Answers to Reviews Regarding Manuscript "Measuring molecular singlet oxygen ($^1O_2^*$) from atmospheric photosensitizers: Intercomparison of techniques, irradiation setups, data analysis and protocol recommendations"

Reply Legend:
Black: reviewer comment
Blue: author response
Blue + italics: text modified

Reviewer 1:

Gemmell et al. compared singlet oxygen ($^1O_2^*$) measurements from four photosensitizers across four photoreactor setups at three institutions. Using their results, they determined the factors influencing the rates of light absorbance, $^1O_2^*$ steady-state concentrations, and quantum yields. Consequently, they made five recommendations to improve the accuracy and reproducibility of $^1O_2^*$ measurements, which include considering wavelength-dependent quantum yields, avoiding suppression of $^1O_2^*$, controlling and reporting photoreactor temperature, considering light scattering from nanoparticles, and conducting control experiments. These recommendations will help standardize $^1O_2^*$ measurements across different laboratories in studying photochemical processing of atmospheric aerosols and droplets. In general, this is a thorough and valuable intercomparison study. The authors have conducted rigorous control experiments and thoughtfully addressed potential artifacts. This manuscript makes a valuable contribution to standardizing $^1O_2^*$ measurements. The recommendations are practical and well-supported by the intercomparison data. However, there are some points that need clarification before acceptance for publication:

We thank the reviewer for this support and feedback.

Major Comments

- Scattering artifacts: The supplement's Section S8 and Figures S15-S17 address a previously underappreciated artifact. The sensitivity analysis showing up to 48.8% error in Rabs for lignin is compelling. However, I notice that the lignin absorbance before and after 0.22 μm filtration (Figure S15) shows negligible difference, yet the Mie scattering modeling (Figure S16) suggests significant scattering contributions. This apparent contradiction needs explanation in the main text. I suggest that the authors clarify that scattering can occur from particles smaller than the filter pore size, and that the absence of filtration effect does not rule out scattering artifacts. This nuance is important for readers who might incorrectly conclude that filtration alone solves the problem.

We thank the reviewer for highlighting this point. What the reviewer has stated is exactly the point we intended to convey, so we've clarified the text which now reads:

"Light scattering should be considered a source of uncertainty in UV–Vis absorbance measurements, even in filtered samples, as particles smaller than filter pore size (0.22 µm here) can still contribute to scattering and filtration alone will not necessarily eliminate this effect. Dissolved organic matter can form colloidal structures or aggregates smaller than the filter pore size, which remain in solution and can scatter light. The formation and optical properties of these colloids depend on the composition and source of the organic matter, and thus filtration does not guarantee removal of all scattering effects (Sec. S8, Fig. S15, S16) (Bieber et al., 2024)."

- UCD photon flux calibration (Section S11): This section reveals a significant methodological challenge that deserves more attention in the main text: The observation that "the ratio of the peak in photon flux at 548 nm to the peak at 347 nm varies from 2.0 to 5.2" across 60 measurements, and that they had to use perinaphthenone to constrain the long-wavelength flux. I suggest adding a brief discussion in Section 3.2.2 or 3.2.3 about the importance of validating spectrophotometer measurements with chemical actinometry or reference sensitizers, especially when internal reflections or positioning variability may affect spectral shape. This is a practical recommendation that would be useful for home- built photoreactors.

  Good point. We modified Section 3.2.2 to explicitly discuss this issue and indicate how we optimized the photon flux by combining measurements from the spectrophotometer, 2NB actinometry, and the perinaphthenone quantum yield for singlet oxygen. The entire section has been edited for clarity and flow, and to address the reviewers comment the following text was added:

  "Calculating absolute irradiance required combining the spectrophotometer measurements of relative photon fluxes as a function of wavelength with chemical actinometry. UCD found significant variability in the relative photon fluxes for measurements made on the same day but with different optical probe positions in the sample chamber (see SI Section S11). We believe that this variability was due to internal reflections within the UCD illumination chamber. To determine the most correct relative photon fluxes, we used experiments to determine the singlet oxygen quantum yield from perinaphthenone to constrain the 548 nm/347 nm intensity ratio, which we used as a marker of the photon fluxes at long and short wavelengths (SI Section S11 and Fig. S21). The combination of actinometry (to get the short-wavelength region) and a reference photosensitizer (to characterize the long-wavelength region) allowed us to constrain the UCD photon flux by identifying the influence of internal reflections on the spectral shape. By testing if experiments with two actinometers yielded equivalent photon fluxes, and by

ensuring that experiments with reference photosensitizers yielded published values, this tested the photon flux across a wide range of wavelengths. This highlights the utility of actinometry and model photosensitizers as robust tools to constrain the photon flux in an experimental illumination system."

