We thank both reviewers for their valuable comments. Our point-by-point responses are provided below. Reviewer comments are in black, our responses are in blue, and the revised text is quoted in blue italics.

Reviewer(s)' Comments to Author:
Reviewer: 1

General comments

The authors present comparative results of a new photoreactor designed to enable an understudied regime of aqueous phase aerosol chemistry. Overall the manuscript is both clear and thorough, and the results indicate a promising revision to previous approaches using similar setups. Given the number of labs interested in this kind of work, increasing access to such a technique will be impactful.

A few of the figures could use improvements for clarity and there are small technical corrections.

Specific comments

Section 2.4 Chemical Analyses - the authors have used an aerosol mass spectrometer to analyze the cloud water (and ALW) mimics, by aerosolizing the liquid samples so they can be sampled by the AMS. Likely, the reason for this is because the only HRMS available *is* an AMS and not because it is a particularly good method of sample prep. Or, possibly, it is to enable a direct comparison to ambient samples collected behind a CVI. Given that using an AMS to analyze an aqueous solution is not the obvious choice, it would be helpful to indicate just briefly why the authors selected this method (e.g. "to leverage our HRMS, which is an aerosol mass spectrometer, samples were…). This way, those unfamiliar will not assume this method is beneficial or confers certain advantages.

We thank the reviewer for this suggestion as additional context behind the choices made in our methodology would be helpful to future readers. The following text has been added to section 2.4:

"The use of an AMS allows for direct measurements of the condensed-phase components of the phenolic SOA and for more direct comparisons to the broader literature of both real-time and offline measurements of SOA."

The color scale of Figure S5 need not go below 0.5 based on the correlation coefficients, it seems, because the current use of the full range compresses the color-based comparison of coefficients to the point of ineffectiveness.

The choice of setting the range from 0-1 was made to show the typical range of R values in general. However, we agree this choice compresses the actual range of range of data, obscuring the distinctions between PMF factors discussed in the main text. We have modified Figure S5 so that the color scale ranges from 0.5 to 1.

Figure 5 would be clearer if there was a shaded block behind the first 3 bars to indicate they are replicants and should be directly compared, perhaps with an extra space before experiment 2.

An additional dashed line has been added to segregate the first 3 bars. This is visually consistent with the dashed lines that segregated other groups of experiments. Also, the objective of the dashed lines has been clarified in the figure caption.

The results of the PMF analysis showing the disappearance of the 1st generation product, the appearance and then disappearance of the second generation product, and the slow appearance of the third generation product/s was really impressive.

We appreciate the kind words. The GA and DMB photoreaction system has proven to be a robust platform for investigating aqueous-phase phenolic photochemistry.

Lines 338-340 seem to be the same sentence, twice, but rephrased.

The following line has been removed to fix this repetition:

"The effects of salts on excited-state production are often system-specific, depending on the nature of the organic and ionic species involved."

Technical corrections

The Supplemental Information contains an abstract that is actually the journal's instructions to authors, not an abstract.

This was a template error. The abstract in the Supplemental Information has been removed entirely.

Figure S4 Caption reads "error! Reference source not found"

Also Figure S7 and Figure S8

Thank you for pointing this error out. It has been rectified.

Reviewer: 2

Comments:

The key technical innovation of this work lies in the development of a short-pathlength photoreactor that overcomes optical screening and thermal artifacts, enabling controlled aqueous-phase photochemistry under strongly light-absorbing, high-ionic-strength ALW conditions that were previously inaccessible. The experimental concept and reactor design are well motivated and technically sound. The discussion part could be strengthened to better emphasize the broader relevance of the new reactor beyond the GA/DMB system and to more clearly extract its general advantages from the experimental results. In addition, the comparison with previously used reactors (e.g., RPR-200 and the small tower reactor) would benefit from a brief introduction of their key features and limitations, as well as a clearer explanation of the specific optimizations implemented in the short-pathlength photoreactor. Details comments as below:

We thank the reviewer for this insightful comment and agree that the discussion can more clearly highlight the broader applicability and advantages of the new short-pathlength photoreactor beyond the GA/DMB system.

