

General changes by the authors:

We sincerely thank the Editor and Reviewers for their time, thorough reading, and feedback where needed. Your comments helped us improve the clarity and overall quality of this manuscript.

Reviewer 2:

No.	Comment	Response
1	Page 1, Line 1: Title: in	This was corrected in the title in the revised version.
2	Page 1, Line 19: Abstract section: What precisely do you mean by constrained? Uncertain, perhaps? Not studied that much?	Abstract has been revised with a more descriptive sentence Page 1, Line 21-22: Yet, to our knowledge, OA has not been measured directly or assessed in the SML.
3	Page 1, Line 19: Abstract section: I think you mean buffer - modulation has other connotations in science.	We removed this in the revised version of the Abstract.
4	Page 1, Line 23: Abstract section: Not sure that you meant to say this.	We agree the original wording was ambiguous. The sentence conflated the definition of the bloom phases with the biological processes occurring within them. In the revised version of the abstract, we now state plainly that the phases are defined by chlorophyll <i>a</i> concentration: Page 1, Line 22-23: Three distinct bloom phases are presented based on chlorophyll <i>a</i> concentration: pre-bloom, bloom, and post-bloom.
5	Page 1, Line 23: Abstract section: I'm not sure that you can call this identification.	The word used before "Identified" has been replaced by "infer" as follows: Page 1, Line 23-24: Salinity-normalised dissolved inorganic carbon and total alkalinity were used to infer the dominant biological processes across each bloom phase.
6	Page 1, Line 25: Abstract section: Not sure what this means.	To clarify which biological process dominates the system, we revised the sentence. Page 1, Line 23-25: Salinity-normalised DIC and TA were used to infer the dominant biological processes across each bloom phase, which in turn framed our interpretation of the acid-base functional groups of DOM associated with the observed OA.
7	Page 1, Line 26: Abstract section: This is pretty certainly not what you mean to say.	We removed this brief description of how we measured OA concentration from the revised version of the abstract.

No.	Comment	Response
8	Page 1, Line 27: Abstract section: Try: By reaching concentrations of OA in the SML was persistently enriched above that of the ULW.	The previous sentence commented here “OA in the SML was persistently enriched (Enrichment Factor (EF) > 1) and reached concentrations up to 264 $\mu\text{mol kg}^{-1}$ ” has been replaced in the abstract as follows. Page 1, Line 27-28: OA was persistently enriched in the SML relative to the ULW (enrichment factor: EF > 1 on nearly all sampling days) and contributed, on average, 8.1% of the TA, compared with a low 3.1% in the ULW.
9	Page 1, Line 28: Abstract section: Concurrently with what?	The word “Concurrently” has been removed in the revised version of the abstract.
10	Page 1, Line 30: Abstract section: Probably better to keep enrichment as a word.	We adopted the term enrichment throughout the text for easy reading.
11	Page 2, Line 44: Introduction section: high biologically-derived? Moreover, is 'high, on its own, enough - are they high-C, or poly-carboxylic	The qualifier ‘high’ was removed. We split the paragraph into a separate paragraph that reports multiple studies on OA and its influence on pH, in the context needed for the discussion. We moved this paragraph to: Page 2, Line 45-47: Multiple studies (Cai et al., 1998; Hernández-Ayón et al., 2007; Kim and Lee, 2009; Muller and Bleie, 2008) have shown that biologically derived organic matter can contribute a non-negligible fraction of TA, which modulates pH in productive, organic-rich marine environments.
12	Page 2, Line 44: Introduction section: Perhaps this whole sentence should be: Multiple studies (Cai et al., 1998; Hernández-Ayón et al., 2007; Kim and Lee, 2009; Muller and Bleie, 2008) show that in organic-rich marine environments high biologically-derived organic acids and bases can contribute a greater fraction of TA to that usually expected in the bulk water beneath, and that this can regulate pH in the SML.	As noted above, we split the paragraph into a separate paragraph that reports multiple studies on OA and its influence on pH, in the context needed for the discussion. We move this paragraph to: Page 2, Line 45-47: Multiple studies (Cai et al., 1998; Hernández-Ayón et al., 2007; Kim and Lee, 2009; Muller and Bleie, 2008) have shown that biologically derived organic matter can contribute a non-negligible fraction of TA, which modulates pH in productive, organic-rich marine environments.
13	Page 2, Line 46: Introduction section: Try: Given this, taken together the available evidence suggests that particular attention needs to be given to the role of the organic acid-base system of the SML in controlling air-sea exchange of CO ₂ .	This was addressed in the same paragraph as above. Page 2, Line 50-51: Given how acid-base functional groups modify pH, particular attention is needed to how this occurs in the SML in controlling air-sea CO ₂ exchange.