- Temperature dependence: Figure S19 is particularly striking: the 30°C vs. 22°C experiments show dramatically different $[^1O_2^*]_{ss}$ even after applying temperature-corrected rate constants. This suggests that temperature affects not just the probe kinetics, but also potentially the sensitizer photophysics and/or $^1O_2^*$ production efficiency. The recommendation to control temperature within 20 to 25°C seems sound, but the manuscript should acknowledge that the underlying causes of this temperature sensitivity are still not fully understood and warrant further investigation. Also, the recommendation to control "within a minimum range of 20 to 25°C" is vague. What is the acceptable variability within an experiment? Across experiments? I suggest the authors consider providing quantitative guidance (e.g., ±1 °C, ±2 °C).

  Great points. The range of 20 to 25°C comes from the UBC photoreactor's design, which uses liquid N2 cooling through a copper coil, and makes it harder to control the temperature precisely. The temperature in the UBC photoreactor is also susceptible to environmental temperature in the laboratory. On the other hand, the cooling systems at UCD and Ircelyon use water cooling and are able to control within ±2 °C. However since temperature influences steady state concentrations of $^1O_2^*$ beyond what is captured in temperature corrected rate constants, we can only recommend temperature control that is practically viable for each experimental set up. To make this point more clear, the text has been updated to say:

  "We recommend that photoreactor setups be temperature controlled to avoid deviation from the temperature-dependent rate constant of furfuryl alcohol with \SO.\citep{appiani_aqueous_2017}. Our use of a range of 20–25 °C is based on practically achievable temperature control across cooling systems. For example, UBC's liquid N$_2$ through the copper coil system is less precise than UCD and Ircelyon's water cooling system. In addition, there are temperature effects beyond furfuryl alcohol's rate constant, likely involving impacts on the photophysics of the excitation. (Fig. \ref{fig:SI_kd}, \ref{fig:SI_T_Dependence})."

- Line 580: "[FFA]0 < 145 μM": I understand that this threshold comes from Ossola et al., but is it universally applicable? I think the appropriate concentration may depend on the photosensitizer's $^1O_2^*$ production rate and the light source intensity? I suggest the authors consider adding guidance on how to verify that probe scavenging is negligible for a given system.

We thank the reviewer for highlighting this point. Indeed, this concentration of FFA is not universally applicable and depends on the sinks of $^1O_2$* in the system. The main text has been updated to read:

*"2. **Chemical probe concentration:** We recommend using concentrations of furfuryl alcohol such that the reaction of $^1O_2$* with the probe accounts for less than 1% of the total $^1O_2$* loss, ensuring that the probe does not perturb steady-state $^1O_2$* concentrations. This condition can be evaluated by calculating the fraction of $^1O_2$* lost to FFA relative to other sinks (Sec. S12), which corresponds to [FFA]0 < 27 μM (at 25 °C)."*

The following text was added to the SI to clarify: "*When using the chemical probe FFA to quantify $^1O_2$* concentrations, it is essential to determine if the probe perturbs the steady-state $^1O_2$* concentration. This can be done by calculating the fraction of $^1O_2$* lost to FFA in a given experiment. The main $^1O_2$* sinks in dilute photosensitizing solutions include $^1O_2$* quenching by water ($k'_{1O2*,H2O}$ = 2.76(0.02)×10^5 M^{-1} s^{-1}, Appiani et al. 2017), $^1O_2$* quenching by dissolved organic carbon (DOC, $k_{1O2*+DOC}$ = 1×10^5 M^{-1} s^{-1}, Ma et al., 2023), and $^1O_2$* reactions with FFA. The fraction of $^1O_2$* lost to FFA ($f_{1O2*,FFA}$) can be calculated with*

$$f_{1O2*,FFA} = \frac{k_{1O2*+FFA}[FFA]}{k_{1O2*+FFA}[FFA] + k'_{1O2*,H2O} + k_{1O2*+DOC}[DOC]}$$

