Response to Reviewers for the manuscript of "Photochemistry of the sea-surface microlayer (SML) influenced by a phytoplankton bloom: A mesocosm study" by Jibaja Valderrama et al.

We thank the reviewers for their constructive evaluation of our manuscript. We believe that their insightful comments have strengthened the quality, clarity and scientific rigor of the revised submission. Please find below our detailed point-by-point responses addressing the reviewers' recommendations. The comments from the reviewers are shown in red, our responses in black, and any changed or amended text *in blue*. Line numbers of *blue* comments correspond to the continuous line numbering of the revised black manuscript.

Reviewer: 1

Comments:
The article by Jibaja et al. conducted a mesocosm study that investigated the photochemical production of carbonyl compounds influenced by a phytoplankton bloom. The study measured the concentrations of carbonyl compounds in both surface microlayer (SML) and underlaying seawater (ULW), as well as production/loss rates after samples collected from different time points were irradiated after 5 hours. The authors also measured photooxidation capacity and concentrations of two trace metals (Fe and Cu). The experiments and the analysis are well designed and executed, I have several comments for the authors to consider:
We sincerely thank the reviewer for the careful and constructive evaluation of our manuscript. We appreciate the recognition of the experimental design, analytical approach and overall execution of our study. The reviewer's suggestions have been very valuable for improving the clarity, depth and scientific rigor of our manuscript. We have addressed each comment and implemented the suggestions as described below. We believe that these revisions have strengthened the manuscript and enhanced its overall quality.

R1C1: The authors selected 17 carbonyl compounds in this study. However, several carbonyl compounds listed in the introduction (formaldehyde, acetaldehyde, acetone) are not among the targeted list. It is not clear whether they were not measured, or measured but results were insignificant. Considering the carbonyl concentrations in this work is pretty high, I doubt that these were below the detection limit, and therefore I suggest that the authors add brief explanation for why formaldehyde, acetaldehyde and acetone were excluded.
A-R1C1: Formaldehyde, acetaldehyde and acetone have been mentioned in the introduction provide context on the photochemistry of carbonyl compounds in the marine environment. Formaldehyde was not analysed in the present study. Acetone and acetaldehyde were initially considered as target compounds, but they were ultimately excluded from the quantitative analysis due to poor linearity in their calibration curves, likely related to their high volatility and potential background contamination from laboratory air. We believe that the exclusion of these

three compounds does not affect the conclusions of our study, as the investigated 17 carbonyl compounds capture the unique photochemistry of the SML with respect to ULW. The following text was added in the revised version of the manuscript:

Page 3, Line 95-97: "Even though acetaldehyde and acetone were initially also considered as target compounds, they were ultimately excluded from the final quantitative analysis since their calibration curves showed poor linearity, likely related to their high volatility and potential background contamination from laboratory air. Formaldehyde was not analysed in the current study."

R1C2: The photoreactor comprises a 1000W Xenon Lamp and an air mass filter. Is the expected light output reaching the sample ~1 sun?

Also, not sure whether the AM1-5G filter out all of the IR emitted by the lamp. Is the temperature inside the bulk phase reactor measured during the 5 hours to ensure the samples didn't get too hot?

A-R1C2: We thank the reviewer for these important observations:

Light output reaching the sample: The solar simulator employed (LS0806, LOT-Quantum Design) consisted of a 1000 W Xenon lamp (LSB551, LOT-Quantum Design) coupled with an air mass filter (AM1-5G). According to the manufacturer's technical specifications, this configuration has been designed to produce an output power equivalent to 1 sun.

Temperature inside the reactor: The experiments were performed using a jacketed temperature-controlled aqueous-phase cylindrical glass photoreactor, where the temperature was controlled using a thermostat (RCS, Lauda). This ensures that the observed changes in carbonyl concentrations are driven by photochemical processes and not affected by any thermal effects.

We have amended the revised manuscript text as follows:

Page 6, Line 156-161: "For carbonyl compound photochemistry investigations, ambient SML and ULW samples were irradiated for 5 hours with a light source that simulated the actinic radiation in the sea surface. A jacketed, temperature-controlled (25 ± 0.5°C) aqueous-phase cylindrical glass photoreactor (length: 9.5 cm, internal diameter: 6 cm) coupled with a thermostat (RCS, Lauda), were used to ensure constant temperature during irradiation. The solar simulator (LS0806, LOT-Quantum Design) consisted on a 1000 W Xenon lamp (LSB551, LOT-Quantum Design) coupled with an air mass filter (AM1-5G) that was positioned 20 cm away from the photoreactor (Fig. 2). This system has been designed to produce output power equivalent to 1 sun."

R1C3: The photoproduction rates are all expressed in nM h-1, which is hard to interpret by readers without carefully examining the light dose and the CDOM absorbance. Is it possible to calculate the apparent quantum yields, since light and absorbance were both measured? The calculated AQYs can be listed in the supplement if too confusing in the main text. Also, there is no error bars for the production rates in figure 4 and 5. I understand the SML sample volume is limited but error bars should be presented for the ULW samples. If AQYs cannot be calculated, I suggest normalize photoproduction rates to CDOM or DOC. Currently I cannot tell whether the enhanced rates are due to increased photoreactivity (or photoproduction efficiency, respectively), or just simply high abundance of chromophores.

A-R1C3: We thank the reviewer for this constructive comment. We agree that the given suggestions would greatly contribute to the interpretability of our results and expand the depth of our analysis:

Apparent quantum yields: Following the reviewer's recommendation, we have calculated the AQYs for all the investigated compounds using the approach presented by Zhang and Blough for polychromatic light. AQYs have been derived from the measured photoproduction rates, the absorbance spectra of each unfiltered sample, and the spectral irradiance of the Xe lamp (Zhang and Blough, 2016). A detailed description of the methodology and the obtained AQYs are now presented in the revised Supplementary information (*Section S6*, *Figure S5*).

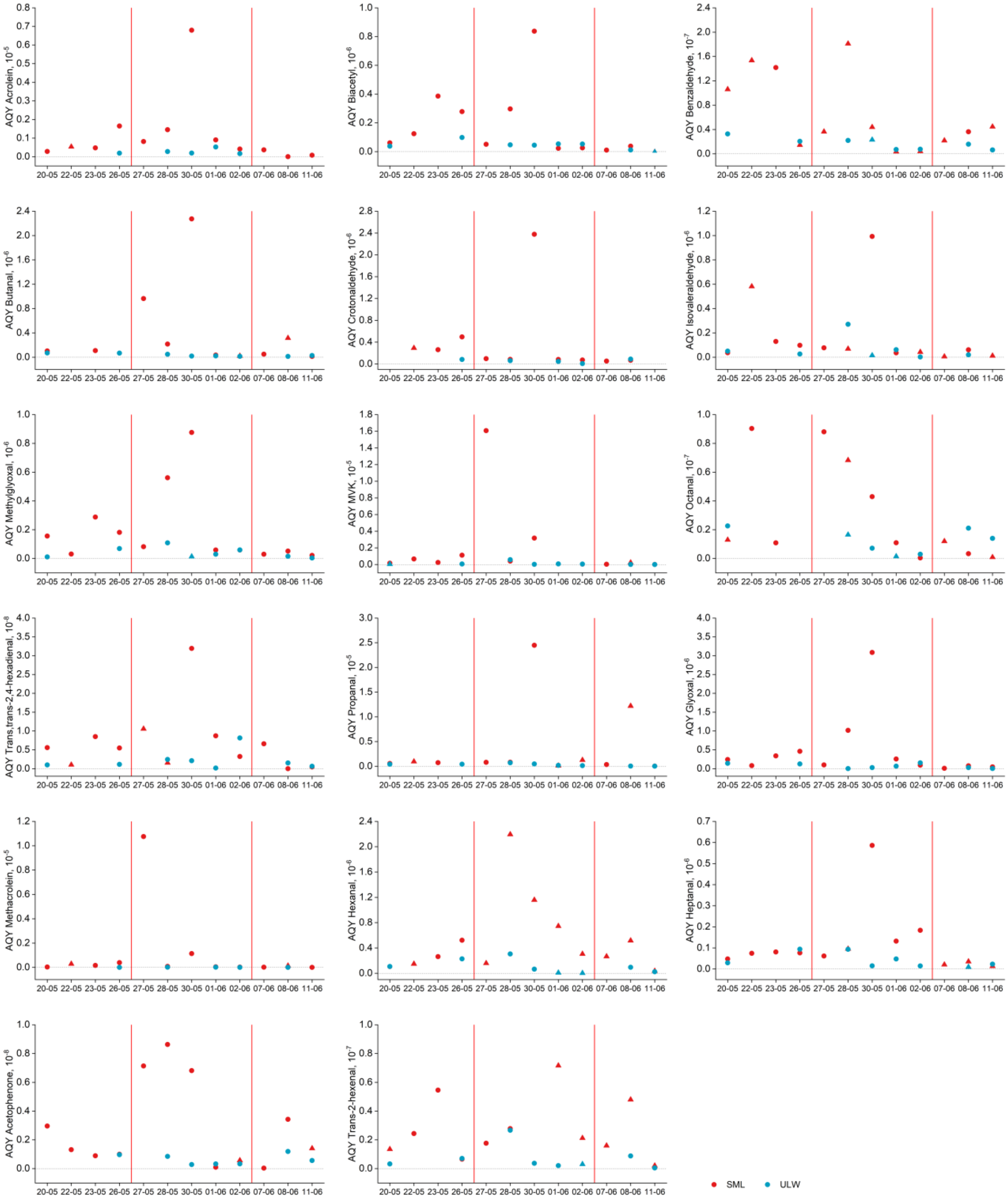


Figure S5: Calculated apparent quantum yields of the carbonyl compounds for each of the investigated SML (red) and ULW (blue) samples. Circles represent photochemical formation and triangles represent photochemical degradation.

As all the irradiation experiments were conducted using unfiltered samples, the calculated AQYs represent the effective photochemical efficiencies of the total organic matter pool, integrating the contributions from both dissolved and particulate organic matter. Therefore, AQYs normalize for both the chromophore absorbance and the light dose, reflecting the intrinsic photochemical efficiency of the system under natural conditions. The obtained AQYs reveal that the SML is generally more photochemically efficient than ULW, particularly in the bloom phase of the mesocosm study. To further address whether the enhanced photochemical activity could be attributed solely to organic matter abundance, AQYs were compared with the dissolved organic matter (DOC) concentrations reported by Bibi et al. (2025), as CDOM data were not available. No systematic relationship was observed between AQYs and the reported DOC concentrations (*Figure S6* in the revised Supplementary Information), indicating that the enhanced photochemical activity of the investigated compounds cannot be only explained by higher organic carbon abundance. Instead, these results suggest that differences in organic matter composition and reactivity in the SML, particularly in the bloom phase, play a more important role.

