Point-to-point answers to the comments of Referee #2

We thank Referee #2 for the time and effort dedicated to reviewing our manuscript, as well as for the constructive comments and valuable reference suggestions. We are particularly grateful for the insightful remark in Comment **RC2: 21**, which prompted a substantial revision of the findings presented in this work. We believe that addressing the referee's suggestions has significantly improved the clarity and quality of the manuscript.

General comments

RC2: 1)

The reader remains frustrated as the study focusses on results at pH 5.4-5.6 since their solution at pH 8 did not sufficiently buffer to work with this pH under stable conditions. Further, the announced study in function of the salinity, is contradicted and resumed by a simple sentence 'The SFG study also showed that the salt concentration of the bulk accelerates the photo reaction. It is not the focus of this paper to discuss the details of the salinity effect on the photochemistry at this surface, we only register the observed phenomenon' (P11,L28 - P12,L2). This is contrary to the statements in the conclusions and the abstract of the paper, and really limits the scope of the paper. It would have been very interesting and novel to explore more in detail the influence of salinity on this reaction, especially since the preliminary results in the SI seem encouraging. Since the experiments discussed finally neither fully explore the effect of pH nor salinity, the paper can no longer claim that it is providing insights for interfaces of diverse natural water systems.

AC1:

We thank the referee for this thoughtful and constructive comment. We acknowledge that the Abstract and Conclusion in the original manuscript did not fully reflect the actual scope and core findings of the study. In response, we have revised both sections to more accurately represent our primary focus on interfacial photochemistry, and to clearly delineate the extent to which the influences of light spectrum, pH, and salinity were addressed.

Salinity:

While a detailed analysis of the salinity effect was beyond the intended scope of this study, we agree that its influence is scientifically relevant and warrants further investigation. Our current data showed a clear trend of salinity accelerating the interfacial photoreaction, which we have now clarified in the revised manuscript. We view this observation as a valuable preliminary result and have included it in order to motivate and support future studies, including our own planned work, contingent on funding availability.

pH:

Regarding pH, we have refined the manuscript to better explain the differences observed between low and high pH conditions. Although high pH conditions were challenging to *maintain due to uncontrolled carbonation, we were able to indirectly assess their effects on interfacial structuring and photoproduct formation. In the revised version, we now include additional analysis based on SFG data fitting, highlighting the behavior of the aromatic band (~3070 cm^{-1}) at both pH 5.4 and pH 8 (P13, L6-12 and Figure 4b in the revised manuscript). This comparison demonstrates a more pronounced increase in the aromatic signal at pH 5.4 following identical light exposure (AM0, 150 minutes), indicating that lower pH conditions are more favorable for the formation of surface-active aromatic species. We attribute this trend to the higher availability of protons at lower pH, which facilitates the formation of the* $C_{14}H_{11}O_3\bullet$ *radical from photoexcited 4-BBA (see Eq. 1 in the revised manuscript). This radical plays a key role in subsequent surface reactions, as detailed in the "Tentative reaction pathways" section in the revised manuscript.*

We believe these revisions provide a more accurate representation of the study's scope and clarify how our findings contribute to the broader understanding of interfacial photochemistry.

RC2: 2)

There are further no citations in the discussion section, although quite a few works work using this photosensitizer exist which could help clarify the observations made. This is particularly the case when the authors propose reaction mechanisms that seem quite original and rather unlikely. Citing previous works that have observed or proposed mechanisms would make their propositions more convincing. In several places, the discussion section is repetitive and the reasoning seems to turn in circles, in particular when discussing the SFG spectrum features of the aromatic band and the OH group. The discussion section needs thorough reworking, in light of all remarks in this review (here and following). Once this is done, the abstract and the conclusion section should be reworked as well to better reflect the main points developed in the work..

AC2:

In response to the referee's comment, we have thoroughly revised the manuscript to improve clarity, reduce redundancy, and better substantiate our interpretations. Specifically, we have merged the "Results" and "Discussion" sections into a single integrated section. This restructuring has enhanced the logical flow of the manuscript by aligning the interpretation of findings more directly with the corresponding experimental results.