where $k_{1O2*+FFA}$ is the rate constant for the reaction of $^1O_2$ with FFA, [FFA] is the initial FFA concentration, and [DOC] is the concentration of dissolved organic carbon. In this work, DOC concentrations were small and therefore DOC is a negligible sink, though this is not always the case in concentrated particulate matter extracts. The system is considered unperturbed by the addition of FFA when the fraction of $^1O_2$* lost to FFA is less than 1% of the overall $^1O_2$* loss, which corresponds to an FFA concentration of less than 27 μM (at 25 °C). Ossola et al. (2021) have a similar, though less strict threshold of ensuring FFA incurs less than a 5% decrease in the steady-state $^1O_2$* concentration, corresponding to an FFA concentration of 145 μM (at 25 °C). If the probe concentration is greater than this threshold, then quenching will need to be accounted for (De Laurentiis et al., 2013; Frimmel et al., 1987)."*

- Line 225: The statement that "the triplet state of perinaphthenone does not react with furfuryl alcohol" is supported by Schmidt et al., but is this universally true across all conditions (pH, concentration ranges)? I suggest the authors consider adding a brief note about the conditions under which these holds.

  The triplet state one-electron reduction potential of perinaphthenone is 1.03 V SHE, making it a weakly oxidizing triplet. Additionally, the triplet energy of perinaphthenone

is 1.70 eV, which is also relatively low for oxidizing triplets (Mcneill & Canonica, *Environ. Sci.: Processes Impacts, 2016*). Finally, perinaphthenone has no acid base functionality so its triplet reactivity is not expected to exhibit a pH dependence. The text has been updated:

"Additionally, the triplet state of perinaphthenone does not react with furfuryl alcohol under typical experimental conditions (concentrations in the μM range) meaning that furfuryl alcohol loss reflects only reaction with singlet oxygen. This greatly simplifies steady-state and quantum yield calculations by enabling relative rate comparisons between singlet oxygen production and furfuryl alcohol consumption (Schmidt et al., 1994; Ossola et al., 2021). Finally, perinaphthenone possesses no acid-base functionality; therefore, its triplet reactivity is not expected to exhibit a pH dependence, further supporting its use as a robust reference photosensitizer."

- Relative vs. Absolute quantum yield methods: This paper presents both methods but it could more clearly guide readers on when to use each approach. The statement that values were "consistently 15% within each other" (line 458) is helpful, but what is the threshold for "acceptable" agreement? Providing more specific guidance will be useful.

  Since this is the first study to compare the relative and absolute quantum yields of singlet oxygen the only guideline we can provide is the agreement we observed for each individual photoreactor set up, which is 15%. Text was added to make this point more clear:
  "*... were consistently within 15% of each other for all sensitizers, and we thereby suggest 15% as a reasonable metric for acceptable agreement between quantification methods (Tables S1 - S4).*"

Specific Technical Comments

- Units' consistency: Table S1 reports R_{abs} for perinaphthenone in units of $\times 10^{-6}$ mol_{photon} L^{-1} s^{-1}, which is consistent with the main text Figure 4a. However, equation 1 in the main text gives units of $mol_{photons}$ cm^{-2} s^{-1}. This discrepancy should be resolved. There should be consistency between the equations, text, and figures.

  We thank the reviewer for noting this discrepancy. To resolve this discrepancy, equation 1 has been changed to give units of mol_{photon} L^{-1} s^{-1}. Now the text reads:

$$“R_{abs} = \sum_{\lambda} (I_{\lambda,0} \cdot \alpha_{\lambda} \cdot \Delta\lambda \cdot 2.303 \cdot 10^{3})$$

where α_{λ} is light absorption coefficient of the sample (cm^{-1}}, baseline corrected), $I_{\lambda,0}$ is the spectral irradiance of the light source ($mol_{photons}\, cm^{-2}\, s^{-1} nm^{-1}$), $\Delta\lambda$ is the interval between adjacent wavelengths, and the values 2.303 and 10^{3} are conversions for base and units, respectively.”

- Blank controls (Section S1, Figure S1): All three labs show negligible FFA decay in blank controls, which is reassuring. However, the Ircelyon blank appears to show a slight downward trend. Is this within experimental uncertainty? Also, to avoid any confusion, I suggest renaming “Lyon Blank” in the figure’s legend to “Ircelyon Blank”.

  The reviewer is correct that the Ircelyon blank data show a slight downward trend (k_{obs} = 2.48 x 10^{-6} s^{-1}). However, this trend falls within experimental uncertainty. The slope of the blank measurement is a factor of 2 smaller than the smallest decay slope observed for a photosensitizer (Ircelyon lignin, k_{obs} = 5.08 x 10^{-6} s^{-1}), indicating that the trend is negligible relative to the measured photochemical signals.

