

## Response to Referee 1

The authors' responses were not completely satisfactory. In several cases they simply repeated lines from the text instead of addressing the reviewers' concerns, or a response was given but no change was made to the manuscript to clarify the issue which was raised. As such, there were several missed opportunities to make the manuscript stronger in this round of revisions.

Even in cases where the authors think a comment was made based on a reviewer's misunderstanding of the text or the intent of the study, rather than just dismissing the comment, realize that there may be an issue with the clarity of the manuscript which the authors don't perceive, but the reviewers do, as outsiders to the project. Use these instances as opportunities to clarify the text to eliminate reader misunderstandings in the final version.

I will point out a few specific issues here but this is not the full extent of the missed opportunities for improving the manuscript. I suggest the authors read through the response and consider carefully where they could be more thorough.

- As previously stated by the reviewer, "neutral" or "non-acidic" is not an environmentally realistic property of atmospheric aerosols, and not always for cloud droplets. The authors need to include a statement in the manuscript to this effect rather than ignoring this comment.

*We added the following sentence (line 211): "The pH of pure  $K_2SO_4$  aqueous particles or cloud droplets that form on them is close to 7, which is not representative of typical atmospheric aerosols, but simplifies interpretation of experiments for systems with significant pH dependence."*

- "OFR254 mode" is jargon that has no meaning outside the OFR community. If you wish to use this terminology it's important to also include a general definition.

*We revised that sentence. It is now: "When used as an OFR, the APPA reactor is operated with lamps producing only 254 nm UV (and not also 185 nm; often referred to as OFR254), with OH produced from photolysis of  $O_3$  that is produced externally by an  $O_3$  generator (Jelight Co., Inc., Model 610) and introduced into the reactor."*

- Both reviewers suggested moving several figures to the SI, with explicit suggestions for figure removal made by both reviewers. The authors disregarded most of these recommendations from both reviewers, keeping a total of 14 figures, which is still too many.

*We also moved Figure 10 to the Supplement, leaving 13 in the main manuscript now.*

## Response to Referee 2

My responses to the author's replies are in red text below. – Referee #2

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While the APPA OFR appears to be capable of generating sulfuric acid from the aqueous-phase  $SO_2/O_3$  reaction, its ability to initiate aqueous-phase OH oxidation chemistry was not conclusively demonstrated here. The authors did investigate SOA generated from gas-phase OH oxidation of benzene, followed by partitioning of OVOC/SOA into ALW/droplets. While this is a novel application that the APPA OFR seems to be well suited to, this is not a demonstration of aqSOA formation according to even the authors' own definition: "water-soluble products of gas-phase chemistry [that] enter cloud droplets or aerosol liquid water and react in the aqueous phase with the hydroxyl radical (OH) or other oxidants" (L83-L86). In that

regard, I think they should have used  $K_2SO_4$  seed particles containing  $H_2O_2$  and/or  $H_2O_2/FeSO_4$  to initiate aqSOA formation (e.g. Nguyen et al., 2013; Daumit et al., 2016), then repeated the same experiments without  $H_2O_2/FeSO_4$ , and inferred the difference in aerosol loading and composition as aqSOA. It is not clear to me why this was not done here – this is what I would need to see to be convinced that the APPA OFR can be used to investigate aqSOA formation.

**RESPONSE WITH FIRST REVISION:** *We certainly recognize that it is challenging to isolate the contribution of aqueous phase chemistry in a system in which it is occurring simultaneously with gas phase oxidation. But that is exactly the type of chemical system the APPA was developed to study. It is true that water soluble products of gas phase oxidation will preferentially partition into the aqueous aerosol and droplets, but without further oxidation those species will evaporate with the water as the aerosol/droplets exit the reactor, pass through two Nafion driers, and travel through a few meters of stainless tubing prior to measurement in the SMPS or AMS. Though the precursor studied was different (isoprene), Lamkaddam et al. (2021) reported that the aqSOA formed in their wetted-wall flow reactor could not be explained as simply the result of dissolution of products of gas phase oxidation: "...the dissolution of isoprene oxidized vapors cannot explain the aqSOA production and provides strong evidence that aqSOA results from OH reactions of the dissolved species in the aqueous phase." Adding  $H_2O_2$  and/or  $H_2O_2/FeSO_4$  would be challenging for this system. As is described, the seed particles/droplets are always produced through size classification of an atomized and dried aerosol.  $H_2O_2$  from the atomizer solution would be lost to evaporation unless the aerosol were not dried below the ERH of  $K_2SO_4$  of approximately 65%. Uncertainty in the calculated change in mass concentration of the aerosol following processing in the reactor would be substantially higher if a correction for the water content of the aerosol when initially classified is required. The alternative would be injection of gas-phase  $H_2O_2$  into the reactor, but then estimating how much gets into the droplets and how much is lost to the walls would be difficult. Furthermore, even with  $H_2O_2/FeSO_4$  in the aerosol/droplets, it is likely that the source of OH near their surface where more reactive species would be oxidized would still be that from the gas phase (which is needed to generate the oxidation products) and so interpretation of the with/without  $H_2O_2/FeSO_4$  would be difficult.*

