Anonymous referee #1

(accepted as is)

The authors considered the reviewers comments and substantially improved the manuscript. Therefore, I suggest publication.

Thank you for recommendation. We did make additional changes in response to the suggestions by the anonymous referee #2 (described in a separate document).

Anonymous referee #2

(accepted subject to minor revisions)

I thank the authors for considering and implementing my suggestions, especially with respect with structure of the materials and methods, and interpretation of UV-vis and MS data.

Before accepting the manuscript for publication, I advise the authors to clarify a few minor points that I highlighted in orange in the comments list below. The remaining items mostly are typos and suggested rephrasing (for clarity).

Abstract and intro

Line 23: Faster photobleaching with respect to ..? Please, add the comparison term.
This change has been made.
Line 48-49: Rephrase as following: "For example, photodegradation of pyruvic acid in high ionic strength and low pH values (< 4) results in the red shift of its major absorption band." (it is unclear what "peak intensity" is: is it increase in the molar extinction coefficient of its absorption band? Clarify or remove)
This statement has been updated.
Line 53: Can you specify the wavelengths?
As the two studies looked at different compounds in the presence of different salts, they observed different wavelengths. We therefore feel it would muddle the point of the sentence to add specific wavelengths for each study.
Line 60: Rephrase as following: "However, no photodegradation studies have been conducted in the presence …"
Thank you for the suggestion. It has been implemented.
Line 62-63: Change "broken down" to "degraded"
This change has been made on line 67, which we believe is what the reviewer is referring to.
Line 72: On which substrate was the photolysis conducted? Please, change "OH radicals" to "hydroxyl (OH) radicals." (OH has not yet been defined)
Thank you for catching this. It has been fixed.
Line 72: Change "with strongly" to "concluding that strongly"
This has been added.
Line 79: Change "dry" to "dry (i.e., organic)"
This clarification has been made.
Line 88: Change "slowed under these conditions" to "slowed as compared to the experiment in pure water."
This adjustment has been made.

Materials and methods
Line 96: Remove the comma after "chamber" (or change as following: "… chamber described in Malecha and Nazadorovick, 2017")

This has been done.

Line 130: Add “Further experimental details on the two setups are provided in the following sections.”

Thank you for the suggestion. We have included it.

Line 139: Move “water” right after “MilliQ”; How much water did you add/how much total volume did you obtain?

This has been updated.

Line 149: Change “solvent” to “water”

This change has been made in line 154, which we believe is what the reviewer is referring to.

Lines 156-160: From my experience, (pure) water and acetonitrile are quite soluble with each other’s: how did you manage to separate the two solvents after adding the 2.5 mL of ACN? Was the presence of salt in water helping phase separation? If so, how could you reproduce the same procedure with the pure water isolate? I recommend clarifying these points in lines 156-157.

We are sorry for the confusion. There was no phase separation into aqueous and organic fractions. Rather, there was very little water present after rotary evaporation (maybe a few microliters), and when ACN was added most of the ammonium sulfate precipitated (because it is not as soluble in ACN) and the remaining water was removed with the ACN. This has been clarified in the revised text.

Line 168: Why was this filter extracted in ACN (while for the others you used water)? Do you think this may introduce a bias in your UV-vis spectra? Do you have data showing that UV- vis spectra in ACN and water are similar for these filter extracts?

We are sorry for being unclear. Both sets of filters were extracted in ACN. However, in the case of the aqueous samples, the ACN was removed and water or 1 M ammonium sulfate was added to the sample before photolysis. We have added a clarification to the section about the aqueous photolysis experiments restating that the filters were extracted using ACN. All UV-Vis data for the filter experiments reported here was taken in ACN and the comparison between the water and ACN solvents can be seen in Fig. S4. They are very similar.

Line 174: Change “with photolysis” to “during photolysis”

This has been changed.

Line 177: Change “the whole setup” to “the cuvette”

This has been changed.

Line 180-182: I think you can delete the part in parenthesis: it is sufficient to say that you used the same 0.5 cm cuvette. I would rather add that these samples were measured in ACN.

This has been deleted and we have added in that the UV-Vis measurements were conducted in ACN for the filter samples.

Results and discussion

Figure 1b: Can you specify in the caption if this graph was obtained using the dark-corrected or the uncorrected spectra?

Thank you for the suggestion. We have updated the caption.

Line 271: Change “absorbance” to “normalized absorbance”; change “rate constants” to “first-order rate constants”

Thank you for the corrections. We have implemented them.

Line 272: Change “absorbance” to “normalized absorbance

Thank you for the correction. We have implemented it.

Paragraph starting at line 275 (until "… from the data."): Rephrase as following: "Based on this analysis, we observed a considerably slower photolysis on filter than in the aqueous phase. However, for the filter sample we could only collect 4 datapoints, which may introduce a bias in our analysis. In particular, the filter data did not include the 0.5 h timepoint, which characterizes the fast-reacting chromophores pool in the aqueous sample."

We have rephrased as suggested.