  The figure legend has also been updated to read “Ircelyon Blank” to avoid any confusion.

Minor Comments

- Figure 5 caption: "Normalized to peak (i.e., peak value = 1)": The authors should consider adding "for each photoreactor setup individually" to clarify that normalization is per setup, not global.

  Thank you for flagging this unclear wording. The figure caption has been updated to read: *“Normalized to peak for each photoreactor setup individually (i.e., peak value = 1)”*

- Atmospheric implications section: This section is somewhat general. The authors should consider adding a more concrete example of how the recommendations would improve model parameterization.

  This section points explicitly to Zhang et al.’s modeling study of SOA processing by oxidants including $^1O_2$* and we highlight here how a key uncertainty in this modeling is the concentration of $^1O_2$* . We also point to Manfrin et al.’s lifetime calculations of key

functional groups. We state that, "this work enables more robust inter-study comparisons and facilitates integration of $^1O_2$* chemistry into multiphase chemical models." and our goal is here is to help constant the *concentration* of $^1O_2$* to expect from the photochemistry of BrC. Nevertheless, to help clarify the focus on concentration, we've added the following sentence:

"Ultimately, we need to better constrain the concentrations of $^1O_2$ and $^3C^*$ generated from different types of BrC to better predict aerosol photochemical aging."*

- Building a new photoreactor Section: This is interesting but feels disconnected from the rest of the main text. The authors should consider integrating it into the recommendations or moving to SI.

  We thank the reviewer for this valuable comment. We think it is a fair point, and have removed this section and incorporated it into the recommendations section. We've also added a reference to Niedek's et al.'s recent photochemical setup:

  "Short pathlength photoreactors have also recently been developed (Niedek et al., 2026), which reduce light attenuation in strongly absorbing solutions by minimizing optical pathlength while maintaining temperature control. "

- Recommendation 5 (Control experiments): The authors should consider stating that results from deoxygenated experiments should be interpreted cautiously since removing O_2 changes the system fundamentally (e.g., $^3C^*$ lifetime increases, other pathways may emerge). The absence of FFA decay in N_2-purged samples confirms no $^3C^*$ + FFA reaction, but I don't think it proves that $^3C^* + O_2 \rightarrow {}^1O_2^*$ is the only pathway in oxygenated conditions.

  We agree that results from deoxygenated experiments should be interpreted with caution, as the removal of O_2 alters the photochemical system, including increasing ^3C* lifetimes and potentially enabling alternative reaction pathways. We also agree that the absence of FFA decay under N_2 does not demonstrate that the $^3C^* + O_2 \rightarrow {}^1O_2^*$ pathway is the only mechanism contributing to FFA loss under oxygenated conditions. Rather, these control experiments primarily indicate that direct reaction between ^3C* and FFA is negligible in our system. To clarify this point, we have revised the manuscript to acknowledge that, while $^1O_2$* is expected to be the dominant oxidant under oxygenated conditions, additional pathways such as reactions involving ^3C*, •OH (even we added a quencher), or other reactive oxygen species, cannot be fully excluded.

These changes have been incorporated in the revised manuscript as: *"Although it is not possible to completely isolate the reaction of $^1O_2$* with furfuryl alcohol, incorporating these control experiments ensures that measured probe decay can be primarily attributed to the intended reactive species. However, results from deoxygenated experiments must be interpreted with caution, as the removal of oxygen may fundamentally alter the system, for example by increasing ^3C* lifetimes and allowing other reaction pathways to emerge. Nevertheless, these controls enhance the reliability and intercomparability of $^1O_2$* quantification."*

- Section S8.2: The sentence "Using a particle concentration of 1.18×10^{13} m^{-3} and a mean particle diameter of 142 nm (values scaled from Bieber et al. (2024))". The term "scaled" implies modification. Please clarify whether these are directly from Bieber et al. or adjusted for this study. If adjusted, the authors should explain the scaling rationale.

  The term "scaled" was used to indicate that the particle concentration used for the scattering analysis was adjusted to account for dilution and to match the concentration of lignin used for our study (20 mg/L). The mean particle diameter is directly from Bieber et al. The text has been updated to read:

  "Using a particle concentration of 1.18×10^{13} m^{-3} (accounting for dilution to 20 mg/L of Lignin) and a mean particle diameter of 142 nm (Bieber et al., 2024) …"

- Section S11, line 86: "... perinaphthenone 1O2* quantum yield" There is a typo here (missing superscripts and subscripts). Should be "$^1O_2{}^*$".