We have also refined the proposed reaction mechanisms and included relevant citations in the revised ***Section 3.2.3 (Tentative reaction pathways)*** *to support and contextualize our interpretations within the existing literature.*

We acknowledge that the previous discussion of the SFG spectral features, particularly concerning the aromatic band and the OH group, was overly detailed and at times unclear. Our original aim was to reconcile the absence of an aromatic SFG signal from 4-BBA in the presence of NA with earlier findings by Tinel et al. (2016), who reported the surface partitioning of 4-BBA under similar conditions.

In the revised version, we have streamlined this discussion, focusing specifically on comparisons with the reference study. We now provide a clearer and more concise interpretation, supported by data fitting, figures, and appropriate citations

The relevant text of the revised manuscript where this comparison is now explicitly highlighted include:

P10, L18-25

P16, L16-18

P20, L16-19

P22, L5-8

P24, L7-9

P25, L5-10

Tables S4 - S6

The abstract and conclusion have also been updated to reflect the key points and improved structure of the revised discussion.

Specific comments:

RC2: 3)

L10: ‘volatile organic compounds (VOCs) can make up a significant fraction of atmospheric aerosols, particularly in urban and industrial areas.’ As is, this statement is incorrect to my knowledge. I think the authors mean that the secondary reaction products of VOCs can contribute significantly to aerosols. Please adjust.

AC3:

We thank the reviewer for this valuable observation. The sentence has been revised for accuracy and now reads:
“It has been estimated that the secondary reaction products of volatile organic compounds (VOCs) can contribute significantly to secondary atmospheric aerosols (SOA)…”

P3, L7-9 in the revised manuscript

RC2: 4)

L19-20: the CDOM references are very old and it has since been shown that CDOM is not always enriched at the surface, see for Van Pinxteren et al.[1], Stolle et al.[2] or Tilstone et al.[3] for more recent work on this. Please modify the sentence to reflect this.

AC4:

We thank the reviewer for highlighting this important point. The sentence has been revised to reflect the more current understanding of CDOM distribution. The revised sentence:

"It was previously believed that CDOM is more concentrated at surfaces than in the bulk (Carlson, 1983; Carlson and Mayer, 1980), however, more recent studies have shown that CDOM is not always enriched at the surface (van Pinxteren et al., 2020; Stolle et al., 2020; Tilstone et al., 2010)."

P3, L26-29 in the revised manuscript

RC2: 5)

P4, L3-4: please add some more recent and environmentally relevant references for the existence of SML and its contribution to seaspray (e.g. review by Tinel, L. et al. Impacts of ocean biogeochemistry on atmospheric chemistry. Elementa: Science of the Anthropocene 11, 00032 (2023) and Sellegri, K. *et al.* Influence of open ocean biogeochemistry on aerosol and clouds: Recent findings and perspectives. *Elementa: Science of the Anthropocene* **12**, 00058 (2024)).

AC5:

We thank the referee for the helpful suggestion. The following sentence has been added to the revised manuscript along with the recommended citations:

"Recent studies have highlighted the critical role of ocean biogeochemistry in shaping atmospheric composition and influencing aerosol–cloud interactions. In particular, the sea surface microlayer has been recognized as a key interface for biologically driven gas emissions, with important implications for their representation in large-scale atmospheric models (Tinel et al., 2023). Moreover, oceanic biogeochemical processes have been shown to affect aerosol formation and cloud properties, thereby contributing to climate-relevant feedback mechanisms (Sellegri et al., 2024)."

P4, L16-21 in the revised manuscript

RC2: 6)

P4, L18-20: the list of publications is not well reflecting the work 'in recent years' – please update the references, in particular the paper by Freeman-Gallant, et al. (Photooxidation of Nonanoic Acid by Molecular and Complex Environmental Photosensitizers. *J. Phys. Chem. A* **128**, 9792–9803 (2024)) is of interest for the current manuscript and should be included in the introduction.