No.	Comment	Response
14	Page 2, Line 48: Introduction section: Try: The seawater pH buffering system is maintained primarily by carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) species which account for most of the TA (Dickson, 1981; Millero et al., 1993).	We revised the sentence for clarity. Page 2, Line 52-53: The seawater buffer capacity to resist pH changes is maintained primarily by bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) species, which account for most of the TA as inorganic alkalinity (Dickson, 1981; Millero et al., 1993).
15	Page 2, Line 57: Introduction section: Disjoint between sentences	Corrected. The sentences were rewritten so each species is described in its own complete sentence within the same paragraph about the phytoplankton species. Page 3, Lines 67-74: Two phytoplankton species, particularly relevant to the North Sea and Jade Bay, Germany, illustrate how biological organic matter production can directly modify the MCS. Coccolithophores (<i>Emiliana huxleyi</i>) calcify by using Calcium (Ca^{2+}) and DIC, mainly precipitating HCO_3^- to build up calcite coccoliths. This calcification is mediated by acidic, Ca^{2+}-binding polysaccharides (De Jong et al., 1979), whose carboxyl and sulphate groups are proton-active once released to seawater and can thus contribute to the organic matter (Passow, 2002). As another example, diatoms (<i>Cylindrotheca closterium</i>) release predominantly polysaccharide-rich exudates containing uronic acids and sulphate ester groups (Staats et al., 1999). Both types of exudates carry weak-acid functional groups that can contribute to TA as OA, linking bloom dynamics directly to the MCS variability in the SML.
16	Page 2, Line 65: Introduction section: over? Says: OA concentrations range from $\mu\text{mol kg}^{-1}$,	We overlooked this issue with a missing value; we addressed it in the revised version of the manuscript.
17	Page 3, Line 67: Introduction section: findings ... suggest that ... will lead to errors in the calculation	This missing part was added as follow: Page 3, Line 83-85: At such high concentrations, OA can bias other MCS parameters, such as pH, by $\sim 0.03 - 0.26$ pH units (at $p\text{CO}_2$ 30 – 1590 μatm; Ko et al., 2016) and by up to ~ 0.78 pH units under low-salinity conditions (Kerr et al., 2021).
18	Page 3, Line 76: Introduction section: demonstrated a 63% suppression of CO_2-transfer by the presence of surface enrichment.	This was improved to be more specific as follows: Page 3, Line 91-92:

No.	Comment	Response
		For example, Mustaffa et al. (2020) demonstrated that CO ₂ gas transfer velocity is suppressed by up to 62% under surfactant-enriched SML conditions.
19	Page 3, Line 77: Introduction section: one s in surfactant!	This grammatical error was corrected as follows: Page 3, Line 86: The SML is consistently enriched in surface-active organic material.
20	Page 3, Line 80: Introduction section: Do you need to mention Case studies? Can't you just mention the authors?	We agree and have corrected accordingly. Page 3, Line 93-94: In the Yellow Sea, multilayer sampling revealed DIC ranged from 20 to 50 $\mu\text{mol kg}^{-1}$ higher in the SML than at 1 – 5 m depth, with pH correspondingly lower by ~0.01 – 0.03 units. (Gong et al., 2007).
21	Page 3, Line 82: Introduction section: Complicated sentence, this! Try: to our knowledge, the implications to air-sea CO ₂ exchange of changes to the acid-base system within the SML has not been assessed.	This issue has been clarified. Page 3, Line 98-99: To our knowledge, organic-rich marine environments are known to modify the seawater acid-base system; yet the implications for air-sea CO ₂ exchange of OA-driven pH changes within the SML have not been assessed.
22	Page 3, Line 92: Introduction section: OA?	This issue has been clarified. Page 3, Line 98-99: To our knowledge, organic-rich marine environments are known to modify the seawater acid-base system; yet the implications for air-sea CO ₂ exchange of OA-driven pH changes within the SML have not been assessed.
23	Page 3, Line 93: Introduction section: 'compared to the ULW' could be erased?	This issue has been clarified in the revised paragraph. Referring specifically to the vertical pH difference between the SML and ULW and not comparison. Page 4, Line 104-105: We tested whether OA enrichment was associated with the vertical pH differences between the SML and the ULW.
24	Page 3, Line 93: Introduction section: We propose a 3-layer model	This issue has been clarified in the revised paragraph. Page 4, Line 107-108: we propose a conceptual three-layer model (air-SML-ULW).
25	Page 3, Line 94: Introduction section: I think that you are going to introduce OA	This issue has been clarified in the revised paragraph.