Table 2: I suggest reporting the results with 2 significant digits if the first significant digit of the error is < 4. In other words, I suggest adding an additional significant digit to all tau1 values and of tau2 of AS. Furthermore, I suggest moving the lifetime of the filter under tau_2, as, based on the text above, you are only obtaining the "slow reacting" pool. (you can consider changing "A_2" to "A_1" in line 277.

Thank you for the recommendations and noticing an inconsistency in indexing the coefficients. They have been added.

Line 301: Change "A large" to "Under all conditions, a large"

Thank you for the suggestion. This has been completed.

Line 306: Why for some peaks you give a formula but not a name? Is it correct that there are two C7H7NO3 compounds in Figure 2 (but only the one at 10.36 is identified as nitrocresol)? Can you indicate with an asterisk the formulas for which you could identify the associated chemical name in Figure 2?

Only the 5 most intense peaks were originally given a name. We have updated the paragraph so all peaks for which the name can be reasonably assigned based on previous studies are given a name. The two peaks which are not named are marked with an asterisk.

Figure 2: I now understand the rationale for showing twice the unaged and water photolysis results. However, I am surprised to see such a large discrepancy from the two filters for the same treatment (e.g., unaged). (In panel (a), all peaks also appear less resolved, maybe due to some chromatographic issues, which makes them appear more different than they probably are). Can you add a sentence to the main text (maybe at the end of section 3.2.1) explaining why the unaged chromatograms of the two filters are different? Will this affect your conclusions?

Over the course of these experiments, we experienced some degradation of the HPLC column, which is under very frequent use in this shared instrument. The samples in panel b were taken about a year before the samples in panel a. We believe we may have been able to identify and discuss more peaks if the column degradation had not occurred, but our conclusions as presented here will still be valid because we only included peaks which were reproducible between the two trials. We have excluded the data for peaks which we could not resolve in panel a. We have added a brief explanation of this to the paragraph preceding the figure.

Line 336: Change "on filter" to "on filter (from filter 3)"

This change has been implemented.

Line 337: Change "sulfate" To "sulfate (from filer 4)"

This change has been implemented.

Line 344: I suggest pointing out that these are also the compounds identified in Figure 2 as being the most abundant (provide the names as well, if possible)

Thank you for the suggestion. This has been added.

Line 345 and entire section 3.2.2: How did you evaluate the difference between the various conditions? Is a visual/qualitative comparison of the highest peak intensities? The same comment applies also for the discussion of VK diagram results.

The analysis was a qualitative comparison of visual observations. We have added this clarification in both places.

Figure 3 and 4, caption: Clarify that it is from Filter 3 and 4, respectively

Thank you for suggesting this clarification. We have implemented it.

Figure 5: I appreciate that the authors took up my suggestion of using KV diagrams. I have a follow up suggestion: for the figure in the main text, do you think it be useful to show only datapoints above a certain intensity threshold? This will allow cleaning up the diagrams and better highlight differences among treatments.

Thank you for the suggestion. We have removed points with intensities less than 1% of the maximum intensity in the unaged samples from the plot in the main text while keeping all points in the SI Van Krevelen diagrams.

Line 406: Change "with on-filter" to "during on-filter"

This has been changed.

Line 407: Change "The purpose of this analysis was to directly contrast the difference in composition changes with photolysis" to "Differently from HRMS, this analysis allowed characterizing bulk changes in composition during photolysis"

We have elected to keep the previous sentence.

Line 408: Change "observe dramatic differences" to "dramatic changes in chemical composition"

This has been updated.

Line 431: Then you think that during on-filter photolysis nitro groups are converted to gas-phase N species? It would be good to add some sort of conclusion to the discussion.

This is what we suspect, and we agree that this paragraph would benefit from a conclusion. We have added a discussion stating we think it is likely the N-containing products are being lost to the gas phase, and added a few relevant references about HONO formation from nitrophenols.

Line 458-459: Please revise as following: "In spite of the *slower* nitrophenols photodegradation (assessed via HRMS, offline-AMS, and FTIR analyses), the overall photobleaching (assessed via UV-vis analyses) was actually *faster* in the aqueous phase as compared to on-filter photodegradation."

Thank you for the suggestion. It has been implemented.

Line 463: This fact may also agree with the larger decrease in the unresolved baseline absorption that you observed for the aqueous samples (- 35% and – 45% for pure water and AS) as compared to the filter isolates (- 21%). It would be good to point this out.

Thank you for the suggestion. We have added a brief statement to this effect.

Line 483: Change "and a large fraction of photorecalcitrant fraction is likely." To "and likely results in the formation of a photorecalcitrant faction."

This has been changed.

Line 484: Change "by SOA." To "of this type of SOA."

Thank you for noticing this. We have updated it.

Line 488: Change "faster photobleaching" to "faster overall photobleaching (assessed by

UV-vis analysis)."
This has been updated.
Line 490: Change as following: "Based on previous studies, we propose that the difference … sample matrices."
This change has been made.
Line 500: remove "photochemical"
This has been updated.
Line 505-504: "(Hems et al., 2021)" should be placed after "days".
This has been moved.
Line 502: Change "photobleaching" to "overall photobleaching"
Thank you for the suggestion. This has been changed.
Line 504: delete "with respect to photobleaching and lifetimes"
Thank you for catching this. It has been changed.