AC6:

Thank you for the suggestion. The outdated citations have been removed in the revised manuscript. We have incorporated the recent study by Freeman-Gallant et al. (2024), which presents new findings on the NA–4BBA system and offers relevant insights following the earlier reference work. The updated text now reads:

“Tinel et al. (2016) demonstrated that the photosensitized degradation of fatty acids at the air–water interface, specifically nonanoic acid (NA) in the presence of 4-benzoylbenzoic acid (4-BBA) and imidazole-2-carboxaldehyde as model systems, enhances VOC emissions and secondary aerosol formation (Tinel et al., 2016). A subsequent study by Alpert et al. (2017) reported the formation of SOA particles through photochemical reactions and ozonolysis of saturated long-chain fatty acids and alcohol surfactants at the water surface (Alpert et al., 2017). More recently, Freeman-Gallant et al. (2024) showed that the efficiency of NA photooxidation in thin films depends on the type of organic photosensitizer, with 4-BBA identified as the most effective among those tested (Freeman-Gallant, et al., 2024).”

P4, L32 – P5, L6 in the revised manuscript

RC2: 7)

P5, L13-15: this sentence relates results obtained and does not seem at its right place here; I suggest to remove.

AC7:

We agree with the referee and removed the mentioned sentence.

RC2: 8)

P5, L18: what do the authors consider a ‘normal pH’ ? Please specify.

AC8:

The phrase "normal pH" was a typographical oversight. During the refinement of the introduction to better align with the study’s core focus, we removed the entire sentence in question.

RC2: 9)

P5, L23: Did the authors take any precaution as to the purification of nonanoic acid? This is important to precise, since Saito, S. *al.* (Impurity contribution to ultraviolet absorption of saturated fatty acids. *Science Advances* **9**, eadj6438 (2023)) reported that impurities can play a role in the photochemistry observed.

AC9:

NA was used as received, without additional purification. We did not observe any evidence that impurities in our NA sample influenced the photochemical reactions under the irradiation conditions used in this study. This information has been added in the revised manuscript (P6, L4-7).

RC2: 10)

P6; 2.2: how was the temperature kept stable upon irradiation?.

AC10:

The irradiation cell was mounted on a large metal table that acted as an efficient heat sink, within a temperature-controlled laboratory environment. Quartz windows were used to allow light transmission during irradiation. The LED light source, emitting only at wavelengths below 550 nm, generated negligible thermal radiation. Additionally, cooling air from the light source electronics was directed away from the measurement cell to avoid thermal influence. This information has been added in the revised manuscript (P6, L33 – P7, L3).

RC2: 11)

P7, section 2.4: the transfer of the sample with a syringe of a surface-active solution can induce biases due to more or less sampling of the surface layer and adsorption to the syringe (or filter). Can the authors detail what part of the solution was sampled with the syringe and if they assessed the reproducibility of this sampling + measurement method?.

AC11:

In the MS experiments, distinguishing surface-derived signals from bulk-phase contributions is inherently challenging. To ensure that the sampled liquid solution was representative of the entire system, the solution was thoroughly stirred prior to sampling to homogenize any surface-enriched compounds with the bulk. The syringe tip was then inserted into the center of the bulk phase to draw the sample. In contrast, the SFG technique is intrinsically surface-specific due to its selection rules, which exclude contributions from the isotropic bulk. This distinction underscores the complementary nature of the two methods. In the revised manuscript, we have clarified how SFG data help identify surface-active compounds among those detected by MS.

Sampling from the liquid phase has been revised in P8, L9 -12 in the revised manuscript.

RC2: 12)

P10, L1-9: Have the authors tried to increase the strength of the buffer solution to try and stabilize the pH at 8?.

AC12:

Yes, we attempted to stabilize the solution at pH 8 using a buffer. While the pH remained stable, the SFG experiments showed no detectable changes upon irradiation. Additionally, we had concerns that the use of a pH 8 buffer in the photochemical system involving NA and 4-BBA could quench reactive intermediates or alter the surface activity of both reactants and products. This may suppress or modify interfacial photochemical pathways that are central to the observed reactivity.