My opinion is that conclusive demonstration of the APPA's ability to mimic aqueous phase OH processes was not shown in this manuscript. OH was generated in the gas phase and its reaction with benzene and its oxidation products also occurred in the gas phase. Given diffusional limitations of OH to the surface of the particles, it is not clear to me how significant aqueous phase OH oxidation could have occurred here.

Analogous to the aqueous  $\text{SO}_2/\text{O}_3$  reaction presented by the authors,  $\text{H}_2\text{O}_2$  or  $\text{H}_2\text{SO}_4/\text{FeSO}_4$  are, to my knowledge, the canonical precursors for initiating controlled aqueous phase OH oxidation in laboratory studies. In my opinion, to demonstrate the APPA OFR for this type of application, the experiments could have, and should have been designed to accommodate their use by working around their limitations. It is a fair point that drying/size selecting the aerosols, and/or interpreting results with/without  $\text{H}_2\text{SO}_4/\text{FeSO}_4$ , could make it challenging to implement them. However, there are other ways that these aqueous OH precursors could have been used: for example, seed aerosols could have been maintained above the ERH of  $\text{K}_2\text{SO}_4$ , or polydisperse seeds could have been used, and aerosol compositional changes with the AMS could have been measured with and without illumination of  $\text{H}_2\text{O}_2/\text{FeSO}_4/\text{K}_2\text{SO}_4$  particles mixed with SOA surrogates or water-soluble SOA extracts rather than needing to generate the SOA in the gas phase as was done here.

In its current form, in my opinion, the revised paper adequately demonstrates the APPA's ability to study the aqueous phase  $\text{S(IV)}/\text{O}_3$  reaction because the gas-phase  $\text{SO}_2 + \text{O}_3$  reaction rate is negligible. It is hard for me to come up with any alternative explanation other than that  $\text{S(VI)}$  formation is occurring via aqueous phase  $\text{O}_3$  oxidation processes. I don't think the same can be said for the benzene/OH reaction, so I think it is misleading to claim that the APPA can be used for this type of application.

Similarly, how did the authors conclude that aqueous phase OH oxidation was responsible for the increase in ambient OA oxidation state as RH was increased from 40%-->85%-->100% (Fig. 17 and related text)? Hypothetically, couldn't this change have been driven by the higher RH (and LWC) promoting more efficient partitioning of low-volatility gas-phase oxidation products into the aerosol?

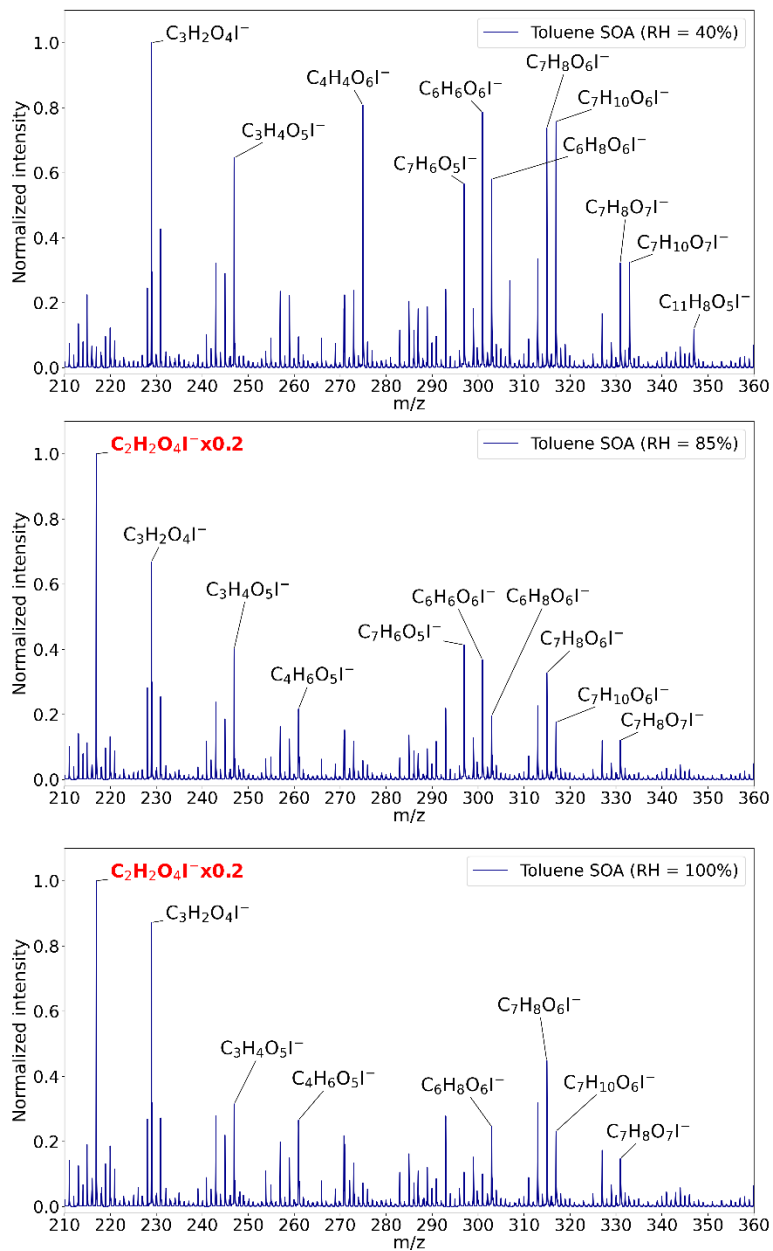
For the reasons mentioned in above comment, it is not clear to me that this evolution in OA oxidation state was in fact due to aqueous phase oxidative aging in the APPA OFR. Similar to part of the response to the above comment, without subsequent oxidation in the aqueous phase, water-soluble products of the gas phase oxidation are expected to evaporate when the aerosol/droplets are dried prior to measurement in the SMPS and AMS. It is also unclear why preferential partitioning to the aqueous aerosol/droplets would be more pronounced for more oxidized (and presumably lower volatility) species.