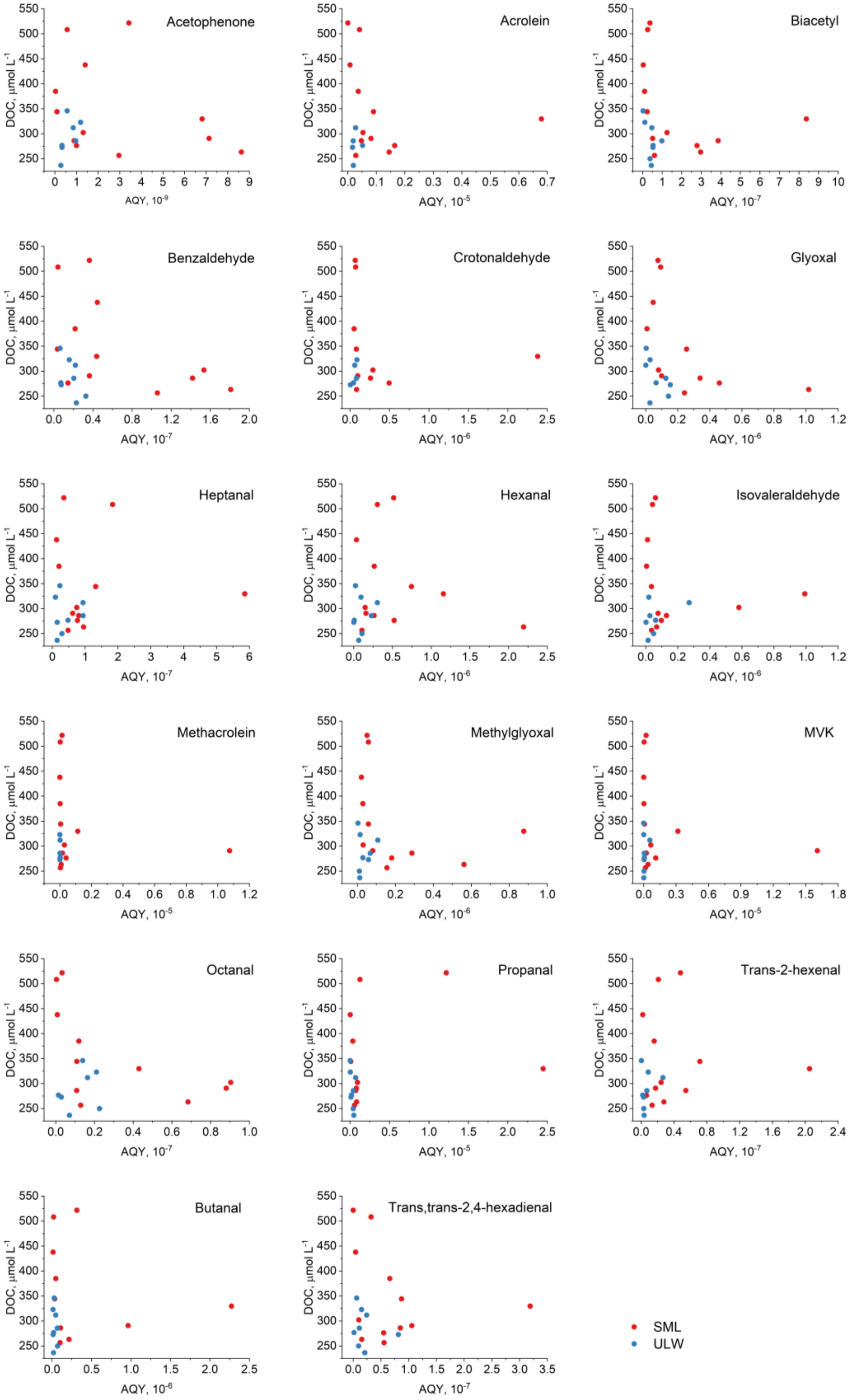


Figure S6: Calculated AQYs of the carbonyl compounds compared with the DOC concentrations.

The following has been added to the revised manuscript:

Page 18, Line 470-476: "Apparent quantum yields (AQYs) were calculated from the measured photoproduction rates and the absorbed photon fluxes (Supplementary Information, Sect. S6). Because the experiments were conducted using unfiltered samples, the derived AQYs represent effective photochemical efficiencies of the total OM pool. The results confirm that the SML is a more photochemically-efficient environment compared to ULW, particularly during the bloom phase. No systematic relationship was observed between AQYs and DOC concentrations (Supplementary Information, Figure S5), suggesting that OM abundance alone does not control the efficiency of these photochemical processes."

We also mentioned AQYs and their relation to DOC concentrations in the *Conclusions* of the revised manuscript:

Page 24, Line 631-634: "The calculation of AQYs suggests that the SML is a more photochemically efficient environment compared to ULW, particularly in the bloom phase of the study. No systematic relationship was found between AQYs and DOC concentrations, which indicates that OM abundance alone does not control the efficiency of the investigated processes."

Error bars in Figure 4 and Figure 5: We appreciate this important observation. Error bars can indeed be added for the rates in ULW samples; however, they are not readily visible when plotted on the same scale as the SML data due to the large contrast between the rates in both layers. Our intention to keep the same scale is for the reader to clearly visualize the differences between the photochemical activity in the SML and ULW. In order to address the comment from the reviewer, we have added a figure to the revised Supplementary Information (*Figure S4*), in which the rates in ULW have been plotted on an expanded scale with clearly visible error bars representing analytical and sample handling uncertainties.

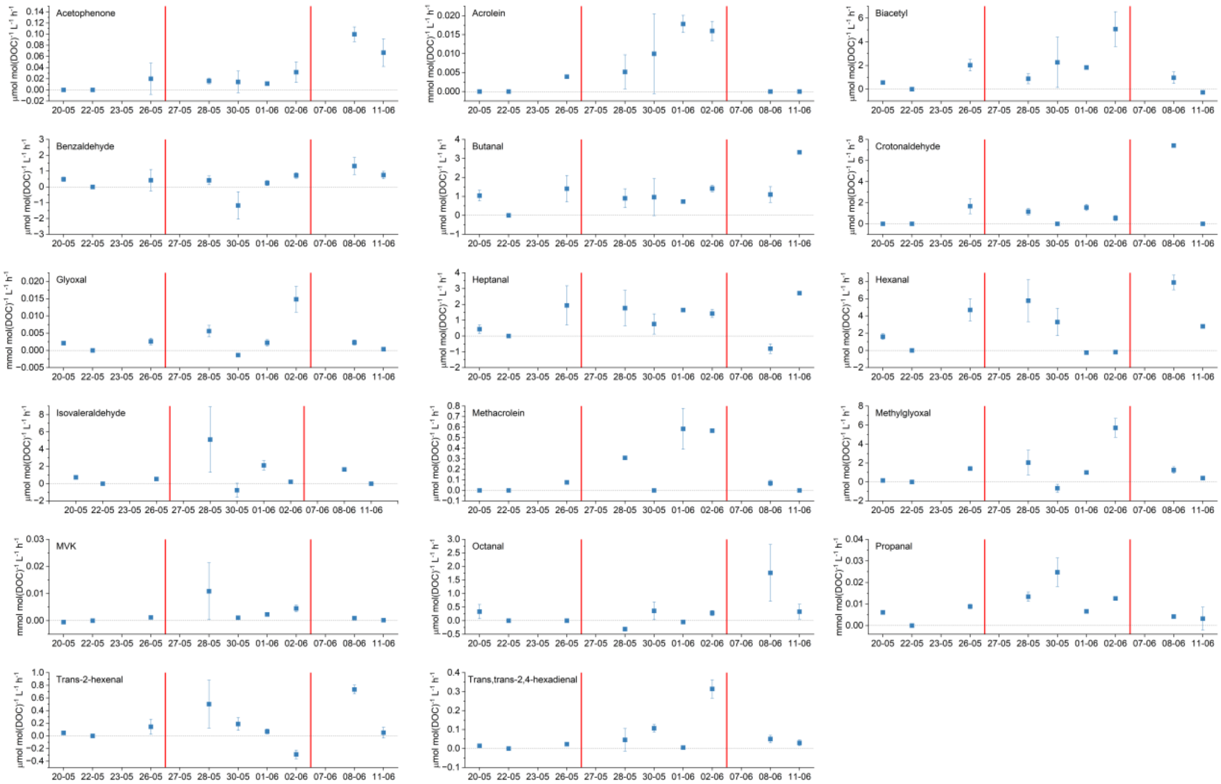


Figure S4: Photochemical production and degradation rates in the ULW samples on an expanded scale, including error bars that reflect analytical and sample-handling uncertainties.

The following has been added in the revised manuscript as part of the caption of *Figure 4* and *Figure 5*:

Page 16, Line 421-423; Page 17, Line 436-437: "Photochemical production and degradation rates in the ULW samples on an expanded scale, including error bars that reflect analytical and sample-handling uncertainties, are shown in Figure S4 in the Supplementary Information."

Normalization of photoproduction rates: In addition to the AQY calculations, photochemical formation and degradation rates have been normalized to DOC concentrations reported by Bibi et al. (2025) and shown in *Figure 4* and *Figure 5* in the revised manuscript.

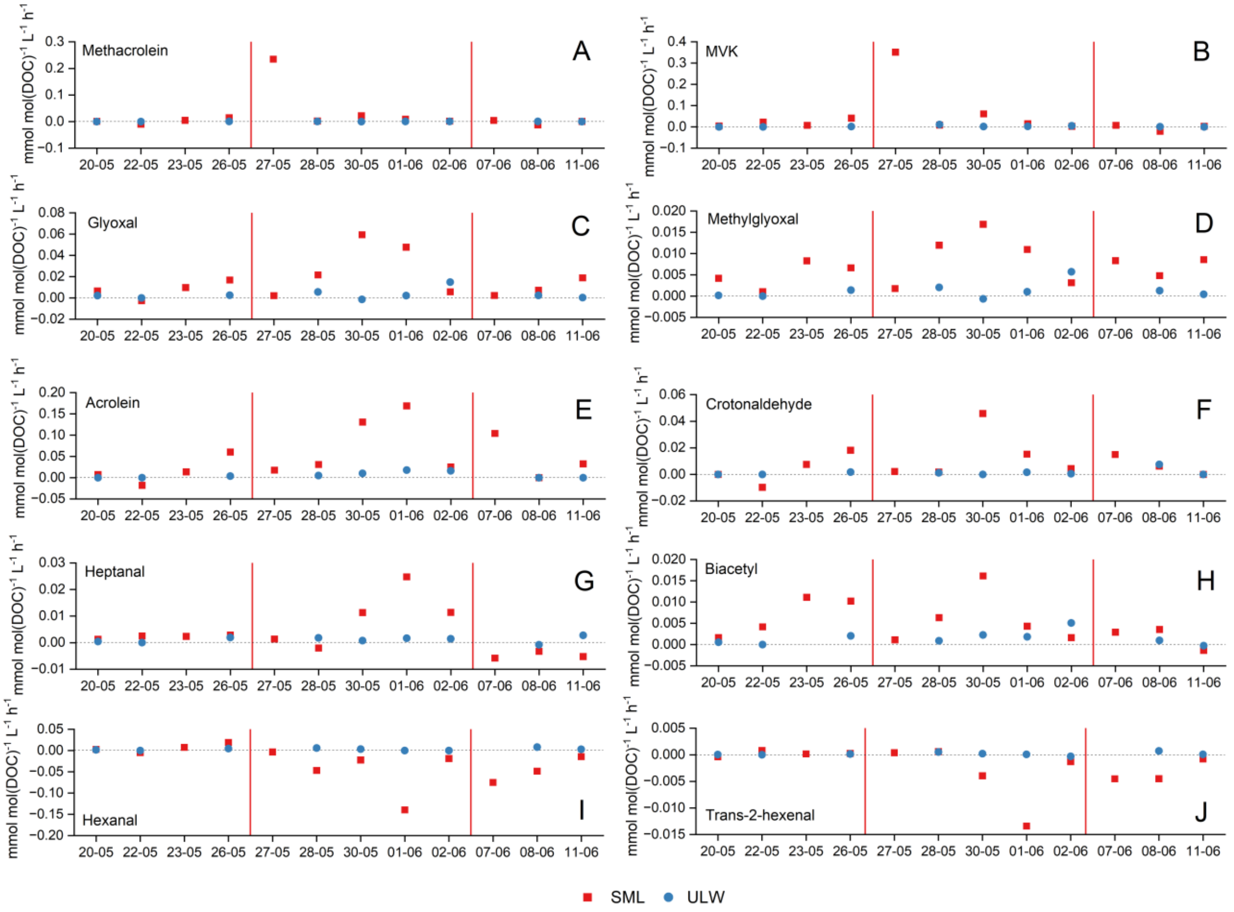


Figure 4: Comparison of photochemical formation and degradation rates of methacrolein (A), MVK (B), glyoxal (C), methylglyoxal (D), acrolein (E), crotonaldehyde (F), heptanal (G), biacetyl (H), hexanal (I) and trans-2-hexenal (J) in the SML (red) and in ULW (blue). The red vertical lines separate the three phases of the mesocosm study: pre-bloom (20-05 to 26-05), bloom (27-05 to 02-06) and post-bloom (08-06 to 11-06). Photochemical production and degradation rates in the ULW samples on an expanded scale, including error bars that reflect analytical and sample-handling uncertainties, are shown in Figure S4 in the Supplementary Information.