RC2: 13)

P11, L26-P12, L2: this does not seem an appropriate conclusion to this section. Please state clearly what the main observations are from the study under different wavelengths. The influence of the salinity should be discussed separately or be omitted altogether.

AC13:

13.1

We would like to clarify that the statement on P11, L26–L28 ("The individual irradiation wavelengths have both different wavelengths and intensities, which was done on purpose to mimic the corresponding solar irradiance for each wavelength.") was not intended as a conclusion but rather as an explanation for the choice of irradiation settings. This point is further elaborated in the Discussion section (P18, L17–25) of the original manuscript. In the revised version, where the "Results" and "Discussion" sections have been merged, this part has been restructured to more clearly present the observations related to the effects of different irradiation wavelengths (P14, L9 – P15, L5).

13.2

Regarding the salinity effect mentioned in the sentence, "The SFG study also showed that the salt concentration of the bulk accelerates the photoreaction (see Sect. S5 and Fig. S14),…" we acknowledge the reviewer's concern. As noted in our response AC1, this is a preliminary observation and not the central focus of the current study. Nevertheless, we felt it was important to document the finding and share it with the community to encourage further investigation. We have reworded the statement in the revised manuscript to clarify that we are reporting the phenomenon without drawing detailed conclusions (P15, L10-14). We are also open to the reviewer's suggestion for a more appropriate placement of this statement within the manuscript.

RC2: 14)

P13, section 3.2.1: the authors discuss aqueous products under irradiation of NA solution and NA+BBA solutions, however in the previous section the changes in spectra with only NA at pH 5.8 are not discussed. Did they see changes there and expected products to be formed from pure NA solutions? Do they see evidence of impurities as well, as discussed by Saito, S. et al. (Impurity contribution to ultraviolet absorption of saturated fatty acids. Science Advances 9, eadj6438 (2023))?.

AC14:

We partially addressed this point in our response to Comment AC9. NA was used as received, without further purification. Under the irradiation conditions applied in this study, we observed no evidence that photochemical reactions were taking place upon the UV absorption of impurities in the NA sample. When NA was irradiated in the absence of 4-BBA, the product signals remained at background levels, indicating minimal or no photochemical activity.

*We acknowledge that a typographical error in the first sentence of Section 3.2.1 may have contributed to the reviewer's confusion. The original sentence, "**The products of the photochemical reactions of NA were detected under different irradiation and at a fixed pH of ~5.8.**", was missing the phrase "**in the presence of 4-BBA**" This has been corrected in the revised manuscript. The updated sentence now reads: **"The products of the photochemical reactions of NA in the presence of 4-BBA were detected under different irradiation and at a fixed pH of ~5.8."** (P 16, L12-13)*

RC2: 15)

P13, Fig 6: the caption currently reads 'concentrations of each of the photoproducts': since quantifying with CIMS is particularly challenging, especially for compounds for which no standards are available, I suggest to replace this by 'normalized intensities of each…'. Further, it is unclear what the error bar for the sum of products indicates here.

AC15:

The authors agree with the Referee, it should be the "normalized intensities", as already indicated on the y-axis label. We have rephrased the figure caption to indicate the normalized intensities and also clarified in the caption that the error bars represent the analytical uncertainty associated with the measurements.

Note: Figure 6 in the original manuscript has become Figure 7 in the revised manuscript.

RC2: 16)

P13, L24-26: the much larger increase of some products under O2 conditions, is probably also indicative of primary and secondary products formed; hence it looks like $C_8H_{12}O_4$ could be one of the primary products formed and the other products secondary products, that are more limited due to the lack of oxygen available. Did the authors also see new products formed under oxygen low conditions? This would be interesting to help elucidate formation mechanisms.

AC16:

We did not observe the formation of new products under low-oxygen conditions. Only changes in the relative contributions of the main products listed in Table S4 to the total $C_xH_yO_z$ signal were detected. Signals from other compounds remained at background levels and did not indicate the emergence of additional products under these conditions.

