In this manuscript, Kloht and co-authors investigate the effect of sample matrix on the photobleaching of brown carbon generated in a smog chamber (toluene + NOx) via UV-vis spectroscopy and liquid chromatography coupled to both UV-vis detection and high-resolution mass spectrometry (HRMS).

This study addresses the broader question on how to correctly model photobleaching of brown carbon in the atmosphere, where presence of a broad range of matrix complicates the understanding and modeling of these processes. Previous studies have mostly focused on cloud-water conditions, and the few that focused on aqueous aerosols conditions used individual compounds, not atmospherically relevant organic mixtures (i.e., organic aerosols). Furthermore, most used salts other than ammonium sulfate, some of which of limited environmental relevance. Kloht et al.’s contribution addresses this knowledge gap by investigating the photodegradation process of a lab-generated organic aerosols under cloud-water, aqueous-aerosol, and dry-aerosol conditions, in the presence and absence of ammonium sulfate.

While motivations and quality of this work certainly justify publication in Atmospheric Chemistry and Physics, I believe that the paper would greatly benefit from a more quantitative analysis of the available data. My largest criticism concerns the analysis of the HRMS data. Based on the information provided in the text, the authors based their conclusions on “naked-eye”, qualitative differences in MS spectra between two experimental conditions. While I acknowledge that performing quantitative analyses of HRMS data of environmental mixtures is not straightforward, I still think the authors can obtain useful (semi-qualitative) information from their spectra. In other environmental chemistry fields, typical analyses include changes (also only qualitative; see Laszakovits and MacKay, 2022) in the population of Van Krevelen diagrams and changes in total number of identified formulas, among other things. I advise the authors to check, e.g., Thorsten Dittmar’s publications (Uni Oldenbourg) to identify which analyses are most suitable for their dataset (e.g., see Merder et al., 2020).

In addition to HRMS data, I think that the manuscript would benefit of a more quantitative analysis of UPLC-PDA data (Figure 3) and of additional analyses of UV-vis data (Figures 1-2). Specifically, UPLC-PDA data should be discussed in terms of changes (i.e., photolyzed sample – unaged sample) in the number of detectable peaks and in total areas (either the area of the unresolved baseline feature alone, unresolved baseline + all defined peaks, and, in case, defined peaks of interest). Furthermore, based on their method description, the authors should be able to assign a molecular formula to all well-defined peaks in Figure 3 (a few are briefly mentioned in lines 267 – 270). In theory, commercially available compounds could also be quantified (and/or their structure could be confirmed); thus, for these peaks, changes in concentrations, not only areas, could be provided. (While this would be a valuable addition, I acknowledge that it will require additional lab work that the authors may or may not wish to undertake.) These additional pieces of information will give a better understanding of which molecular structures/molecules behave differently under various experimental conditions – which may provide further insights into the underlying photodegradation mechanism (see comments below).

Concerning UV-vis data (Figure 1-2), I have two main suggestions. First, the authors should consider analyzing how all chromophores change during irradiation, not only the band at 350 nm. While I understand the rationale that they provide (even though Lin et al. gives
absorbance maximum values from 292 to 360 nm, not only 350 nm), the authors are using a complex mixture, not with a pure nitrophenol. To achieve this, they can consider variations in the total area ≥ 300 nm (or ≥ 290 nm) as a function of irradiation time (corrected for variations occurring in the dark). Repeating their calculation at selected wavelengths (in addition to the 350 nm one) is also an option. The results in Table 2 should then be referred to all chromophores, not only to the ones at 350 nm (the authors can also discuss variations in lifetime when considering specific wavelength or all chromophores).

A second suggestion concerns the choice of the fitting equation. While I agree with using a biexponential decay equation (indeed, this is common in the aquatic photochemistry community; see, e.g., Del Vecchio and Blough3. The authors may consider highlighting the parallelism between dissolved organic matter and SOA photobleaching in their text), I found the rational for excluding some components of the equation rather arbitrary. Instead, I suggest fitting all datasets with the general equation (eq 2), and then use parameters related to the goodness of the fit (e.g., R² or others) to justify the use of other fitting equations. I also advise the authors to remove y₀ from eq 2 (unless strictly necessary to have a good fit) and limit their analysis to the 5 h irradiation data. Indeed, I do not agree with their justification for setting y₀ = 0 for the aqueous solutions samples: by looking at the ammonium sulfate data in Fig S4, at 24h the amount of absorbance left is still half of that at 5h. I thus believe that more datapoints are required to confidently assess the presence of a photorecalcitrant fraction.