  We thank the reviewer for flagging this typo. The superscripts and subscripts have been updated to the correct formatting.

Reviewer 2:

This work investigates key aspects of photochemical experiments such as repeatability and reliability of measurements across multiple light sources and actinometry methods for one of the most critical photochemical oxidants, singlet oxygen. Quantum yields for singlet oxygen were measured using both chemical probe experiments and phosphorescence measurements. Results suggest that reaction conditions and the selection of the light source can have strong impacts on observed, and hence predicted, levels in atmospheric scenarios such as wildfire aerosol emissions. This work is thorough and makes clear the importance of inter-lab comparisons across multiple approaches. The considerations for singlet oxygen assessment are valuable.

We thank the reviewer for their praise of our work.

However, the presentation quality is frequently problematic, particularly if this work is to be generally helpful to researchers with a wide range of backgrounds. At times poor wording and detailed lines of logic that omit key points may give rise to misapplication of the important points this manuscript seeks to demonstrate. I recommend this manuscript for publication, but not without such numerous corrections, listed below, as to amount to major revisions, whether in effort or importance. This work seems to be focused on getting the details right, which is absolutely commendable, yet the quality of presentation can work against this.

We thank the reviewer for their fair comments and have worked diligently to improve the presentation of the information throughout the manuscript, including all the comments listed below.

General Comments

Some of the applicability to a wider range of systems seems limited, in terms of the recommendations.

How can the suggestion “less than 1% of photosensitizers” be applied to more complex systems when the sample itself includes photosensitizer species? The production rate of singlet oxygen would also seem to be an important metric. Perhaps the authors can also suggest ways to diagnose whether quenching of singlet oxygen is a problem in more complex samples. Much more could be said in the final recommendations as to the utility of relative yield measurements in complex systems.

The suggestion of less than 1% of photosensitizers was not an accurate description of what we were trying to convey. Rather, our intent was to limit the probe concentration to account for less 1% of the total $^1O_2^*$ loss. The main text has been updated to read: *“2.* ***Chemical probe concentration:*** *We recommend using concentrations of furfuryl alcohol such that the reaction of*

$^1O_2$ with the probe accounts for less than 1% of the total $^1O_2$* loss, ensuring that the probe does not perturb steady-state $^1O_2$* concentrations. This condition can be evaluated by calculating the fraction of $^1O_2$* lost to FFA relative to other sinks (Sec. S12), which corresponds to [FFA]0 < 27 µM (at 25 °C).”*

The following text has also been added to section 3.3.6 to address the point of determining if quenching of singlet oxygen is a problem in more complex samples:

“Phosphorescence measurements can also be used to diagnose whether quenching of $^1O_2$ is significant in complex samples (Madhiyan and Moor, 2026). Although not conducted here due to the use of single molecule sensitizers, $^1O_2$* can be generated using a known sensitizer at a wavelength outside the absorbance range of the sample matrix and the phosphorescence signal at 1270 nm compared in the presence and absence of the sample. A reduction in the signal when the sample is present indicates additional quenching of $^1O_2$* and this approach is complementary to chemical probe methods. For example, in systems that do not absorb above 500 nm, Rose Bengal can be excited at 550 nm to generate $^1O_2$* and evaluate quenching by the sample matrix.”*

Can more be said about the universality of furfuryl alcohol as a chemical probe and what other chemical probes would be useful in some applications? Are there limitations, perhaps chemical compatibility to consider?

We thank the reviewer for this valuable comment. Text has been added to Section 3.3.1 to address the universality of furfuryl alcohol as a probe and potential alternatives:

“Furfuryl alcohol is widely used as a chemical probe for $^1O_2^*$ due to its well characterized and selective reactivity (Haag et al., 1984; Appiani et al., 2017). Recent work has expanded the family of furan-based probes. For example, Arciva et al. (2025) reported singlet oxygen reaction kinetics for 17 furan derivatives, highlighting that alternative probes may be selected for specific experimental constraints. For example, less volatile probes such as 2-methylfuran-3,4-dicarboxylic acid may be advantageous in open systems where volatility is a concern, although this was not an issue for the capped solutions used here. To the best of our knowledge, chemical compatibility has not been systematically explored as a limitation of FFA as a probe for $^1O_2^*$.”