RC2: 17)

P17, L13-14: the authors state that the study was done in conditions '…similar to the real environment at sea water and droplets in the atmosphere.' I'm not convinced this is indeed the case, as most experiments were done without no salinity and at pH 5.8 and irradiation at AM0, conditions that are neither representative for aerosol, droplets nor sea surface. I suggest to nuance this statement..

AC17:

This sentence has been removed from the revised manuscript.

RC2: 18)

P18, L22-25 and P25, L13-15: do the authors suggest that differences due to different wavelengths (through geographical location, time etc) are currently not taken into account in models? What kind of models are they thinking of here? The reference is not correctly cited as well.

AC18:

We do not suggest that differences in spectral power distribution, arising from factors such as geographical location or time of day, are currently excluded from models. Rather, our intention is to emphasize the importance of accounting for such variations, as they can significantly influence photochemical processes at the air–water interface. The citation has been corrected in the revised manuscript.

RC2: 19)

P18, L31: the authors suggest that the reason for the rapid decrease of the pH is the decarboxylation of 4-BBA. This is a little surprising to me, as this is not the main pathway for 4-BBA reactions (which is expected to be a reduction of the carbonyl group, e.g. Calvert & Pitts, 1966), and should thus only be a minor CO2 source. It should be noted that NA can also undergo decarboxylation, which is a likely a major pathway, as expected for an aliphatic organic acid (and seen some major products observed are C8). Could the authors make a quantitative estimate of how much CO2 they need to change the pH as observed and what sources they think contribute (solubilisation of gas vs decarboxylation) ? This could help better understand how much 4-BBA or NA is expected to disappear.

AC19:

*We thank the referee for this insightful comment and acknowledge that the original paragraph was unclear. The discussion referred to the behavior of the "**mixture of NA and 4-BBA**" under UV exposure, rather than 4-BBA alone, as can be seen in Figure S12 (in the original manuscript), which was cited in the paragraph. We have now revised the text for clarity and scientific accuracy.*

To maintain the focus of the main manuscript, we have moved the entire section previously titled "4.2. Evolution of pH values", including the corrected paragraph, to the revised Supporting Information, now under section "S4. Changes of pH with time and UV exposure."

See revised SI P11, L22 – P12, L7

Note: Figure S12 in the original SI has become Figure S13 in the revised SI.

RC2: 20)

P19, L12: 'Normally NA is only partially dissociated' Can the authors please precise here what 'normal' they referred to? It would be good to relate this behaviour to the pKa of NA at 5.23, pH at which NA will thus be present at a proportion of 50/50 in ionic and deprotonated form.

AC20:

In this context, we meant that nonanoic acid (NA) in aqueous solution is partially dissociated across a wide range of pH values (see P12, L13-15 in the revised SI). To clarify, we now include a plot (Fig. S13b) showing the dissociation fraction of NA as a function of pH. As expected, the dissociation fraction increases with pH, which corresponds to a decrease in NA's surface activity, and vice versa.

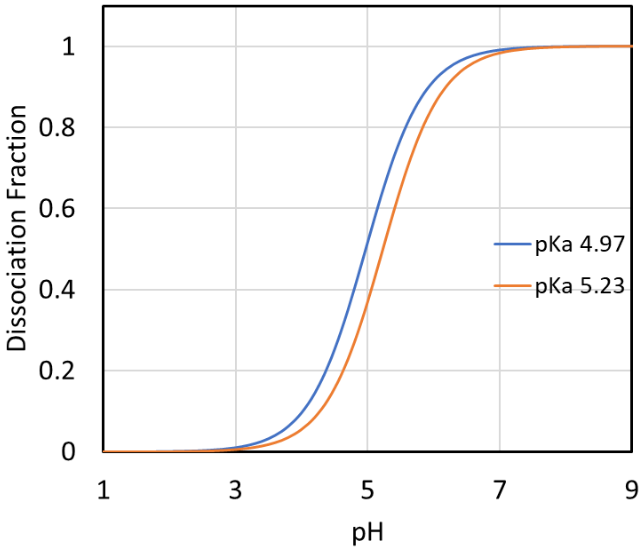

Fig. S13b (here we include the pKa value cited by the referee (5.23) and the pKa value 4.97 from the literature (Luo et al., 2020; Wellen et al., 2017) for NA).