In response, we have added several additional points of discussion throughout the *Results and Discussion* section and details missing from section 2.2 to highlight that the reactor design and performance demonstrated here are not specific to GA/DMB chemistry but are broadly relevant to a range of aqueous-phase and multiphase photochemical systems (see below for the additional discussion text that has been added). The revised discussions also underscore how the reactor's short optical pathlength, high photon flux, and modifiable ambient conditions make it particularly suitable for studying photochemical aging of diverse organic and inorganic precursors under atmospherically relevant conditions.

We further expanded the comparison with previously used reactors (e.g., RPR-200 and small tower designs) to briefly summarize their key limitations (e.g., longer optical pathlengths, lower or less uniform photon flux, larger solution volumes) and to clarify the specific motivations for developing the short-pathlength reactor.

Section 2.2:

"Samples are illuminated horizontally rather than from above using 2 cm cuvettes. The RPR-200 photoreactor employs three sets of fluorescent lamps centered at 300, 350, and 419 nm to crudely simulate solar radiation, generating triplet excited state carbon ($^3C^*$)

levels ~7 times higher than typical wintertime ambient conditions (George et al., 2015; Jiang et al., 2021). The reaction vessels are 110 mL with 5 cm diameters."

Section 3.1:

"While more traditional photoreactors ca be made airtight, modifying ambient conditions inside the reaction chamber can be challenging. Additionally, given the large liquid volumes typically required with standard cuvettes, the ambient conditions, solution composition, and ionic strengths reached here with the SPP represent a significant step forward in laboratory-based explorations of atmospherically relevant condensed-phase chemistry."

"This represents an advantage over more traditional photoreactors where the pathlength is set by cuvette dimensions and may be difficult to modify."

"This represents an advantage over more traditional photoreactors where the pathlength is set by cuvette dimensions and may be difficult to modify, making light screening a significant impediment in solutions with moderate-to-high absorbance"

"While the remaining sections focus on a model system of GA and DMB photochemistry, the ability to easily swap light sources opens up a broad spectrum of photochemical systems."

Linear 39, any range information for that "higher ionic strength."

The following edit to this line has been made:

"...resulting in higher ionic strength (up to ~20 M)..."

Line 59, Please add a short line, reminding the difficulty in controlling ionic strength, to connect context.

The following edit has been made:

"However, accurately reproducing the optical and chemical environment of ALW in the laboratory, particularly the high ionic strength conditions, remains a significant experimental challenge."

Line 174, please add a short description of the methods for internal standard, SOA yield calculation and PMF solution selection, instead of using citation here only.

The following lines have been added for clarification on the use of an internal standard, SOA yield calculation, and PMF selection:

"Briefly, a known quantity of $^{34}SO_4$ was added to each aliquot prior to HR-AMS analysis. The $^{34}SO_4$ signal, measured concurrently with the organic aerosol signal in the AMS, serves as

an internal reference to quantify the liquid-phase concentration of organics in the aliquot. The SOA yield was then determined from the increase in the AMS-measured organic signal relative to the corresponding decrease in GA concentration measured by HPLC."

"Selecting fewer factors led to high residuals while selecting more factors led to factor splitting. The four-factor solution minimized the sum of the weighted squared residuals."

Line 179, it is not clear whether the authors intend to state that the whole PMF results, including factor number and spectrum, are internally consistent with Jiang 2021 et al, or only that one factor primarily represents the unreacted GA fit. Clarification is needed.

We appreciate the reviewer's comment and agree that our original statement was not clear. Our intent was to covey that the overall PMF results – including both the number of factors and their corresponding mass spectral profiles – are broadly consistent with Jiang et al., 2021. We chose to focus on results from Experiment 7 because this experiment showed the most extensive GA decay and the most pronounced evolution of SOA as identified by the PMF analysis. In contrast, other experiments showed less GA decay, limiting the observation of later generations of SOA. Nevertheless, to the extent that they were observed, the factor structures and their temporal behavior were consistent across all experiments performed in this study and aligned well with Jiang et al., 2021. This point has been clarified in section 2.5.3 (see new text below) and is further discussed in section 3.2.2.