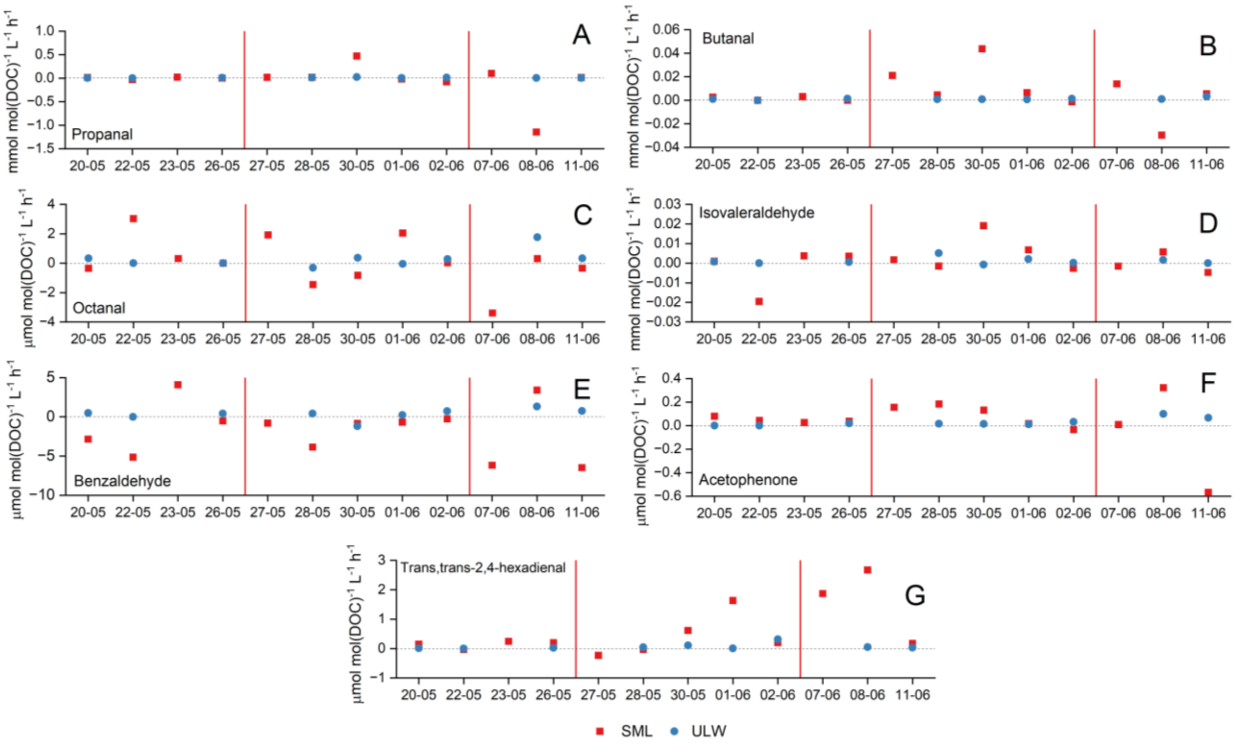


Figure 5: Comparison of photochemical formation and degradation rates of propanal (A), butanal (B), octanal (C), isovaleraldehyde (D), benzaldehyde (E), acetophenone (F) and trans,trans-2,4-hexadienal (G) in the SML (red) and in ULW (blue). The red lines separate the three phases of the mesocosm study: pre-bloom (20-05 to 26-05), bloom (27-05 to 02-06) and post-bloom (08-06 to 11-06). Photochemical production and degradation rates in the ULW samples on an expanded scale, including error bars that reflect analytical and sample-handling uncertainties, are shown in Figure S4 in the Supplementary Information.

This modification is also clearly mentioned in the text:

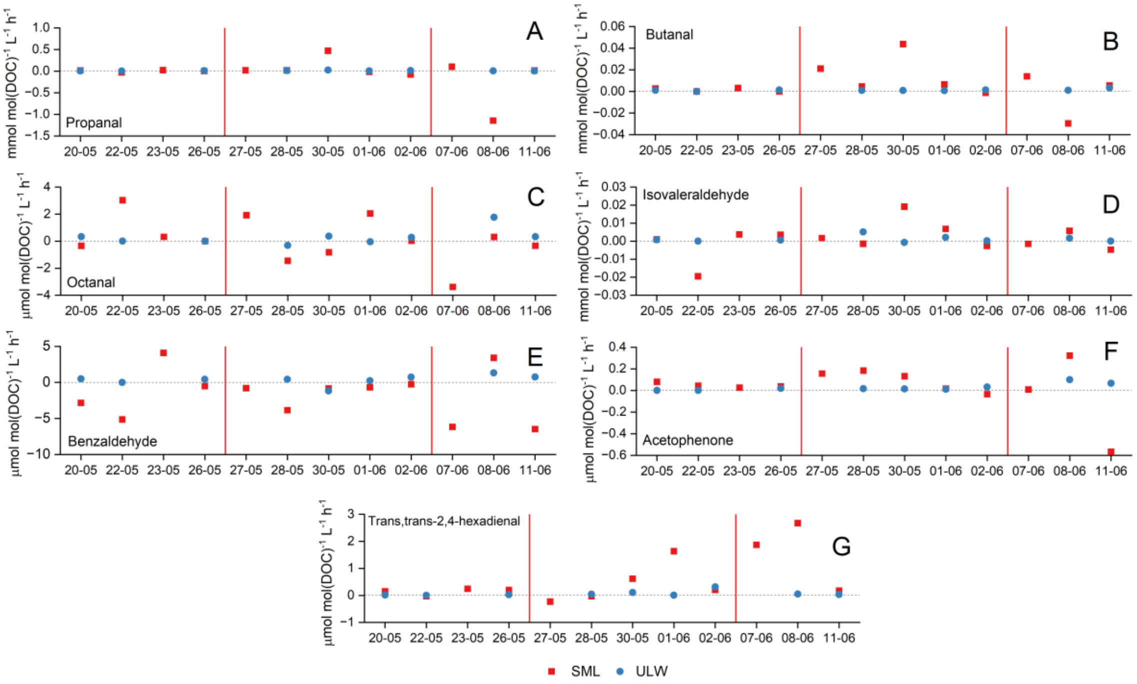
Page 13, Line 350-351: "We investigated the photochemical formation and degradation rates of the 17 carbonyl compounds in both SML and ULW samples (Fig. 4 and Fig. 5, expressed in mol mol(DOC)$^{-1}$ L^{-1} h^{-1})."

Absolute rates expressed nM h^{-1} have been maintained in the text for discussion of the results in order to facilitate the comparison with values reported in previous studies. The plots with the non-normalized rates have been moved to the revised Supplementary Information (*Figure S8* and *Figure S9*). We have added the following text in the revised manuscript to explain this:

Page 18, Line 458-459: "To facilitate comparison with existing literature, the non-normalized rates were also calculated and are provided in the Supplementary Information (Figure S8 and Figure S9)."

R1C4: Apparently, a wrong figure 5 was inserted. The Fig5 in the manuscript is a duplicate of Fig. 4.

A-R1C4: We thank the reviewer for identifying this mistake. In the original manuscript, Figure 5 was unintentionally duplicated from Figure 4. We have replaced it with the correct *Figure 5* in the revised manuscript (*Page 17*, *Line 430*).



R1C5: Section 3.2.1 is all literature review. The authors did an excellent job summarizing the carbonyl sources and sinks but there is a lack of connection with the actual results obtained in the work.

A-R1C5: We value this constructive comment. We agree that the original version of Section 3.2.1 was largely descriptive and not connected to the experimental results. To address this, we have revised the manuscript and integrated this literature discussion with observed photochemical production and degradation trends. To be more specific, the content of Section 3.2.1 has now been moved to *Section 3.2* of the revised manuscript. This restructuring strengthens the interpretation of our results by explaining how known formation and degradation pathways are also reflected in the experimental observations.

R1C6: For the gas-transfer rate estimations, it appears that the authors assume all carbonyls produced in the surface microlayer (SML) are transferred to the gas phase according to equilibrium partitioning. While I appreciate the simplicity of this assumption, I am not convinced it accurately represents the process, as in situ carbonyl loss (abiotic + biotic) within the SML (e.g., via photolysis or further reactions) may be rapid and could substantially reduce the effective transfer rate. An alternative and potentially more realistic approach would be to estimate the transfer flux based on the predicted concentrations on both sides of the air-water interface.

A-R1C6: We thank the reviewer for raising this important point. We agree that our equilibrium-based assumption simplifies the studied transfer processes and does not fully represent what occurs in ambient conditions. Assuming that all carbonyl compounds photochemically-produced in the SML are potentially transferred to the atmosphere neglects the contribution of other abiotic and biotic in situ loss processes in the SML (e.g., photolysis or microbial consumption), which can indeed decrease the fraction of carbonyl compounds that are actually available for volatilization under ambient conditions. However, we would like to emphasize that the intention of this study was not to provide an accurate representation of ambient air-sea fluxes, but rather to derive upper-limit estimates to point to the potential enhancement of air-sea exchanges influenced by a phytoplankton bloom and motivate future modelling efforts. Neither our dataset nor the existing literature allows us to resolve individual loss pathways to make a more realistic estimation on how air-sea exchanges can be influenced by the presence of phytoplankton blooms. Existing predictions, unfortunately, do not yet elaborate on how concentrations in the atmosphere may be impacted locally by biological events. Nevertheless, in order to address the reviewer's suggestion and explore a more realistic alternative, we have implemented an additional transfer estimate using concentration gradients for glyoxal as a case study. Minimum and maximum concentrations of glyoxal in bloom and non-bloom conditions for non-irradiated SML samples were taken as the aqueous-phase concentrations in the interface. For the concentrations in the air interface, we used the value of 10 ppt reported for the tropical Atlantic boundary layer (Walker et al., 2022). The gas transfer velocity (*k*) has been estimated using the aqueous-phase diffusion coefficient of glyoxal (Curry et al., 2018) and an assumed SML thickness of 100 µm. Details of these calculations are provided in the revised Supplementary Information (*Sect. S5.2*). Using this approach, the estimated transfer fluxes ranged between (1.7 – 20.8) × 10^{-4} nmol cm^{-2} s^{-1} in non-bloom conditions, and (4.1 – 29.4) × 10^{-4} nmol cm^{-2} s^{-1} during the bloom. While still being a simplified approach due to the limited data, this gradient-based estimate integrates the net effect of other formation and degradation processes influencing total glyoxal concentrations in the air-sea interface. In contrast, the rates of transfer of photochemically-produced carbonyl compounds from the SML to the gas interface calculated using equilibrium partitioning (revised Supplementary Information, *Sect. S5.1*) are explicitly limited to the photochemically-produced carbonyl compounds.