In support of this, the offline experiment shown in Fig. S13a demonstrates this behavior. The gray curve represents a mixture, initially at pH 8.4, irradiated with 280 nm UV light. After two hours, the pH decreased by approximately 20%, indicating a measurable shift in NA dissociation during the experiment. By contrast, the green curve, corresponding to a mixture starting at pH < 6, shows a stable pH throughout. This suggests that, in our SFG and MS experiments under low pH conditions the dissociation fraction of NA remained constant over the course of the experiments.

The new dissociation plot referenced above has been included in the revised (SI).

RC2: 21)

P20, L2-5: The formation of the C9H10O5, suggested to be an aromatic compound, from irradiation of 4-BBA alone is quite surprising. Are the authors sure this is not contamination from a previous experiment (e.g. rinsing several times, repeated results)? If precautions were taken to avoid contamination, further investigation is needed to better understand this unusual reaction mechanism. The reaction mechanism proposed P22, L11 (and also L16) indicates an addition of bicarbonate. The probability of this reaction taking please again depends on the concentration of CO2 expected to be dissolved (see remark above). Bicarbonate would also be majorly under its fully protonated form at pH 5.4, and should thus better be written as H2CO3.

AC21:

We sincerely thank the Referee for this insightful and constructive comment. It prompted a careful revise of our mass spectrometry data, which in turn led to more accurate and supported interpretations. Based on this review, we confirm the following:

1. ***$C_9H_{10}O_5$ was not produced by the irradiation of 4-BBA alone.***
2. ***It was also not the result of contamination****, as appropriate rinsing procedures were followed, and the finding was consistently reproduced across independent experiments.*
3. ***$C_9H_{10}O_5$ was exclusively observed in the irradiation experiments of NA + 4-BBA****, with its relative abundance varying depending on irradiation conditions and the presence or absence of oxygen. (see P20, L21-24 in the revised manuscript)*

In light of these findings, we have revised the proposed reaction pathways accordingly in the manuscript (see section 3.2.3 Tentative reaction pathways).

Furthermore, we now attribute the aromatic band observed in the SFG spectra to $C_9H_{10}O_5$ rather than benzaldehyde. While our original hypothesis suggested benzaldehyde as the source of the interfacial aromatic signal, its detection in the gas phase makes this assignment less likely. In contrast, $C_9H_{10}O_5$ is non-volatile and may possess amphipathic, surface-active aromatic characteristics. This makes it a more plausible candidate for the origin of the interfacial aromatic signal, as now described in the revised manuscript.

RC2: 22)

P22, L8-11, L13-17: it would be very helpful to have a developed reaction mechanism schematic instead of the brut formulas here. There are several steps that seem unrealistic, notably the additions of bicarbonate as mentioned before, and in particular L16 where the addition of bicarbonate on an RO2 radical leads to further unsaturations. This could also help clarify the quite unclear discussion of the mechanism P23, L10-14.

AC22:

As noted in our response to comment AC21, the proposed reaction pathways and corresponding text have been revised in the updated manuscript. A schematic representation of the refined reaction mechanism is now provided in the revised Supporting Information (Fig. S15). Additionally, the unclear discussion in pages 23–24 has been removed to improve clarity and focus, as they lacked sufficient supporting evidence and detracted from the main interpretation of our findings.