"While the same PMF methodology was applied to all experiments, Section 3.2.2 focuses on results from Experiment 7. This experiment exhibited the most extensive GA decay and, consequently, the most pronounced SOA evolution, allowing clear resolution of all three generations of GA-derived aqSOA described in Jiang et al., 2021. In other experiments with less GA decay, only the first and second generations were partially resolved."

Line 206-214, The description of RH control is potentially misleading. The manuscript implies that liquid water mass is controlled "via salt deliquescence," which suggests that salt behavior plays an active role in RH regulation. In reality, salt deliquescence appears to be used as a passive validation of equilibrium water uptake under externally controlled RH. This distinction should be clarified.

We agree the presentation of RH control is not clear. The following edits have been made:

"The SPP also allows for regulation of the liquid water mass in the reaction system via RH control and salt deliquescence."

Line 215, In Figure 3, the agreement between measurements and predictions varies among different salts. For LiCl in particular, the measurements do not show a clear trend with

increasing predicted values. Here need to add some discussion to clarify before the statement of agreement.

We agree that the agreement between measured and predicted water uptake is variable and the LiCl data points on their own do not follow a clear trend. Our goal with this set of experiments was only to see if water uptake of salts inside the SPP would recapture expected behavior in general. Overall, the agreement is moderate and adequate for our purposes. The following line has been added to Section 3.1 to re-emphasize this point:

"The measured water uptake values exhibit moderate agreement with those predicted by the osmotic coefficient-based model (Figure 3). While LiCl displays the largest deviation, the correspondence between predicted and observed values across all salts is generally good under the experimental conditions examined."

Line 225, maybe use log scale for x-axis for better display of all data

We appreciate the suggestion for Figure 4. However, given the relatively narrow range of values on the left y-axis (~0.01-0.03), applying a log scale would likely reduce interpretability, even though the data would be less vertically compressed.

Line 240, does this thermal control refer to the temperature curve in Figure 2? In this four-day test, the temperature does not stop increasing at the right end of x-axis. Do author has longer data set to show the stability of the SPP system in temperature control? So far the data set is not convincing enough. Also in this chapter, the major discussion is around topic of RH/ liquid water mass and optical control. Please modify this conclusion.

The line you refer to does refer to the thermal control shown in Figure 2. While it is true that the temperature is increasing at the right end of the x-axis, the overall up-and-down swings of the temperature trace were attributed to changes in room temperature affecting our measurement of the changes in internal, SPP temperature. This is mentioned in lines 189-190 and now has been further clarified with the following edit:

"In practice, the chamber temperature stabilized slightly above the setpoint (22 – 24 °C), likely due to the continuous influx of warm, humid N_2 and minor fluctuations in ambient laboratory temperature that tracked the day-night cycle."

Additionally, our model system of guaiacyl acetone and dimethoxybenzaldehyde is a radical-driven reaction and is not known to be particularly temperature sensitive, and given the range of observed temperature fluctuations (~±2 °C), we believe the temperature control presented in Figure 2 is adequate for all data presented after.

Line 266, Figure 5(b), the sulfate difference was marked twice, by the color of Exp ID and the size. The author needs to rethink the way to separate the experiment marker. Using

color to differentiate Exp ID is less helpful; better use color, transparency, and size of marker to indicate the key parameters, GA, GA/DMB, and SO4. Same for Figure 7.