Sunlight itself is not a single, constant light source, as it varies with solar zenith angle. Using a solar simulator to reproduce sunlight is certainly a good approach, but it is still a single light source that does not apply to all solar conditions.

The following text has been added to address this point:

"We note that solar irradiance is not constant in either intensity or spectral distribution, as it varies with solar zenith angle and season. Although irradiation sources that span wavelength ranges similar to natural sunlight can help reduce wavelength dependent quantum yield artifacts, it remains difficult to perfectly reproduce solar radiation under laboratory conditions."

More Specific Comments

Equation 1

While numerically the values may work out, this equation is very, very poorly expressed. The reference (Kaur 2019b) does this much more clearly, and the authors would do best to follow that example exactly.

Absorbance does not have units. It seems this should be absorption coefficient.

The summation over the wavelengths approximates the integration over wavelength, meaning that the 1/nm units are canceled via multiplication by dλ . Add a Δλ in units of wavelength.

The goal of this paper is very clear validation, and these seemingly small shortcuts may quickly lead to poor application of the principles this manuscript is working to support.

The reviewer is correct, absorbance does not have units and was an oversight on our part to not change this to absorption coefficient. The equation has been changed to be absorption coefficient, and Δλ was added. Thank you.

Equation 3

This equation is also problematic.

The final equivalence should be kobs*t, not just kobs.

The slope of the log plot is the observed rate constant.

This is correct, and we thank the reviewer for catching this typo. The equation has been corrected accordingly.

Equation 5

Absorbance does not have units, again, this should have absorption coefficient, not abs. The reviewer is correct. The equation has been changed to be absorption coefficient, not abs.

The screening factor should be more clearly defined, in particular its general purpose, which would include the reduction of light available to the photosensitizer. It would seem in the spirit of this manuscript to assume the audience is not strictly photochemists, but rather atmospheric chemists more broadly (or others) who need to consider the wider impacts of UV irradiation on their experiments.

We thank the reviewer for suggesting this important change. Text has been added to more clearly define the screening factor and why it is important: *"Internal light screening due to light absorption is the reduction of light intensity within a sample as photons are absorbed before they can reach the entire irradiated volume. The light screening of the sample depends on the light absorbance of the sample, the path length of the light through the sample, and the irradiance from the light source."*

Equation 8

All terms, especially the rate constants, must be clearly defined

We thank the reviewer for pointing out that not all terms in this equation were clearly defined. The text has been updated now to read:

"where Φ_{ISC} is the fraction of excited singlet photosensitizer molecules that undergo intersystem crossing to the excited triplet state, k^T_d is the deactivation of triplets, k_{O2} is the second-order rate constant for the physical quenching of $^3C^*$ with O_2, $k_{O2}[O_2] / k^T_d + k_{O2}[O_2]$ is the fraction of $^3C^*$ that is quenched by O_2, and $f\Delta$ is the fraction of the quenching that leads to the formation of $^1O_2^*$."

Table 2

The table should include a header row indicating "light absorbance equivalent hours," this information should not be solely in the caption.

We thank the reviewer for this suggestion to improve clarity. Table 2 has been updated with a header row.

Table 3 and Section 3.3.6

The apparent low sensitivity of the phosphorescence method is noted, were higher concentrations of photosensitizer and/or oxygen saturation attempted?

Yes, 5 concentrations of the photosensitizer were conducted. The concentrations tested ranged in absorbance from 0.1 – 0.5. Oxygen saturation was not attempted in an effort to keep results as comparable to chemical probe experiments as possible. Text has been added to read:

"To address this, we tested five photosensitizer concentrations (absorbance 0.1–0.5), yet signals remained undetected. Oxygen saturation was intentionally avoided to maintain comparability with the ambient-air conditions of the chemical probe experiments."

The authors should also further address, or at least specifically state for the reader, that 4-nitroanisole was measured to have a much higher yield than juglone using chemical probe measurements, yet phosphorescence measurements of 4-nitroanisole were apparently below detection limits while juglone produced singlet oxygen above phosphorescence detection limits.

We thank the reviewer for highlighting this point. It was an unexpected finding that requires more explanation. The discrepancy in quantum yield measurements from the two techniques is observed for all three nitroanisole compounds. To iterate this point, text has been added to read:

"Notably, for 4-nitroanisole, while a quantum yield of 8.83% was measured using the chemical probe method, no corresponding signal was detected via direct phosphorescence. The relative position of the methoxy and nitro groups are impacting the reactivity of these nitroanisoles, and warrants further experiments to understand why and how".