Last, the authors should acknowledge that the fit for the on-filter photolysis samples includes only 4 datapoints (notably, there is less data at lower irradiation times, where the fast-decay pool would be visible); this may be a reason why their data had to be fitted to a monoexponential decay function. I also recommend adding data for the dark controls in Figure 2.

My last major criticism concerns the structure of the materials and methods. In its current form, the authors mention some techniques whose data was not discussed in the paper (i.e., online AMS data during collection of the aerosol samples), and do not describe techniques that are later presented in the paper (i.e., FT-IR data). Furthermore, there should be a more explicit description of which blanks were collected and which results they provided (e.g., in current section 2.3.1, did the authors also performed photolysis on a blank filter?) Last, I think that a different order of the various subsections will improve readability. Specifically, I suggest following this order (some additions/changes are also indicated for each subparagraph).

2.1 SOA generation – In addition to describe the aerosol generation experiment, as they already do, the authors should also provide and briefly discuss (in the supplement, not in the main text) data related to O₃, NOₓ, AMS, particle size, as it will help other researchers reproducing their results. Furthermore, the chamber used in their experiment should be described (or a reference should be provided to a published description of their chamber). The online AMS analysis (now part of section 2.3.2) should also be in this section (i.e., in the supplement), not as part of the main text (unless the authors wish to discuss AMS data as a part of their results; in this case, a comparison with HRMS and UV-vis data of filters pre-irradiation should also be included). If all this data was already presented and discussed in a publication, they can simply add the reference to the published work. In addition, description of how blank samples are obtained should be added as well.

2.2 Photolysis experiments – Here, the authors should describe the general features of the irradiation setup used for both aqueous and on-filter photolysis (i.e., xenon lamp, now part
of section 1.2.1). In addition to the information already provided, the authors should also add a description of their irradiation experiments – How long where these experiments run for? When did the authors collect aliquots for which analyses? How many replicates were performed?

2.2.1 Aqueous experiments – Here, the authors should describe specific details related to the aqueous-phase experiments, including pre- and post-irradiation sample preparation (now, also in section 1.2.1)

2.2.2 On-filter experiments – Here, the authors should add details specific to irradiation of filters, including post-irradiation sample preparation for further analyses (now part of section 2.3.1)

2.3 Sample and data analyses

2.3.1 UV-vis analyses – Here, there should be a description of the UV-vis spectrometer and data analysis protocol. In the current form, this section requires some changes - in my opinion, there are too few details on actual measurements and too many details on recovery calculation. Missing information on sample collection include the following: how was the UV-vis operated (single beam or double beam)? If in double-beam, which reference was used? Which cuvettes were used (1-cm quartz)? How many replicates were collected for each datapoint? Missing information on data analyses include the following: Did you perform blank subtraction? (If yes, which blank spectrum did you use?) Did you correct for long-wavelength absorption? Did you correct for changes occurring in the dark? (According to Figure S3, there are some substantial variations in UV-vis absorption in the ammonium sulfate kept in the dark.) What is the range of absorbance you detected at your experimental concentrations? (i.e., was within the linear range of the instrument?) Furthermore, the text on estimating SOA recovery from UV-vis analyses should be moved to the supplement.

2.3.2 UPLC-PDA-HRMS analyses – Here, add content of section 2.2.3. Additional data analyses performed (see previous comments) should also be described here.

2.3.3 FT-IR analyses – Please, provide instrument setting, sample analyses, and data analyses details here. This information is currently missing.

2.3.4 Offline AMS analyses – Here the authors can refer to the O’Brien et al. publication describing the system they used.

Below, I provide a list of minor changes that the authors may wish to address in preparing their revised manuscript.

Abstract and introduction

Lines 8-9: Please, change “oxides of nitrogen” to “oxides of nitrogen (NO_x)”.

Line 14: Please, change “UV-B” to “UV” (based on your spectrum in Figure S1, you have also a substantial amount of UVA during your experiments).

Line 24: Please, change “nitrophenol” to “nitrophenols”.

Line 33: Please, change “NO_x” to “nitrogen oxides (NO_x)”

Line 39: Please, specify what “non-cloud conditions” refer to.

Line 44: Please, change “aqueous particles” to “deliquesced aerosol particles”.

Line 45: Please, change “particle phase water” to “water present in deliquesced aerosol particles”.

Line 62: Please specify why ammonium sulfate is a more interesting/relevant salt to use compared to others already investigated in the literature.
The authors may want to point out that also the concentration range of the organics is different, not only the ionic strength; this can have effect on products formation (e.g., oligomers formation is more likely when solutions are more concentrated).