My current interpretation of the results shown here is that the yield of gas-phase benzene/OH oxidation products that partition into aerosol liquid water simply increased as a function of increasing humidity in the APPA, and that this is what is driving the humidity-dependent compositional changes (rather than aqueous-phase OH oxidation).

*We recognized that our assertion that much of the SOA was forming through aqueous phase reactions was not adequate. Reviews are always valuable in highlighting assumptions that are trusted, but not verified. We have made significant changes to the manuscript that we believe demonstrate a significant role of aqueous phase chemistry. Specifically, we replaced the description of SOA formed from oxidation of benzene with that of toluene. Importantly, we collected the aerosol at the exit of the reactor for each RH condition and analyzed it using a FIGAERO-CIMS. Most of the results included in the manuscript for toluene SOA are similar to those for benzene SOA. The rationale for making the*

*change is the CIMS analysis results now included in Figure S7 in the supplement (copied below), which show oxalic acid makes up a substantial fraction of the aerosol formed when aqueous aerosol and cloud droplets were present, but a negligible amount when only dry seed aerosol was. The paragraph added to the text in support of the role of aqueous phase chemistry is:*

*“The observed increase in SOA yield with increasing liquid water content is believed to result from further oxidation in the aqueous phase of the products of the gas phase oxidation of toluene. An alternative explanation that must be considered is that the enhancement is simply a consequence of the increased surface area available for condensation of low volatility products of the gas phase oxidation. Support for a significant role of aqueous phase chemistry comes from the aerosol composition measured with the CIMS. Mass spectra of the SOA collected for the three RH (and liquid water) conditions are shown in Fig. S7. The spectra obtained for the aerosol collected during the 85 % RH and 100 % RH experiments have a dominant peak at the  $m/z$  of oxalic acid (217 with 1) that is more than 5 times higher than the next highest peak, while it is absent in the spectrum obtained for the aerosol from the 40 % RH experiment. Oxalic acid is not produced from gas phase chemistry (Warneck, 2003), but has been shown to be an important product of oxidation of aromatics including toluene in the presence of ALW or cloud water. Specifically, oxalic acid is produced from aqueous phase oxidation of glyoxal, which is formed from the gas-phase oxidation of toluene with a yield of as high as  $\sim 0.4$  (Volkamer et al., 2001).”*



**Figure S7.** Mass spectra of SOA produced from OH-oxidation of toluene in the presence of dry seed particles (40 % RH), aqueous seed particles (85 % RH), and cloud droplets (100 % RH). The aerosol was collected on PTFE membrane filters and then evaporated from a FIGAERO inlet connected to an HR-ToF-CIMS. A peak corresponding to oxalic acid ( $C_2H_2O_4$ ) was dominant for both the 85 % RH and 100 % RH cases but absent for the 40 % RH case (note that the amplitudes of the oxalic acid peaks in both the 85 % and 100 % RH spectra were multiplied by 0.2).