In order to clearly recognize this limitation and avoid any overinterpretation of the provided estimations, the text has been amended in *Sect. 3.4* of the revised manuscript as follows:

Page 23, Line 593-611: "These results aim to serve as a preliminary basis for motivating new experimental efforts and refining air-sea exchange models, particularly by highlighting the role of the SML in the photochemical production of carbonyl compounds and its implications in the formation of SOAs. We note that these estimations neglect the potential contribution of in situ loss processes within the SML, such as photolysis and microbial consumption, which may substantially decrease the fraction of photochemically-produced carbonyl compounds available *for volatilization under ambient conditions. For this reason, the transfer rates presented in the present study shall be interpreted as upper-limit approximations.*

While these equilibrium-based transfer estimates provide useful upper limits, an air-sea transfer estimate based on concentration gradients was explored for glyoxal as a case study, integrating measured SML concentrations under bloom and non-bloom conditions with representative atmospheric values (Supplementary Information, Sect. S5.2). The resulting transfer fluxes range between (1.7 – 20.8) × 10^{-4} nmol cm^{-2} s^{-1} in non-bloom conditions, and (4.1 – 29.4) × 10^{-4} nmol cm^{-2} s^{-1}. In contrast to the rates of transfer of photochemically-produced carbonyl compounds calculated using equilibrium partitioning (Sect. S5.1), the transfer fluxes estimated using the concentration gradient approach consider total glyoxal concentrations measured in the non-irradiated SML and in the atmosphere in the marine environment. This means that the gradient-based transfer fluxes reflect overall values that integrate all possible processes, while the results obtained in Sect. S5.1 are limited to the photochemically-produced compounds.

Overall, the increased transfer rates observed for several carbonyl compounds during the phytoplankton bloom highlight the need to incorporate the complex interplay of biotic and abiotic factors into marine VOC inventories, which may help to reduce discrepancies between model predictions and real-world observations, especially in coastal areas where blooms are frequent."

As we are now implementing a second approach (concentration gradients) to estimate the transfer fluxes, we have explicitly differentiated the first approach (equilibrium partitioning) in the revised manuscript:

Page 22, Line 572-573: "Table 2: Estimated rates of transfer of photochemically-produced carbonyl compounds from the SML to the gas interface (c_{sl}) according to equilibrium partitioning."

Page 22, Line 578-579: "The estimated rates of transfer of photochemically-produced carbonyl compounds from the SML to the atmosphere according to equilibrium partitioning were generally higher during the bloom phase for the majority of the compounds, namely acrolein, biacetyl, butanal, crotonaldehyde, glyoxal, heptanal, methacrolein, methylglyoxal, MVK, propanal and trans-2-hexanal."

R1C7: I don't see any measurement for the phytoplankton community structure in the mesocosms, and how did the authors concluded that initial bloom was dominated by coccolithophore and the subsequent bloom by diatom?

A-R1C7: We thank the reviewer for this suggestion and agree that a detailed biological characterization of the seawater samples is important for properly conceptualizing the observed photochemical transformations in the different phases of the bloom. During the mesocosm study, the daily concentrations of chlorophyll *a* were used as the primary indicator to define the bloom development, and other biological parameters were measured and are reported in detail by Bibi et al. (Bibi et al., 2025), based on the same mesocosm study. The dominance of *Emiliania huxleyi* (coccolithophore) during the initial bloom phase and a subsequent increase of *Cylindrotheca Closterium* (diatoms) during the latter bloom phase were derived from pigment analysis and described in detail therein. In order to address the comment of the reviewer, we have expanded the text in the revised manuscript to include additional information on phytoplankton pigments, organic carbon pools and bacterial abundance and provide the full biological characterization of the mesocosm, with explicit reference to Bibi et al. (2025) to clarify that these conclusions are based on published data.

Page 4-5, Line 117-132: "The concentrations of other phytoplankton pigments in the ULW samples followed similar trends to the ones reported for chlorophyll a. Concentrations of chlorophyll c, a photosynthetic pigment present in haptophytes ranged between 0.07 and 2.10 µg L^{-1}, peaking on May 28th, June 1st and June 3rd. Chlorophyll b and β-carotene were found between 0.04 and 0.40 µg L^{-1}, and 0.04 and 0.30 µg L^{-1}, respectively. Even though chlorophyll b and β-carotene seemed to have a minor contribution to the total phytoplankton mass, they also experienced an increase that reached maximum values between June 1st and June 3rd. Overall, the observed trends support the presence of a nutrient-driven phytoplankton bloom, which consisted of an initial dominance of Emiliania huxleyi (coccolithophore), followed by a subsequent growth of Cylindrotheca Closterium (diatoms) (Fig. 1) (Bibi et al., 2025). To further contextualize the biological development of the mesocosm, dissolved organic carbon (DOC) and particulate organic carbon (POC) concentrations were also analysed. DOC concentrations ranged from 245 to 583 µmol L^{-1} in the SML, and from 207 to 373 µmol L^{-1} in ULW. DOC concentrations increased during the phytoplankton bloom phase, and remained elevated in the post-bloom phase of the study. On the other hand, POC concentrations measured in the ULW samples were between 23 and 173 µmol L^{-1}, and their temporal trend along the mesocosm study was comparable to that of the chlorophyll a concentrations. In terms of bacterial abundance, which includes both free bacteria and bacteria-like material, it peaked in the post-bloom stage and ranged from 481 × 10^{6} to 1468 × 10^{6} in the SML, and from 245 × 10^{6} to 1681 × 10^{6} in the ULW. An enrichment factor (EF) of 1.3 ± 0.7 was found during the phytoplankton bloom. A detailed characterization of the biological parameters in this mesocosm study is provided by Bibi et al. (2025)."

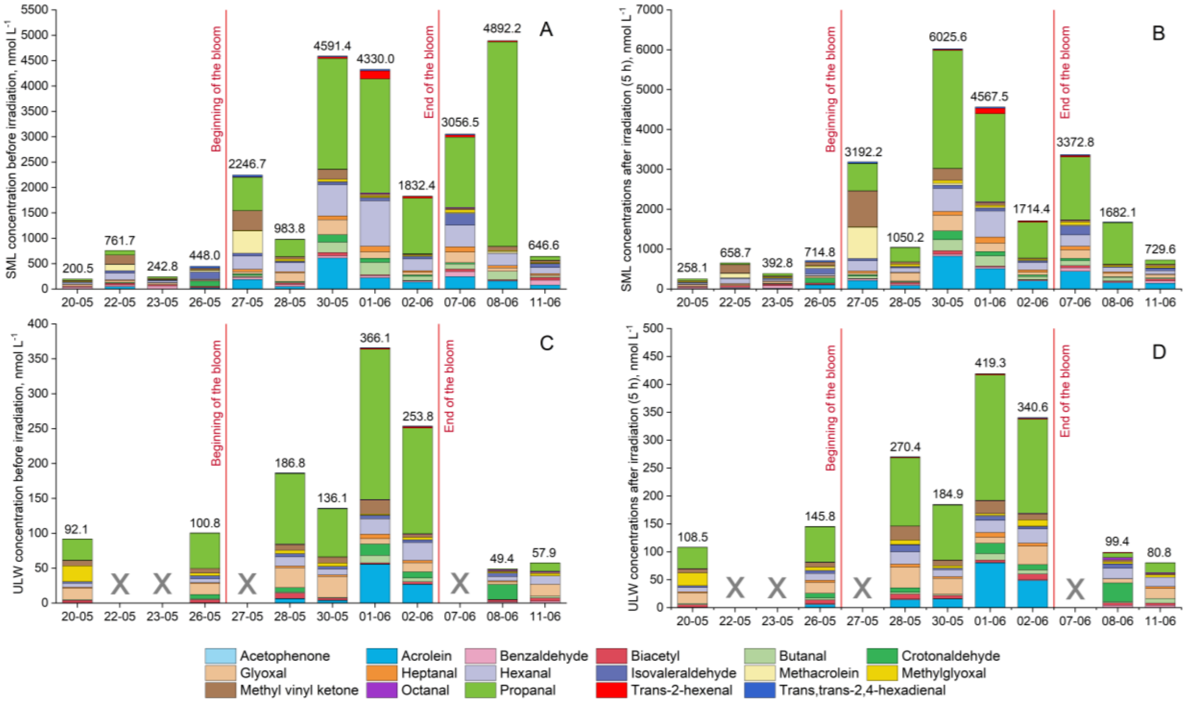
R1C8: The propanal concentrations are indeed very high in the samples, which is a novel finding and I feel that the authors should highlight this more. Also a minor comment is that the name propionaldehyde and propanal are both used in the manuscript and I would pick one to be consistent.

A-R1C8: We thank the reviewer for pointing out this important topic.

High propanal concentrations: We agree that the consistently high concentrations of propanal represent a notable and potentially novel result in this study. A particularly high propanal concentration was observed in the SML sample collected on June 8th, but the overall trend points to propanal as a potentially significant and previously overlooked component of the carbonyl pool in the SML during a phytoplankton bloom and in the post-bloom stage. However, we deliberately refrain from overinterpreting this observation as we think we need further future studies and more replicates to elaborate on what it potentially means. We added the following text to identify propanal as a key outcome that would deserve further targeted investigation:

Page 11, Line 304-307: "Propanal exhibited remarkably higher concentrations with respect to other species, particularly in the SML during the bloom and post-bloom phases. This suggests that propanal may represent an important, yet previously underrecognized, contributor to the carbonyl pool at the air-sea interface. Further targeted studies with increased temporal resolution and replication are required to better understand the specific mechanisms driving its massive production in these conditions."

Propanal vs. propionaldehyde: In the caption of *Figure 3* in the revised manuscript, the name "propionaldehyde" has been changed to "propanal" to ensure consistency in the whole manuscript.



R1C9: The photooxidation capacity is relatively stable across the sampling period. Instead of attribute to influence by metals, maybe the enhanced rate just represents the abundance of chromophores instead of enhanced photoreactivity or photoproduction efficiency? This aligns with my above comment regarding the AQYs. I suggest the authors reconsider this part of the discussion after the AQYs are calculated.

A-R1C9: We thank the reviewer for this insightful observation, which stresses the importance of calculating the AQYs to have a better context on the photochemical processes in the investigated samples. As advised in a previous comment (R1C3), AQYs have been calculated for all 17 carbonyl compounds for each investigated SML and ULW sample. AQYs and DOC concentrations have been compared to evaluate any potential systematic relationship between the photochemical efficiency of the samples and the organic matter abundance, and no correlation has been observed. Similarly, we examined potential connections between the DOC concentrations and the measured photooxidation capacities and found no correlation, indicating that the observed photochemical activity cannot be solely attributed to the abundance of organic matter. This analysis has been added to the revised Supplementary Information as *Figure S7*.

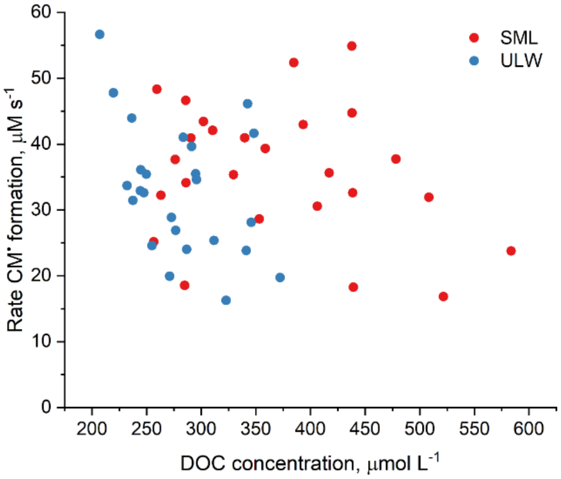


Figure S7: Calculated rates of CM radical formation compared with the DOC concentrations.

While the complexity of the mesocosm seawater samples makes it difficult to attribute the oxidation properties to specific compounds, metal ions are a known class of redox-active species in marine systems that could influence the observed photooxidation capacity. Our study proposes the potential contribution of such processes, but a deeper, more targeted investigation would be required to accurately quantify the role of metal ions and other redox-active components in driving photooxidation. The following text was added to the revised manuscript:

Page 19, Line 504-507: "To evaluate whether these results reflect enhanced photochemical reactivity or simply the highest abundance of OM the measured photooxidation capacities were compared to DOC concentrations (Supplementary Information, Figure S7). No systematic correlation was found, indicating that the observed results cannot be explained solely by the abundance of OM."