Please specify if “near UV” refers to UVA, UVB, or both. Furthermore, in which phase are the SOAs in the discussed studies? (i.e., was the irradiation performed on filters or in the aqueous phase?)

Please change “This” to “This hypothesis”.

Materials and methods

How was hydroxyl radicals steady-state concentrations measured/estimated? This information should be added in the supplement (where additional information related to section 2.1 of the materials and methods are presented).

Is “NOy” a typo? Why not “NOₓ”?

Please, change “location” to “location of further analyses or experiments” in the heading of the first column (or add a new column named “location of the experiment”).

Did the extracts dissolve easily in water (or ammonium sulfate solution), or did the authors sonicate the filters? (If the authors sonicated, for how long and at which power?). The authors should also clarify which type of water was used to prepare their aqueous extract (i.e., deionized water or milliQ; if MilliQ water, information on the generation system should also be provided).

Please, change “µg/mL” to “mg/L”. This applies also to instances in the supplement (e.g., Table S2).

I found it surprising that also the water solution has such a low pH (generally, the pH of deionized water is 5.5 – 6.5 due to dissolved CO₂). Can you explain this lower pH? (e.g., is it due to organic acids parts of your aerosol or to inorganic components? Can the AMS data provide useful insights?)

Please, clarify if the cuvette was irradiated from the top or from the side.

A typical approach to remove salts and prepare samples for HRMS analysis involve solid phase extraction (SPE). Have the authors tried/considered this procedure as well? Are there literature precedents showing that your procedure is better/more convenient?

Please, check that “g/mL” is the correct concentration unit.

Please, provide the brand of the UPLC instrument.

I would add that separating the compounds by LC previous to HRMS allows one also to improve characterization – as you can assign a formula to each peak of the chromatogram.

Results, discussion, and conclusions

I suggest combining Fig. 1 and Fig.2 in a single 2-panel figure, at it will make it easier for the reader to see that Fig. 2 was obtained using data from Fig. 1. Furthermore, I suggest changing the x-axis of Fig. 2 to “time (hours)” (instead of “(min)”), as this is the same unit in the legend of Fig. 1. In the caption related to Fig. 1 data, the authors should specify the conditions under which this data was acquired, instead of referring to “representative conditions” (i.e., say directly that it is was collected during an aqueous-phase experiment in water). In addition, a reference to spectra collected in other conditions (i.e., Figure 3) should be added to the caption.
Line 264: Please, provide empirical evidence for the following statement: “[...] the fastest absorbance decrease with photolysis was observed at 350 nm” – from analysis of their UV-vis data, the authors should be able to justify this choice.

Figure 3: I have two suggestions here: 1. Remove one panel (I found it confusing that the black and blue traces are shown twice); to increase readability, the authors may consider increasing the offset of each peak and normalize the PDA counts to one given, convenient, signal; 2. Indicate on the graphs which are the peaks for which you could assign a molecular formula (and add the formulas/names).

Line 295: Please, explain how you assessed the reproducibility of your analyses.

Line 313 – 315: Here, a total organic carbon analysis before and after irradiation could provide some evidence about this point. If the authors did this analysis or have material left to perform this analysis, it would be good addition to their experimental dataset.

Figures 4 and 5: As for the two panels in Figure 3, I advise the authors to produce one single figure with all four experimental conditions.

Line 343 – 344: Did the authors record FTIR data also for aqueous samples? Can their offline AMS method distinguish between inorganic (e.g., HNO₃) and organic nitrogen-containing compounds? If not, inorganic nitrogen containing products may remain in the aqueous phase contributing to NO⁺ + NO₂⁺ counts.

Figure 6: Please explain why the ammonium sulfate data was not included in this analysis.

Section 3.2.4 and lines 393, 414-415: Please, make clear that the ones discussed are only proposed mechanisms based on previously reported reactivity for nitrophenols. The authors did not perform any experiment to test the underlying mechanism. Instead, this point should be highlighted as an area for further research in the final section. I also highlight that running more analyses to confirm the identity of some of the well-resolved peaks (see my comments above) will allow the authors to collect a piece of evidence for the existence of triplet reactivity – if compounds that they identify are the same for which triplet reactivity has been observed, not only speculated, in previous work.

Lines 375 – 379 (and lines 414-415): Photodegradation of dissolved organic matter generates carbonyls (e.g., Moran and Zepp⁴ or Zhu and Kieber⁵). If the same happens during SOA photodegradation, carbonyls may react with NH₄⁺ to form new nitrogen-containing compounds. Did the authors consider this mechanism while explaining their ammonium sulfate results?
References