Line 28 "potent but oxidant". Please complete the sentence.

The word "but" was a typo, and has been removed from the sentence. Text now reads: *"generating singlet oxygen ($^1O_2^*$), a potent oxidant"*

55

Lack of reproducibility is vague here. Please revise to make this clearer.

Agreed. The text has been revised for clarity: *"The challenge of extrapolating laboratory measurements of $^1O_2^*$ to the atmospheric context is exacerbated by the current lack of reproducibility in environmental samples such as the Suwannee River fulvic acid samples (Partanen et al., 2020), making it difficult to distinguish between variability in $^1O_2^*$ measurements and true inconsistencies in reproducibility."*

95

UBC Setup : "…20 mg/L of lignin were used to make up" It would be clearer if you state something more like "20 mg/L of lignin were the concentrations". The same applies to the other setups.

Thank you for this suggestion to improve clarity. The text has been updated to read (note different concentrations for the different set ups, but generally reads the same):

"Experimental solutions contained 20 µM furfuryl alcohol, 1 mM of isopropanol and 10 µM of either perinaphthenone, Rose Bengal, or 30 µM juglone, or 40 mg/L of lignin."

185

What quencher?

Text has been updated to read: *"due to the use of isopropanol as a quencher"*

221

The use of parentheses to indicate the symbol for the relative quantum yield is confusing here.

Please instead use a set of commas to indicate this use of an appositive.

Commas have been used instead of parentheses. The text now reads: *"In contrast, the relative quantum yield of* $^1O^*_2$ *,* $\Phi^r_{1O2^*}$*, …"*

364

The potential for screening of 2-NBA at the excitation wavelength due to the overlapping absorption of the product during actinometry should be mentioned. Also, it should be made clear that both actinometers should be utilized at low optical depth.

We thank the reviewer for highlighting these points. Text has been added starting on line 357: *"Additionally, both chemical actinometers should be used at low optical depth, and potential light screening by all chromophores, including reaction products, should be considered."*

426

It should be made clearer that "optimized" screening factors indicates reduction sample absorbance. Furthermore, the Ircelyon screening factor is 0.68, far from a value of 1, while this is a value that is reasonable to correct for, this deviation from 1 should be noted here.

We thank the reviewer for flagging this unclear statement. For the Ircelyon photoreactor, the irradiation pathlength through the sample is 3.5 cm leading to screening factors that deviate from 1. Text has been updated to address both points: *"In our case, the screening factors were optimized to be close to 1, by reducing sample absorbance, to specifically avoid screening (Tables S1-S4). However, in the Ircelyon photoreactor, the 3.5 cm irradiation pathlength through the sample produced screening factors that deviated from 1"*

448

It seems this is the "deactivation lifetime". Please clarify.

The reviewer is correct, "deactivation lifetime" is the better term compared to just "lifetime" and has been changed in the text. Thank you.

470-480

Normalizing production yield to the rate of absorption is simply the definition of quantum yield. What is the purpose of this sentence? Is there something else implied here? The second paragraph simply states that the observed quantum yield with lignin and juglone was not consistent with the other photosensitizers. Indeed, the most likely source is some sort of wavelength dependence. These paragraphs could be condensed and edited to greatly increase clarity.

The reviewer is correct in that the purpose of the sentence and section was to highlight the fact that for photosensitizers perinaphthenone and Rose Bengal, we did not observe a wavelength dependent singlet oxygen quantum yield. For lignin and juglone we did observe wavelength dependent singlet oxygen quantum yields. The text has been condensed and edited to improve clarity of the point we are trying to convey:

"Rates of light absorbance and $^1O^*_2$ steady-state concentrations differed by several orders of magnitude across the different laboratories (Fig. 3). These differences reflect variation in photon flux among the light sources, with higher intensity sources producing higher absorbance rates and correspondingly higher $^1O^*_2$ concentrations (Fig. 4 a,b). Despite these order of magnitude differences in Rabs and $[^1O^*_2]_{SS}$, the apparent quantum yield, Φ_{1O*2} , for Rose Bengal and for perinaphthenone were consistent and reproducible across photoreactors and aligned with literature values (Schmidt et al., 1994; Wilkinson et al., 1993) (Fig. 4c), indicating that these sensitizers singlet oxygen generation efficiency exhibit minimal dependence on the irradiation conditions explored here.