Page 20, Line 527-528: "Further targeted studies are needed to quantify the relative roles of metal ions and other redox-active components in influencing seawater photooxidation."

The following has been added to the Conclusions in the revised manuscript:

Page 24, Line 639-641: "After accounting for the differences in DOC levels measured along the mesocosm study, these results indicate that photooxidation capacity cannot be solely explained by variations of OM abundance. Instead, they suggest a dominance of redox-active species, such as metal ions, rather than by biological processes."

Reviewer: 2

Comments:

The study investigates the photochemistry of the sea surface microlayer (SML) and underlying water (ULW) collected during a mesocosm-induced phytoplankton bloom. The authors investigate the photochemical production and degradation of 17 specific carbonyl compounds and the overall photooxidation capacity of the samples. They conclude that selective photochemical activity in the SML possibly reflects a link between photochemical reactivity and bloom-driven changes in DOM composition, while the estimated photooxidation rates highlight the potential role of redox-active species, such as metal ions, in controlling photooxidation capacity.

However, several critical issues concerning sample handling, characterization, and data presentation and interpretation require clarification. Addressing the points outlined below is essential to strengthen the main findings, as in their current form the results are not sufficiently convincing and do not appear to make a meaningful contribution to the field.

We thank the reviewer for the detailed and constructive evaluation of our manuscript. The comments raised important concerns regarding data presentation and interpretation, and the biological contextualization of the mesocosm study, which have been instrumental in strengthening the scientific rigor and clarity of our study. We have carefully addressed each point by revising the manuscript, expanding the contextual and methodological discussion, and refining the presentation and interpretation of the results. We believe that these revisions adequately address the reviewer's concerns and substantially improve the robustness and impact of our manuscript.

R2C1: The unfiltered SML and ULW samples were frozen immediately after collection, then thawed and irradiated without further filtration. Under such conditions, both DOC and POC fractions—including cells, cellular debris, and particulate biological material released due to freeze–thaw rupture—are subject to photochemical transformations. Despite this, the manuscript interprets carbonyl dynamics solely within the context of the DOC pool, while the potentially substantial contribution of the particulate fraction is not addressed. Without accounting for the POC fraction, the interpretation of carbonyl production and degradation remains incomplete, and the overall experimental design—based on irradiation of unfiltered samples—was inadequately conceived for drawing the conclusions presented. I strongly recommend that the authors revise statements throughout the manuscript that rely on assumptions regarding the DOC pool alone, without considering possible contributions from the particulate fraction.

A-R2C1: We thank the reviewer for raising this important point regarding the irradiation of unfiltered seawater samples and the potential contribution of particulate organic matter (POM) to the observed photochemical transformations. We agree that freezing, thawing, and subsequent irradiation of unfiltered SML and ULW samples implies that both dissolved organic carbon (DOC) and particulate organic carbon (POC), including cells, cellular debris and particular biological material released upon freeze-thaw disruption, may contribute to the observed production and degradation of the carbonyl compounds. The experimental design deliberately consisted of irradiating unfiltered samples in order to preserve as much as possible the natural chemical and biological complexity of the SML and ULW. Nevertheless, we acknowledge that this approach does not allow a strict separation between DOC- or POC-derived photochemical processes. That being the case, the observed carbonyl transformations should be interpreted as the result of the combined photochemical transformation of DOM and POM, rather than from the DOC pool alone. To address this point, we have revised the manuscript to explicitly acknowledge that the observed photochemical formation and degradation rates of the investigated carbonyl compounds may reflect contributions from both DOC and POC. We have avoided attributing the observed effects solely to DOC, and have amended the statements where this distinction was implicit. Based on available data from the same mesocosm study published by Bibi et al. (2025), POC concentrations in ULW samples accounted for an average of 17% of the total organic carbon (DOC + POC). While corresponding POC concentrations are not available for the SML, this information suggests that DOC represents the dominant organic carbon pool in the bulk water. However, due to the absence of POC measurements for the SML, we do not attempt to quantitatively separate DOC and POC contributions in our calculations, and the derived rates should then be considered as integrated responses of the total organic matter pool.

Accordingly, we have added the following statement in the *Methods* (*Sect. 2.1*) and *Results and discussion* (*Sect. 3.1*) to clearly frame this interpretation:

Page 5, Line 139-141: "All experiments were conducted using unfiltered samples in order to preserve as much as possible their natural complexity, and the results therefore reflect the combined photochemical processes involving both DOM and POM."

Page 11, Line 294-298: "The observed photochemical transformations of carbonyl compounds likely arise from the combined processing of both the DOM and POM (including intact cells, cellular debris, and particulate biological material potentially released during freeze-thaw cycles). As a result, the reported photochemical rates represent the integrated responses of the total organic matter pool present in the SML and in ULW."

We believe that these amendments and clarifications strengthen the consistency between the experimental design and the interpretation of the obtained results, and ensure that the conclusions are framed within the limitations of the study.

R2C2: The manuscript does not provide essential information about the bloom itself. The authors describe the bloom progression exclusively through chlorophyll a, but do not present phytoplankton cell abundances and community composition. There is also not information about the abundance of heterotrophic bacteria which could be highly enriched in the SML. This lack of biological information raises concerns about how well the biological context of the experiment is constrained. At least, it would be useful to provide more details on this aspect and supplement the data with POC concentrations additionally indicating the pooled biological development during the experiment.

A-R2C2: We thank the reviewer for this important comment and agree that a robust biological characterization of the seawater samples is essential for properly conceptualizing the observed photochemical transformations in the different phases of the phytoplankton bloom. During the mesocosm study, the daily concentrations of chlorophyll *a* were indeed used as the primary indicator of the bloom development in our study. However, we acknowledge that this metric alone does not fully capture the complexity of the biological system. Additional biological parameters, including phytoplankton pigment composition, phytoplankton community structure, POC, DOC and bacterial abundance, were measured throughout the mesocosm study and are reported in detail by Bibi et al. (Bibi et al., 2025). In the original manuscript, we briefly summarized these findings documented by Bibi et al. as follows: "The bloom consisted of an initial bloom where *Emiliania huxleyi* (coccolithophore) was dominant, and a subsequent bloom of *Cylindrotheca Closterium* (diatoms) had higher relevance (Fig. 1) (Bibi et al., 2025). Dissolved organic carbon (DOC) concentrations increased during the phytoplankton bloom phase, and remained elevated in the post-bloom phase of the study.". To directly address the reviewer's concern, we have now expanded *Section 2.1* to provide a clearer picture of the biological development of the mesocosm during the study. Specifically, the revised manuscript now includes (1) pigment signatures supporting an initial dominance of *Emiliania huxleyi*, followed by an increase relevance of *Cylindrotheca closterium*, (2) concurrent increases of DOC and POC during the bloom phase, (3) elevated bacterial abundance. By including these observations, we aim to strengthen the biological context in which the reported photochemical transformations occurred. We have amended the text as follows:

Page 4-5, Line 117-132: "The concentrations of other phytoplankton pigments in the ULW samples followed similar trends to the ones reported for chlorophyll a. Concentrations of chlorophyll c, a photosynthetic pigment present in haptophytes ranged between 0.07 and 2.10 µg L^{-1}, peaking on May 28th, June 1st and June 3rd. Chlorophyll b and β-carotene were found between 0.04 and 0.40 µg L^{-1}, and 0.04 and 0.30 µg L^{-1}, respectively. Even though chlorophyll b and β-carotene seemed to have a minor contribution to the total phytoplankton mass, they also experienced an increase that reached maximum values between June 1st and June 3rd. Overall, the observed trends support the presence of a nutrient-driven phytoplankton bloom, which consisted of an initial dominance of Emiliania huxleyi (coccolithophore), followed by a subsequent growth of Cylindrotheca Closterium (diatoms) (Fig. 1) (Bibi et al., 2025). To further contextualize the biological development of the mesocosm, dissolved organic carbon (DOC) and particulate organic carbon (POC) concentrations were also analysed. DOC concentrations ranged from 245 to 583 µmol L^{-1} in the SML, and from 207 to 373 µmol L^{-1} in ULW. DOC concentrations increased during the phytoplankton bloom phase, and remained elevated in the post-bloom phase of the study. On the other hand, POC *concentrations measured in the ULW samples were between 23 and 173 µmol L^{-1}, and their temporal trend along the mesocosm study was comparable to that of the chlorophyll a concentrations. In terms of bacterial abundance, which includes both free bacteria and bacteria-like material, it peaked in the post-bloom stage and ranged from 481 × 10^6 to 1468 × 10^6 in the SML, and from 245 × 10^6 to 1681 × 10^6 in the ULW. An enrichment factor (EF) of 1.3 ± 0.7 was found during the phytoplankton bloom. A detailed characterization of the biological parameters in this mesocosm study is provided by Bibi et al. (2025).”*

Additionally, we have mentioned the average concentrations of chlorophyll *a* at each stage of the bloom to complement the data presented in Figure 1.

Page 4, Line 112: an initial pre-bloom phase, with lower chlorophyll *a* levels *(average: 2.2 µg L^{-1})* prior to nutrient addition (May 18th to May 26th);

Page 4, Line 114-115: a nutrient-induced bloom phase, (May 27th to June 4th), characterized by a rapid increase in phytoplankton mass *(average: 7.3 µg L^{-1})*;

Page 4, Line 116: (3) a post-bloom phase, marked by the gradual decline in phytoplankton biomass *(average: 1.8 µg L^{-1})* (June 5th to June 16th).

R2C3: Figure 3 is central to interpreting photochemical changes in carbonyl compounds. However, presenting only absolute concentrations before and after irradiation provides limited insight and the figure is difficult to read in its current form. I recommend to consider presenting relative changes (e.g., % increase/decrease) instead, which would allow the irradiation-induced effects easier to interpret. Absolute values can remain in the Supporting Information. Moreover, Figure 3 lacks standard deviations, making it hard to assess whether observed differences are statistically meaningful. While I understand that limited SML volume may constrain replication, at least the ULW samples should include variability between the replicates reflecting analytical and sample-handling uncertainty. Both improvements would substantially strengthen the findings, as in their current form they are not sufficiently convincing .

A-R2C3: We thank the reviewer for emphasizing the central role of Figure 3 in supporting the main conclusions of the study. We agree that improving data presentation and contextualization is essential to strengthening the robustness and interpretability of our results.

Relative changes vs. absolute concentrations: To address the concern that absolute concentrations alone provide limited insights into effects induced by irradiation, we have calculated the irradiation induced relative changes (% increase/decrease) for all quantified carbonyl compounds and now present these data as box plots in the revised Supplementary Information (*Figure S3*).