RC2: 23)

L23, L1-6: this seems like an unnecessary repetition and can be removed

AC23:

Removed

RC2: 24)

P23, L20-P24, L25: The explanation for the appearance of the aromatic band given here is not very convincing; it seems a little far-fetched to use an observed gas-phase product (benzaldehyde) to explain changes in the SFG spectrum at the surface and link these to the lower OH band. It seems like the aromatic band should form with and without NA. Since it is only observed in the presence of NA, this could be due to having less NA at the surface, as it will be more oxidised and hence more solubilised, which would lead to an increase in the aromatic signal from 4-BBA. The appearance of the aromatic band could also be due to other liquid phase products formed from a self-reaction of 4-BBA alone; however, these products are not discussed in the paper explicitly and would not explain why the aromatic band is not observed with BBA alone. Furthermore, benzaldehyde may interact with OH groups from water in a similar way as 4-BBA, since they both have a carbonyl function. This discussion should be revised thoroughly; quantitative (or estimations) of photolysis yields for primary photoproducts from 4-BBA or estimated loss rates of 4-BBA could be helpful in this discussion.

AC24:

Pages 23 and 24 have been removed from the revised manuscript in the light of our refined interpretations (see AC21 and AC22).

Note: The increase in the aromatic band cannot be due to 4-BBA, particularly after having less NA at the surface. 4-BBA is not surface-active. The appearance of the aromatic band is indeed due to other liquid phase products however formed from the photolysis of NA + 4BBA as described in the revised manuscript. This is now discussed in the revised manuscript with the potential reaction path ways.

RC2: 25)

P24, L26-31: it’s unclear what the authors are trying to convey in this paragraph; is this meant to further explain the dangling OH band feature? Or is this supposed to explain photoreaction products (which should be mainly radical reactions however)? It’s also unclear why the presence of catalysts is invoked here.

AC25:

Pages 23 and 24 have been removed from the revised manuscript in the light of our refined interpretations (see AC21 and AC22).

Language and minor edits:

RC2: 26)

P4, L24: nonanoic acid should not take a capital here, to be consistent with other chemicals.

AC26:

Corrected (P4, L33 in the revised manuscript)

RC2: 27)

SI: S6, Table S3: pH =MilliQ, please replace by the measured pH value of the ultrapure water.

AC27: (Table S3 in the revised manuscript)

Replaced

RC2: 28)

P8, L5 & L23: neglectable: should be negligible

AC28:

Replaces (P10, L8 in the revised manuscript)

RC2: 29)

P9, L25: seens the following discussion, I suggest to remove ‘simply’

AC29:

Removed

RC2: 30)

P10, Fig 3a: the legend indicates AM0 but the caption indicates these are dark experiments. Please correct.

AC30:

Corrected (Fig 3a in the revised manuscript)

RC2: 31)

P11, L1: one and a half hours: please write as 1.5 h

AC31:

We replaced it by “90 min” (P13, L21 in the revised manuscript)

RC2: 32)

P16, L12: ‘…(see Table S5). Only…’ this is the same sentence, please remove the capital.

AC32:

This sentence has been reworded in the revised manuscript. (P22, L2-5 in the revised manuscript)

RC2: 33)

P16, Fig. 11: please indicate for which solutions these results are shown.

AC33:

Indicated (Fig 12 in the revised manuscript)

RC2: 34)

P17, L18: the year of the reference is missing

AC34:

Corrected. (P16, L5-6 in the revised manuscript))

RC2: 35)

P18, L28: for solutions with a higher pH value of 8; the whole sentence is not grammatically correct

AC35:

This sentence has been corrected and reformulated in the revised manuscript.

(P11, L15-17 in the revised manuscript)

RC2: 36)

P22, L5: improved: please replace by increased

AC36:

Replaced (P20, L9 in the revised manuscript)

RC2: 37)

P22, L1: please add '…the solution with 4-BB **and NA'**

AC37:

Added (P20, L17 in the revised manuscript)

RC2: 38)

P24, L16: afterword: should be afterwards

AC38:

Pages 23 and 24 have been removed from the revised manuscript in the light of our refined interpretations (see AC21 and AC22).

RC2: 39)

P24, L29: I think I should be a conjugate **base**, not acid?

AC39:

Pages 23 and 24 have been removed from the revised manuscript in the light of our refined interpretations (see AC21 and AC22).

RC2: 40)

SI, S5, Table S1: last column: please correct the units to mM.

AC40:

Corrected (Table S1 in the revised manuscript)