In contrast, lignin and juglone exhibited deviations in quantum yields across photoreactors. Specifically, xenon lamp systems (UCD and Ircelyon) yielded lower Φ_{1O*2} values, whereas the

UV bulb system (UBC) produced higher values. For juglone, this discrepancy was particularly pronounced, as the highest photon flux (UCD; Fig. 4a) corresponded to the lowest measured quantum yield (Fig. 4c, left). These results suggest that, unlike Rose Bengal and perinaphthenone, the apparent quantum yields of lignin and juglone are influenced by the spectral distribution of the light source, consistent with a wavelength dependent mechanism."

480 and elsewhere

It is more descriptive to describe wavelengths as "short" and "long", rather than low and high. Low and high are better adjectives for frequency.

Thank you for pointing this out. All descriptions of wavelength have been updated to be short and long rather than low and high.

493

Combinations of several narrowband excitations allow for the adjustments between changing light source wavelength profiles, while at the same time requiring many more experimental trials. As noted above a solar simulator set to one solar flux profile does not cover all atmospheric conditions either.

Thank you for highlighting the use of several narrowband excitations as a way to assess wavelength dependent quantum yields. The text has been updated to read:

"Due to wavelength dependencies, results obtained using narrow or single wavelength irradiation can be difficult to reliably extrapolate to the broader solar spectrum. Accordingly, using sunlight-mimicking irradiation sources, or combinations of several narrow band excitations are best recommended."

Section 3.3.7

The first paragraph is poorly worded to the point of confusion. The tedious explanation of how to determine the oxygen concentration in solution is not necessary, stating that the dissolved oxygen concentration was determined the atmospheric partial pressure and the Henry's law constant is sufficient, and adjustments to altitude can be noted.

The second paragraph tells us that the discrepancy between chemical and phosphorescence detection discussed in section 3.3.6 is now due to reaction with furfuryl alcohol. I understand the

presentation of results in 3.3.6 and discussion in 3.3.7. Perhaps somehow these sections can be combined in a succinct way to make a clearer presentation.

We agree with the reviewer, and have now rewritten these two sections. Section 3.3.6 is intended to discuss the comparison between the probe method and direct phosphorescence for the measurement of 1O2*, whereas Section 3.3.7 is intended to discuss only the role of dissolved oxygen. It's true that Section 3.3.7 also uses the phosphorescence measurements to make this point, and so although we don't think merging is effective in conveying our 2 messages, we have edited both sections heavily. In particular, we moved the numerical details of section 3.3.7 to the SI as recommended by the reviewer. We also moved most of 3.3.7 discussing the discrepancies between the methods to 3.3.6. We think the text reads more clearly now.

523

Why wasn't an equation noted? Instead "this calculation" is simply stated without clearly indicating what calculation was done. This is insufficient.

We thank the reviewer for flagging this unclear point. The text now reads:

"The calculation of $[O_2]$ in solution led to calculated $^3C^*$ deactivation pathways yields, $k_{O2}[O_2]$, that were 2.8 times larger than k_d^T in Vancouver, and 2.5 times larger in Calgary. "

524-525

If an equation was noted or referenced, it be immediately clear to any reader that lower oxygen concentration leads to a lower quantum yield for any photosensitizer. This statement suggests that something special is occurring here, when this is exactly as expected. Do the authors suggest that there is a unique reason why lower oxygen concentration leads to lower quantum yields?

We thank the reviewer for this clarification. We do not suggest a unique mechanism, and the decrease in quantum yield at lower oxygen concentrations follows directly from the relationship described in Eq. 9. The text has been revised to explicitly reference Eq. 9 to make this connection clearer to the reader.

535

This sentence does not really define photochemical "action spectra". Typically, an action spectrum would refer to a chemical response as a function of wavelength, such as an OH

photolysis yield. The rate of absorption doesn't need a new definition or seem to quite fit the term "action spectrum."

We thank the reviewer for pointing out this oversight on our part. The reviewer is correct, "action spectrum" inherently contains information of photochemical reactivity while our definition does not. All mentions of "action spectra" have been updated to read *"action spectra of light absorbance"*.

600

It should be noted that the solar spectrum is not constant in either intensity or wavelength dependence across solar zenith angles.

The following text has been added to address this point: *"The ideal photoreactor would have 1) an irradiance spectrum that spans a broad range of wavelengths, attempting to reproduce the solar spectrum, such as a xenon lamp"*