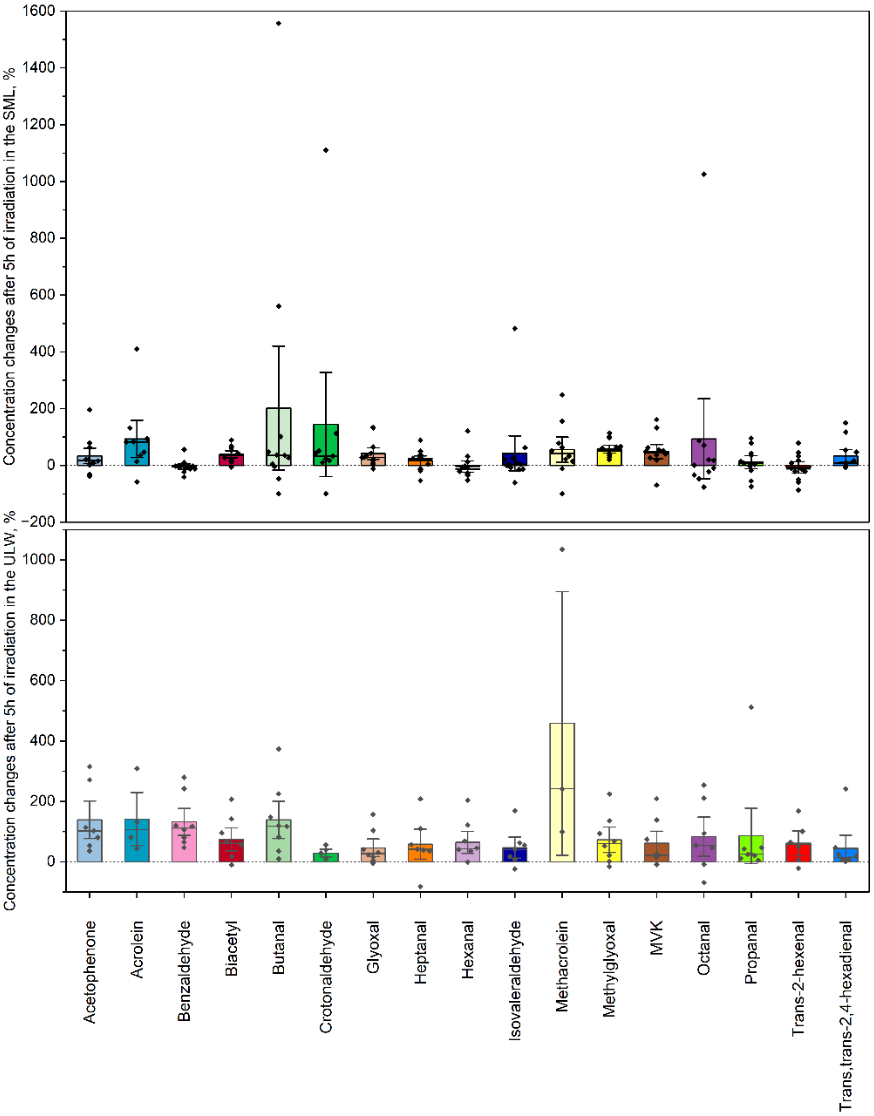


Figure S3: Relative concentration changes (%) after 5 hours of irradiation of 17 carbonyl compounds in the investigated SML and ULW samples. Boxes represent the interquartile range, the line in each box represents the median, and the whiskers extend to 1.5 times the interquartile range.

This representation allows a clearer comparison of photochemical responses across compounds, and directly addresses the reviewer's concern regarding the clarity and interpretability of the effects driven by irradiation. We propose to keep Figure 3 with absolute concentrations in the main manuscript because it allows the reader to directly visualize (1) the temporal evolution of carbonyl compound concentrations as the bloom develops, and (2) differences between SML and ULW before and after irradiation. We believe these temporal and matrix patterns are essential for interpreting the changes in carbonyl speciation driven by the bloom and by irradiation, while the added plots with the relative changes provide a complementary perspective.

The following has been added in the revised manuscript to guide the reader:

Page 11, Line 293-298: "Relative changes induced by irradiation (% increase/decrease) in carbonyl compound concentrations are shown in Figure S3 (Supplementary Information) to facilitate comparison of photochemical responses across compounds."

<u>Error bars for the ULW samples:</u> We acknowledge that the absence of error bars in Figure 3 limits the direct evaluation of the variability induced by analytical and sample-handling uncertainties. As the reviewer mentioned, replicate analysis of SML samples was not feasible since the volume of collected SML was limited. For ULW samples, analytical replicates were available. As including error bars directly in Figure 3 would substantially reduce readability due to the large number of compounds and overlapping bars, we have addressed this limitation by adding a new figure in the revised Supplementary Information (*Figure S4*), in which the photochemical production and degradation rates in ULW samples are shown with clearly visible error bars representing analytical and sample-handling uncertainty.

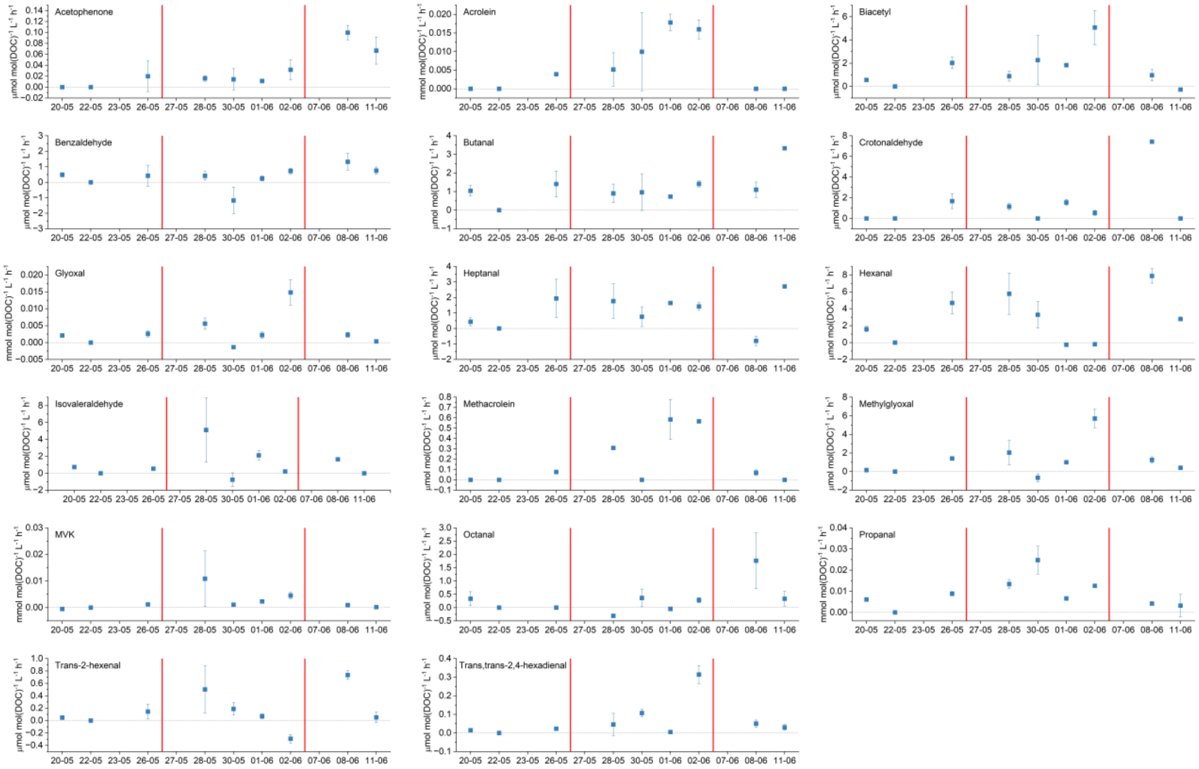


Figure S4: Photochemical production and degradation rates in the ULW samples on an expanded scale, including error bars that reflect analytical and sample-handling uncertainties.

The following has been added in the revised manuscript as part of the caption of Figure 4 and Figure 5 to guide the reader:

Page 16, Line 421-423; Page 17, Line 436-437: "Photochemical production and degradation rates in the ULW samples on an expanded scale, including error bars that reflect analytical and sample-handling uncertainties, are shown in Figure S4 in the Supplementary Information."
These revisions aim to directly address the reviewer's concerns regarding data presentation and uncertainty. We believe that they substantially support the evidential basis of the obtained results and their contribution to understanding photochemical processes in the SML and ULW influenced by a phytoplankton bloom.

R2C4: It is not surprising that higher concentrations of carbonyl compounds were detected during the phytoplankton bloom phase, as overall OM increase during this period as well. It appears that the variability of DOC concentrations resulting from irradiation was not reported. To strengthen the interpretation and conclusion, it would be important to assess changes in the contribution of carbonyls to DOC (%) before and after irradiation. Moreover, it is not surprising that higher photochemical production rates were measured for the SML compared to the ULW due to the SML enrichments in organic matter. Therefore, it is unclear whether and how the authors accounted for initial OC levels when calculating photochemical formation and degradation rates. The same concern applies to the evaluation of photooxidation capacity using the radical probe in the EPR experiments. Because the authors report similar photooxidation rates across bloom phases and between SML and ULW, the influence of differing OC levels on these rates should be discussed. Accounting for above, I strongly recommend that authors reconsider the statements throughout the text, including conclusions.
A-R2C4: We thank the reviewer for this detailed and insightful comment, which raises an important point regarding the influence of initial organic carbon (OC) levels in the interpretation of the carbonyl photochemistry and the photooxidation capacity. In response, we have substantially revised our data analysis and interpretation to explicitly account for differences in OC abundance between SML and ULW samples, and we have reconsidered relevant statements throughout the manuscript.

Normalization of initial OC levels: To address the concern that higher photochemical rates in the SML may simply reflect higher organic matter concentrations, the photochemical production and degradation rates have now been normalized to the corresponding DOC concentrations for each sample, which were reported by Bibi et al. (2025) and shown in Figure 1. Unfortunately, POC concentrations could not be considered for this normalization because they were not measured for SML samples. This modification is reflected in the revised *Figure 4* and *Figure 5*, where the rates are no longer expressed as nM h^{-1}, but mmol mol(DOC)$^{-1}$ L^{-1} h^{-1} or µmol mol(DOC)$^{-1}$ L^{-1} h^{-1}. After this normalization, the temporal trends in the photochemical activity remain similar across the three bloom phases, indicating that the observed patterns are not solely driven by the initial OC concentrations. Absolute rates expressed nM h^{-1} have been maintained in the main text for the description and discussion of the results in order to facilitate the comparison with values reported in previous studies.

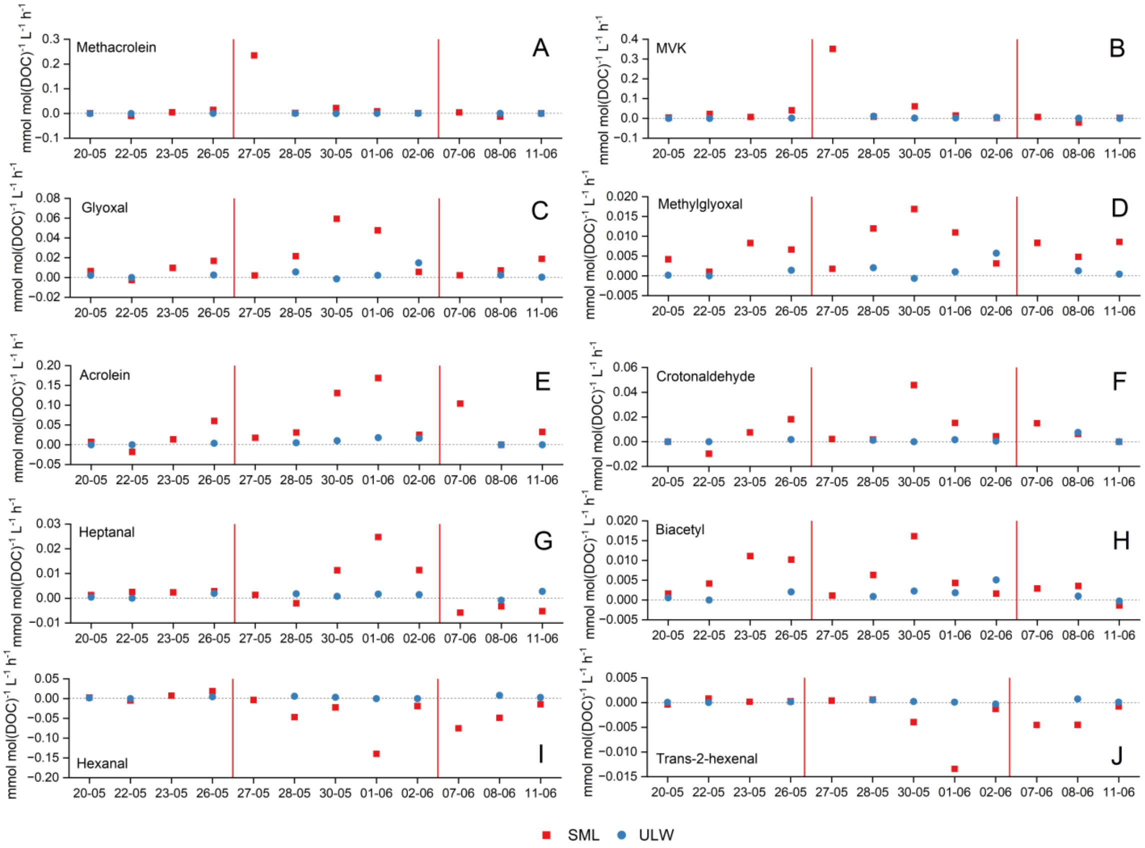


Figure 4: Comparison of photochemical formation and degradation rates of methacrolein (A), MVK (B), glyoxal (C), methylglyoxal (D), acrolein (E), crotonaldehyde (F), heptanal (G), biacetyl (H), hexanal (I) and trans-2-hexenal (J) in the SML (red) and in ULW (blue). The red vertical lines separate the three phases of the mesocosm study: pre-bloom (20-05 to 26-05), bloom (27-05 to 02-06) and post-bloom (08-06 to 11-06). Photochemical production and degradation rates in the ULW samples on an expanded scale, including error bars that reflect analytical and sample-handling uncertainties, are shown Figure S4 in the Supplementary Information.

