from triplet reaction between 300 and 425 nm then induce photobleaching at longer wavelengths, whereas only photobleaching was observed for VAL-aqSOA from $^\bullet$OH reaction?*

We believe this reflects differences in the chemical nature of the aqSOA formed by the two oxidants and/or reactivity differences between the two oxidants. ^{3}C* oxidation of VAL may form chromophores that absorb in that region, while $^\bullet$OH oxidation of VAL may lead to rapid fragmentation. Another possibility may be because the aqSOA by ^{3}C* may by resistant to oxidation by ^{3}C*, while $^\bullet$OH-aqSOA is rapidly degraded by $^\bullet$OH, which is reasonable considering $^\bullet$OH is a nonselective oxidant compared to ^{3}C*.

10. *Line 335: What does this mean, and why would physical quenching be important for FA but not for the other phenols here?*

Physical quenching is when the interaction between the excited triplet state and the phenol does not result in chemical reaction. As explained by Ma et al. (2021), quenching is the dominant FA interaction with the triplet excited state of 3,4-dimethoxybenzaldehyde (^{3}DMB*), probably because energy transfer from ^{3}DMB* results in reversible isomerization of FA. FA is unique compared to the other highly substituted phenols because of its unsaturated, acrylic acid substituent, which increases the rate constant for physical quenching. The same is likely true for FA-aqSOA. We have modified the text to mention these points.

11. *Line 345: How was the overall lifetime of absorbance by phenolic BrC for both $^\bullet$OH and ^{3}C* for cloud and ALW conditions calculated?*

The overall lifetime of BrC was calculated using $\tau_{\mathrm{BrC}} = \dfrac{1}{k'_{Rabs,OH} + k'_{Rabs,3C*}}$. . We have added this equation to our methods section.

12. *Line 350: How does the identity of the precursor phenol play a role in the BrC lifetime? Why would the lifetimes of BrC from TYR and FA, which are classified differently in this work (one is less substituted phenol, and the other is more substituted phenol), be longer than those from other phenols here?*

The short answer is that we don't know why the lifetimes of light absorption by the aqSOA depend on the precursor phenol. But this observation suggests that different ArOH can produce different types of BrC that can have distinct properties and lifetimes. For example, TYR produces BrC that increases in light absorption with multiple generations, unlike the typical photobleaching by other phenols. Also, FA produces exceptionally long-lived BrC, which might be because it undergoes photoisomerization. While we only have results for six phenols, the differences in BrC lifetimes suggests that the chemical nature of the aqSOA is influenced by the precursor ArOH.

Minor:

1. *Line 60: Are these second-order rate constants for highly substituted phenols? Please specify.*

We have modified this sentence to indicate we're referring to all phenols.

2. *Line 65: Which functionalization reactions are unique to the aqueous phase?*

We have modified the sentence to add oligomerization as an aqueous process and removed the idea of "unique".

References:

Jiang et al., 2023, https://doi.org/10.1021/acsearthspacechem.3c00022.

Smith et al., 2014, https://doi.org/10.1021/es4045715.

Yu et al., 2016, https://doi.org/10.5194/acp-16-4511-2016.

Referee #4

This manuscript describes studies of brown carbon formation by 6 substituted phenol species under bulk aqueous photooxidation by OH radicals or triplet carbon species. The data shows that triplet carbon photooxidation produces more brown carbon from each precursor, and that triplet carbon photooxidation destroys brown carbon more slowly than OH radicals. The authors extend their results with useful parameters such as the estimated atmospheric lifetimes of the precursor species under photooxidation by either oxidant as a function of liquid water content (clouds to aerosol particles), and by both oxidants together, at relevant concentrations. The authors conclude that the lifetime of brown carbon are controlled by OH photooxidation in clouds, but by triplet carbon in aerosol. The in-depth analysis and useful parameters make it very likely that this work will be of interest to climate modelers in addition to atmospheric chemists. The work can be published after minor revision to address the following point:

- *Table 1 lists the total R values for the first data point of each study, but the Figures show that this first data point were collected at different times, ranging widely from 20 to 150 minutes. How the times of the first data points collected were selected is not clear. It would seem that each reaction system would go through a maximum R value at some early point in the reaction, so the R values measured for precursors where the first data point was collected later might be expected to be biased low.*

This is a good point. Our goal in each experiment was to have a total reaction time of three half-lives (3 $t_{1/2}$), which we estimated based on the expected oxidant concentration and the known second-order rate constant for the oxidant with the phenol. We then sampled each solution every calculated 0.5 $t_{1/2}$. But this time isn't necessarily the maximum in the rate of light absorption by each oxidant-phenol combination, so our rates of sunlight absorption at 0.5 $t_{1/2}$ are probably lower than the maximum rates. We have modified the text in the discussion of Figure 2 to mention this issue.

Response References

Arciva, S., Niedek, C., Mavis, C., Yoon, M., Sanchez, M. E., Zhang, Q. and Anastasio, C.: Aqueous ·OH oxidation of highly substituted phenols as a source of secondary organic aerosol., Environ. Sci. Technol., 56(14), 9959–9967, https://doi.org/10.1021/acs.est.2c02225, 2022.

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Ma, L., Guzman, C., Niedek, C., Tran, T., Zhang, Q. and Anastasio, C.: Kinetics and mass yields of aqueous secondary organic aerosol from highly substituted phenols reacting with a triplet excited state, Environ. Sci. Technol., 55(9), 5772–5781, https://doi.org/10.1021/acs.est.1c00575, 2021.

Sun, Y. L., Zhang, Q., Anastasio, C. and Sun, J.: Insights into secondary organic aerosol formed via aqueous-phase reactions of phenolic compounds based on high resolution mass spectrometry, Atmospheric Chemistry and Physics, 10(10), 4809–4822, https://doi.org/10.5194/acp-10-4809-2010, 2010.