We appreciate the concern that our scheme for differentiating experiments is not helpful. Based on your suggestion of using color, transparency, and size of marker to described the different parameters, we believe we are currently using a scheme that would be adequate (color, size, and shape of marker) but have failed to describe the point of changing marker color, size, and shape. Rather than change the existing scheme, we have added the following text to the caption of Figure 5 to explain the purpose of the maker shapes and size:

"In (b), maker colors distinguish experimental conditions: circles represent the base experiments where GA and DMB concentrations varied while maintaining a fixed GA/DMB ratio of 20; squares represent experiments where the GA/DMB ratio was modified (by changing either $[GA]_0$ or $[DMB]_0$); triangles represent experiments where $[SO_4]$ was altered while keeping GA/DMB = 20. The size of each triangle scales with $[SO_4]$, allowing visual differentiation of these experiments."

Line 275, for PMF analysis, the final source factor selection criteria are very important, especially here different analysis methods are applied.

We agree the selection criteria are critical for a meaningful PMF analysis. We have added in the standard PMF diagnostic plots for Experiment 7 as a new Figure S5 which is referenced in Section 3.2.2.

Line 282, is there cross comparison of factor mass spectra between this study and previous studies?

A quantitative cross comparison was not performed, instead we opted for a qualitative discussion referencing prior studies. The goal of the PMF analysis was not to reproduce prior results, but to demonstrate that similar results can be achieved with the SPP which uses a different light source and encompassed a different range of experimental conditions compared to previous studies. The reader is instead referred to Figure 2 in Jiang et al. (2021) which shows a nearly identical figure derived from data from a similar experiment.

Line 289-294, The paragraph is somewhat contradictory. The authors aim to highlight the SPP's improvements in simulating real aqueous chemistry instead of surface reactions in previous studies, yet use the similarity to previous results as evidence of its effectiveness. Need to be clarified.

We thank the reviewer for this insightful comment and agree that our intent was not clearly conveyed in this section. Our reference to Jiang et al., 2021 serves as both a

methodological and interpretative benchmark rather than as evidence of novelty. Jiang et al. (2021) is the only published study using the same model photochemical system we with PMF analysis of the HR-AMS spectra of aqSOA, making it a critical reference point for validating our approach under dilute conditions (Exp. 1).

Experiment 1, which replicates the dilute conditions of Jiang et al. (2021), provides a necessary baseline to demonstrate that the SPP can reproduce established results under comparable conditions. The other 12 photochemical experiments and salt-water uptake experiments extend this framework to more concentrated conditions (approaching that can be found in atmospheric ALW). These experiments reveal new kinetics and mechanistic behaviors of phenolic aqSOA formation that have been previously under-explored.

While the overall chemical composition of the aqSOA remains similar across conditions – indicating that aqueous-phase oxidation pathways of phenolic compounds are robust, the kinetics are significantly affected by solution composition. This distinction underscores the SPP's value: it enables controlled exploration of concentration-dependent aqueous-phase processes while maintaining chemical comparability to prior studies.

To clarify this point in the manuscript, the following line has been added to Section 3.2.2:

"While the kinetics of GA decay and aqSOA production are affected by organic concentration and ionic strength, the bulk chemical composition of the aqSOA is relatively insensitive to these conditions suggesting that under more ALW-like conditions, the chemical characteristics of phenolic aqSOA may be fairly constant."

Line 363-370, the description of experiments 11-13 changes between ionic strength and salt effect, which is misleading and needs to be unified.

The distinction between "salt effect" and "ionic strength" in our manuscript is intentional. The references citied in this section discuss a variety of systems involving different salts, cations, and anions, and often report their results in terms of molar concentrations of salts rather than ionic strength. In contrast, in this study, we focused on a single salt and presented our data in terms of ionic strength to more directly reflect the physicochemical property influencing aqueous-phase chemistry. So while "ionic strength" is the most appropriate descriptor for our results, the more general term "salt effect" was used when discussing prior studies that did not explicitly quantify ionic strength. We have revised the text to clarify this distinction and ensure consistent terminology throughout the manuscript.

"While previous studies have reported mixed findings regarding salt effects (a general term meant to encompass ionic strength as well as other salt-related effects described in

previous work), most observed only minor effects at molar sulfate concentrations (Loisel et al., 2021; Ma et al., 2021; Zhou et al., 2019).”