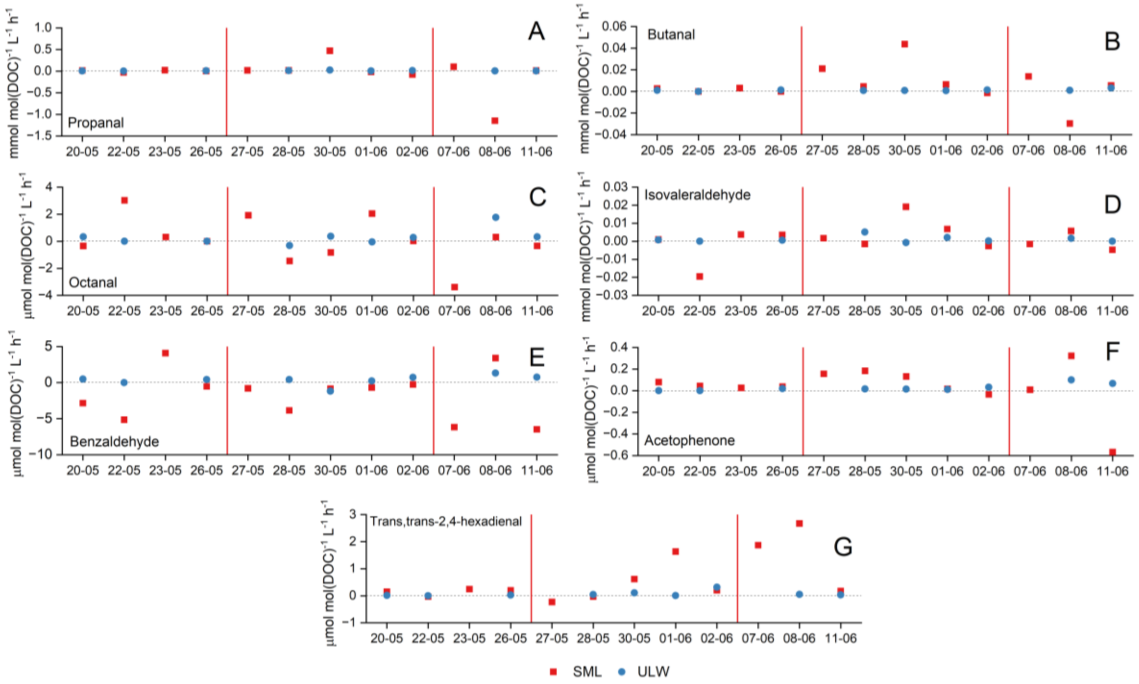


Figure 5: Comparison of photochemical formation and degradation rates of propanal (A), butanal (B), octanal (C), isovaleraldehyde (D), benzaldehyde (E), acetophenone (F) and trans,trans-2,4-hexadienal (G) in the SML (red) and in ULW (blue). The red lines separate the three phases of the mesocosm study: pre-bloom (20-05 to 26-05), bloom (27-05 to 02-06) and post-bloom (08-06 to 11-06). Photochemical production and degradation rates in the ULW samples on an expanded scale, including error bars that reflect analytical and sample-handling uncertainties, are shown Figure S4 in the Supplementary Information.

Additionally, the photooxidation capacity was plotted against the corresponding DOC concentrations for all samples and added to the revised Supplementary Information (*Figure S7*), and no systematic correlation was found. These results suggest that, while the photooxidation capacity may be influenced by the OC abundance, this influence does not seem to be dominant in these samples. DOC concentrations reported by Bibi et al. (2025) were used because CDOM data was not available.

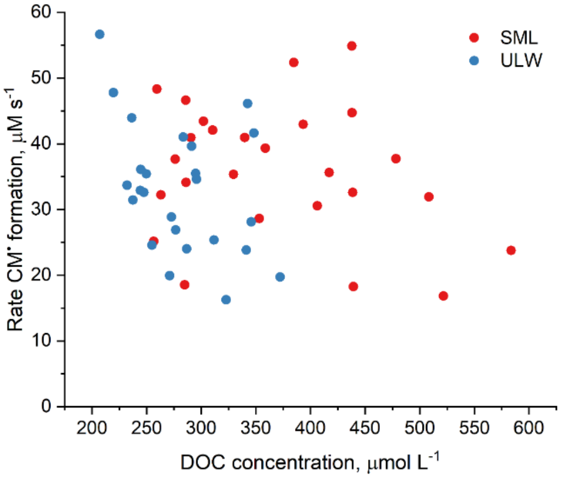


Figure S7: Calculated rates of CM radical formation compared with the DOC concentrations.

The following text was added to the revised manuscript:

Page 19, Line 504-507: "To evaluate whether these results reflect enhanced photochemical reactivity or simply the highest abundance of OM the measured photooxidation capacities were compared to DOC concentrations (Supplementary Information, Figure S7). No systematic correlation was found, indicating that the observed results cannot be explained solely by the abundance of OM."

Page 20, Line 527-528: "Further targeted studies are needed to quantify the relative roles of metal ions and other redox-active components in influencing seawater photooxidation."

The following has been added to the *Conclusions* in the revised manuscript:

Page 24, Line 639-641: "After accounting for the differences in DOC levels measured along the mesocosm study, these results indicate that photooxidation capacity cannot be solely explained by variations of OM abundance. Instead, they suggest a dominance of redox-active species, such as metal ions, rather than by biological processes."

Apparent quantum yields (AQYs): To further decouple OC abundance from intrinsic photochemical reactivity, we calculated the apparent quantum yields (AQYs) for all the investigated compounds using the absorbance spectra of each sample and the absorbed photon fluxes. A detailed description of our approach and the obtained AQYs are presented in the revised Supplementary information (*Sect. S6*, *Figure S5*). To complement the photoproduction rates presented in the revised manuscript, the AQYs normalize the rates for both the chromophore absorbance and the light exposure, reflecting the intrinsic photochemical efficiency. The calculated AQYs reveal that the SML generally had a higher photochemical efficiency than ULW, especially in the bloom phase of the experiment. To assess if this enhanced efficiency is linked to OC abundance, AQYs were compared to the DOC concentrations reported by Bibi et al. (2025) (*Figure S6* in the revised Supplementary Information).

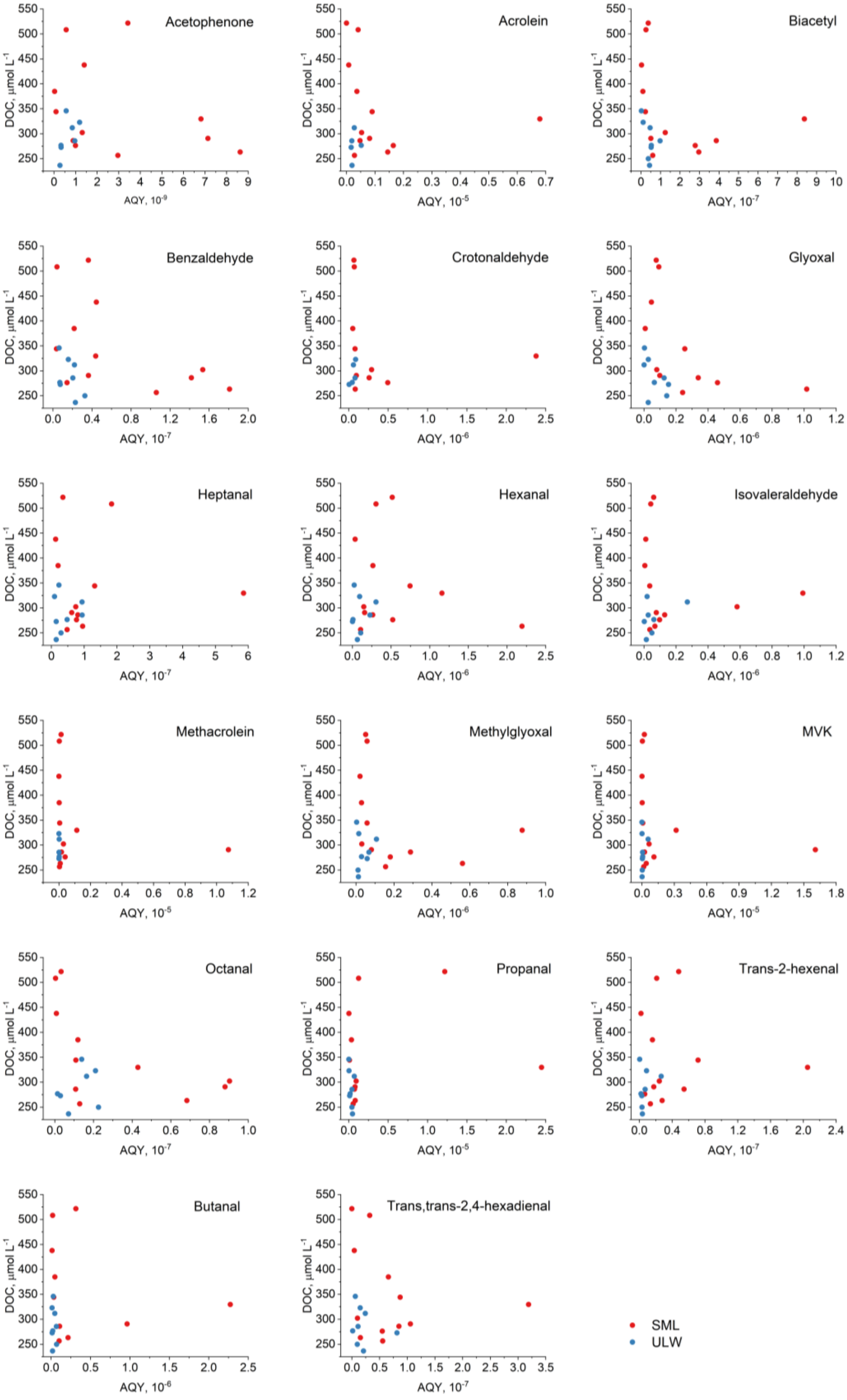


Figure S6: Calculated AQYs of the carbonyl compounds compared with the DOC concentrations.

No correlation was found between AQYs and the reported DOC concentrations, indicating that the enhanced efficiency in the photochemical activity of the investigated compounds cannot be solely explained by higher OC abundance. Instead, these results point to differences in DOM composition and photoreactivity, particularly in the SML during bloom conditions. Based on these additional analyses, we have revised the Results and Discussion and Conclusions to more clearly state that higher OC concentrations do not necessarily imply higher photochemical activity. Instead, the results demonstrate that the photochemical efficiency is strongly influenced by the chemical nature and photoreactivity or organic matter, which appears to differ between the SML and ULW and across bloom phases. The following has been added to the revised manuscript:

Page 18, Line 470-476: "Apparent quantum yields (AQYs) were calculated from the measured photoproduction rates and the absorbed photon fluxes (Supplementary Information, Sect. S6). Because the experiments were conducted using unfiltered samples, the derived AQYs represent effective photochemical efficiencies of the total OM pool. The results demonstrate that the SML is a more photochemically-efficient environment compared to ULW, particularly during the bloom phase. No systematic relationship was observed between AQYs and DOC concentrations (Supplementary Information, Figure S5), suggesting that OM abundance alone does not control the efficiency of these photochemical processes."

We also mentioned AQYs and their relation to DOC concentrations in the *Conclusions* of the revised manuscript:

Page 24, Line 631-634: "The calculation of AQYs suggests that the SML is a more photochemically efficient environment compared to ULW, particularly in the bloom phase of the study. No systematic relationship was found between AQYs and DOC concentrations, which indicates that OM abundance alone does not control the efficiency of the investigated processes."

DOC concentrations before and after irradiation: To assess changes in the contribution of carbonyls to DOC before and after irradiation, we quantified the changes in the relative contribution of the sum of C in the measured carbonyl compounds to non-purgeable organic carbon (NPOC). NPOC was used as the closer operational proxy for DOC in selected, unfiltered SML and ULW samples before and after 5 hours of irradiation, one for each bloom phase.

Table S14: Relative changes in the contribution carbonyl compounds to NPOC in unfiltered SML and ULW samples, before irradiation and after 5 hours of irradiation.

Sample type	**Date**	**Bloom phase**	**Contribution to NPOC before irradiation, %**	**Contribution to NPOC after irradiation, %**	**Changes in contribution to NPOC, %**
SML	May 26th	Pre-bloom	0.21 %	0.22 %	0.01 %
SML	May 30th	Bloom	1.20 %	1.06 %	-0.14 %
SML	June 8th	Post-bloom	1.24 %	0.51 %	-0.73 %
ULW	May 23rd	Pre-bloom	0.05 %	0.18 %	0.13 %
ULW	May 30th	Bloom	0.11 %	0.16 %	0.05 %
ULW	June 8th	Post-bloom	0.04 %	0.10 %	0.06 %

The relative contribution of carbonyl compounds to NPOC was always below 1% and did not increase considerably after irradiation. For the SML, relative changes indicate no net accumulation and suggest rapid photochemical turnover. Changes in ULW were smaller and more uniform, which suggest a limited net accumulation. The obtained results demonstrate that irradiation does not result in a significant enrichment of carbonyl compounds relative to the OC concentrations and indicate that OC abundance alone is not sufficient to explain differences in photochemical rates. This is in agreement with the AQY analysis and the trends in the normalized photochemical rates. These calculations have been added to the revised Supplementary Information (*Sect. S7*, *Table S14*).

R2C5: The authors should discuss the notable increase in Fe concentrations during the bloom relative to pre-bloom conditions. It would be helpful if the authors could also discuss how trace metal complexation in SML vs ULW may have contributed to the redox activity in the EPR experiments.

A-R2C5: We thank the reviewer for highlighting the increase in Fe concentrations during phase and for encouraging a deeper discussion of how trace metal complexation in the SML and ULW may influence the observed redox activity in the EPR experiments.

Increased Fe concentrations in the SML during the bloom: While Cu concentration values reported for both SML and ULW were stable during pre-bloom and bloom conditions, the observed Fe concentrations showed a noticeable increase in the SML sample during the bloom. Because samples were extracted with acid in the method used to determine Fe and Cu concentrations (TXRF method description, Sect. 2.6), the reported values represent total metal concentrations, independent of oxidation state or solubility. As the mesocosm was conducted under open-air conditions during the campaign, the increased iron concentration can be attributed to atmospheric metal deposition over time. In addition to that, we cannot fully exclude minor contamination introduced by the prolonged use of sensors and other instrumentation present throughout the mesocosm study. To evaluate the contribution of Fe and Cu to the photooxidation of the CMH radical probe, control experiments were performed using chloride salts of Fe and Cu (Figure S3 of the Supplementary Information). These experiments showed that Cu has a major effect on CMH oxidation under the investigated conditions, whereas Fe makes a minor contribution. This finding is consistent with the observation that, despite the increase in total Fe concentration in the SML sample during the bloom, the photooxidation capacity measured by EPR remained relatively stable across the three bloom phases and between the SML and ULW.

Metal complexation and redox activity in SML vs ULW: Metal complexation plays a critical role in controlling the redox properties, solubility and photochemical behaviour of Fe(III) and Cu(II) in seawater. In general, photoreduction is enhanced in the presence of organic ligands that form photoactive inner-sphere complexes and enable ligand-to-metal charge transfer (LMCT). While strong ligands such as oxalate are known to significantly increase the quantum yields for the metal reduction, this effect is much weaker for ligands with a lower stability constant (Sun et al., 1998). Generally, the solubility of Fe and Cu ions in ocean water is reduced in the absence of organic ligands due to the formation of hydroxy-oxo insoluble species promoted at typical seawater pH levels. Therefore, the presence of organic matter enhances the photochemistry of Fe and Cu in seawater by increasing the solubility of ions (Millero, 1998; Calza et al., 2014). However, marine organic matter itself comprises fulvic and humic acids, which have photosensitizing properties. Direct photosensitization processes can be suppressed when these photosensitizers are bound to Fe, since LMCT mechanisms will be favoured (Calza et al., 2014). Therefore, the overall effect of Cu and Fe complexation is very complex and system-dependent, a decrease or increase in redox activity cannot be inferred solely from metal or organic matter concentrations. Although organic matter concentrations are supposed to be higher in the SML than in the ULW, Fe and Cu are expected to occur predominantly as organic complexes in both systems. Because dedicated metal speciation and characterization of potential ligands were not the focus of the present work, attributing the observed photooxidation capacity to a decrease or increase in redox activity is not straightforward. The following text was added to *Sect. 3.3* in the revised manuscript:

Page 21, Line 542-555: "Although the control experiments with Fe and Cu chloride salts indicate that Cu has a stronger effect on CMH oxidation than Fe, metal complexation significantly modulates the redox properties and the solubility of both Fe(III) and Cu(II) in seawater. In general, photoreduction is enhanced in the presence of ligands that form photoactive inner-sphere complexes and enable ligand-to-metal charge transfer (LMCT). While ligands, such as oxalate, are known to significantly increase the quantum yields for the metal reduction, this effect is much weaker for ligands with a lower stability constant (Sun et al., 1998). The solubility of Fe and Cu ions in ocean water is generally reduced in the absence of organic ligands due to the formation of hydroxy-oxo insoluble species promoted at typical seawater pH levels. Therefore, the presence of OM enhances the photochemistry of Fe and Cu in seawater by increasing the solubility of ions

(Millero, 1998; Calza et al., 2014). However, OM itself comprises fulvic and humic acids, which have photosensitizing properties. Direct photosensitization processes can be suppressed when these photosensitizers are bound to Fe, since LMCT mechanisms will be favoured (Calza et al., 2014). Consequently, the overall effect of Cu and Fe complexation is very complex. While attributing the observed photooxidation capacity to a specific decrease or increase in redox activity would require dedicated metal speciation and ligand characterization, the stable CMH photooxidation rates observed across bloom phases and between the SML and ULW suggest that changes in total Fe concentrations did not exert a dominant control on the measured redox activity under the investigated conditions."

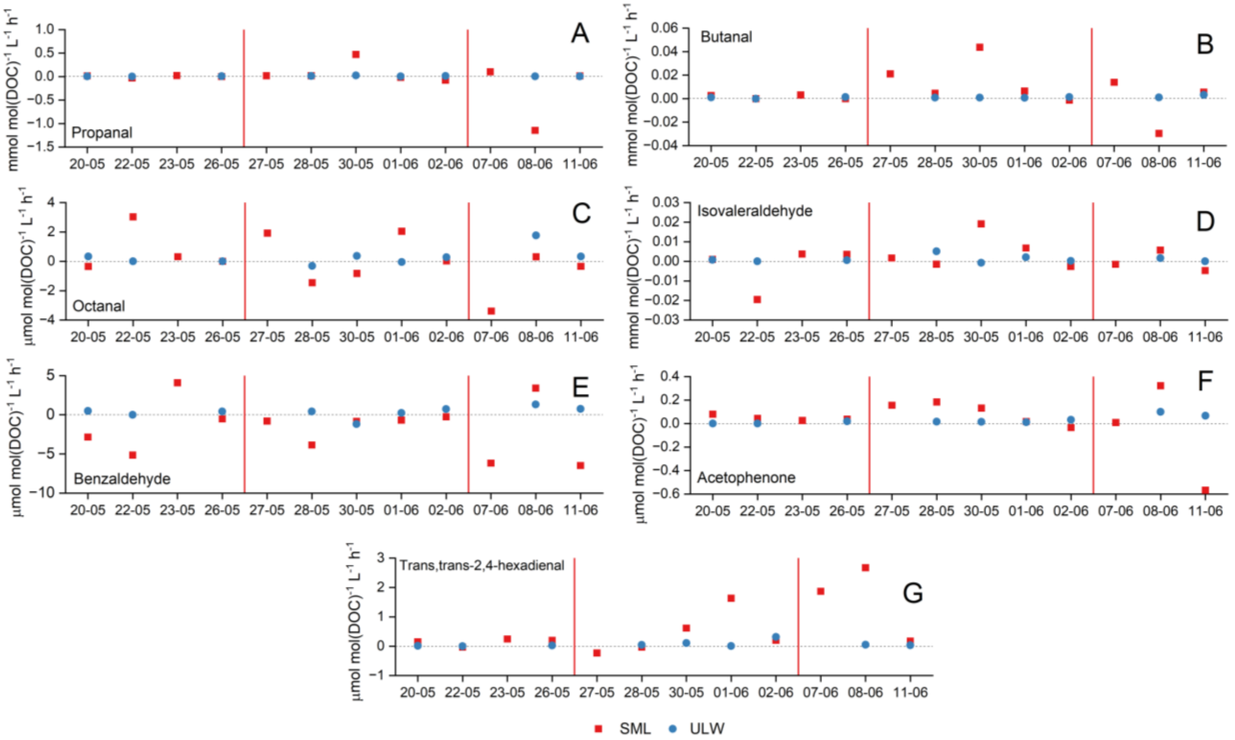
R2C6: Please specify the temperature at which EPR measurements were performed, as well as the method/approach used to maintain temperature stability. Controlled and constant temperature conditions are crucial because temperature fluctuations influence EPR signal intensity, amplitude, and contributions from molecular rotational dynamics.

A-R2C6: We thank the reviewer for emphasizing the importance of temperature control during EPR measurements. During EPR measurements, it was confirmed that the resonator temperature remained stable at 298 K throughout the irradiation. The irradiation in the EPR was made using a 100 W Xenon lamp with radiation filters, coupled to the resonator through an optical fibre, ensuring minimum transfer of infrared radiation. This configuration minimizes the transfer of infrared radiation to the resonator and prevents sample heating during irradiation, therefore maintaining stable thermal conditions during the measurements. The following text was added to include this information:

Page 9, Line 227-230: "During the EPR measurements, it was confirmed that the resonator temperature remained stable at 298 K throughout the irradiation. The irradiation in the EPR was made using a 100 W Xenon lamp with radiation filters coupled to the resonator through an optical fibre, ensuring minimum transfer of infrared radiation and preventing sample heating."

R2C7: Figure 5 seems to be missing and has likely been replaced inadvertently by a repeat of Figure 4.

A-R2C7: We thank the reviewer for identifying this mistake. In the original manuscript, Figure 5 was unintentionally duplicated from Figure 4. We have replaced it with the correct *Figure 5* in the revised manuscript (*Page 17*, *Line 430*).



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