No.	Comment	Response
	into the SML. If that is so, you should say that.... to improve understanding of CO ₂ exchange in organic-rich marine environments.	Page 4, Line 108-109: The model will consider OA influence on SML pH relevant to CO ₂ exchange in biologically active marine environments.
26	Page 4, Line 97: Method section: Is there more than one?	The original writing in plural referred to the different setups for the microsenors, the CTD sensor, and the pump circulation. However, we agree that writing in the singular and referring to the overall Mesocosm study is more appropriate. Page 4, Line 112: 2.1 Mesocosm Study Setup and Data Collection Strategy.
27	Page 4, Line 98: Method section: ICBM - Inter-continental ballistic missile?	We didn't clarify that, but it appears in the affiliation section, which is not part of the manuscript. ICBM stands for Institute for Chemistry and Biology of the Marine Environment, which was included in the revised version Page 4, Line 113-115: The 35-day mesocosm study, 15 May to 16 June 2023, was performed at the Institute for Chemistry and Biology of the Marine Environment (Carl von Ossietzky Universität Oldenburg) in a concrete basin (Sea sURface Facility, SURF: 8.5 m × 2 m × 1 m, ~17 m ³).
28	Page 4, Line 98: Method section: Not defined; it does not tally with Sea sURface Facility	SURF stands for the Sea sURface Facility: https://uol.de/en/icbm/processes-and-sensing-of-marine-interfaces/infrastructures/surf
29	Page 4, Line 98: Method section: This seems to be a surfing school - is this correct?	This acronym has been used in previous studies (Bibi et al., 2025; Gassen et al., 2025) and is now defined in the revised section on the methodologies.
30	Page 4, Line 99: Method section: transmissible	We revised to a more specific description according to in Bibi et al., 2025, which is part of this special issue: Page 4, Line 115-116: The SURF was exposed to ambient light and equipped with a retractable roof of transparent 4 mm polycarbonate plates, highly transmissible to sunlight in the visible spectrum (> 80%; Bibi et al., 2025).
31	Page 4, Line 99: Method section: This excluded wind and rainfall	This suggestion has been addressed as follows: Page 4, Line 116-117:

No.	Comment	Response
		This setup excluded wind and rainfall during the measurements while maintaining ambient irradiance conditions.
32	Page 4, Line 99: Method section: Try: The 35-day, outdoor mesocosm study was made at the Institut für Chemie und Biologie des Meeres der Carl von Ossietzky Universität, Oldenburg (ICBM), in a concrete basin (8.5 m × 2 m × 1 m; ~17 m ³), equipped with a light-transmissible, retractable roof.	This suggestion has been addressed as follows: Page 4, Line 113-116: The 35-day mesocosm study, 15 May to 16 June 2023, was performed at the Institute for Chemistry and Biology of the Marine Environment (Carl von Ossietzky Universität Oldenburg) in a concrete basin (Sea sURface Facility, SURF: 8.5 m × 2 m × 1 m, ~17 m ³). The SURF was exposed to ambient light and equipped with a retractable roof of transparent 4 mm polycarbonate plates, highly transmissible to sunlight in the visible spectrum (> 80%; Bibi et al., 2025).
33	Page 4, Line 103: Method section: beginning Previews sentence referring to: Before begin of the time series, the surface was skimmed with a glass plate technique	The previous version of the sentence was removed from the original version and reads now as follows: Page 4, Line 124: Before the start of the time series ...
34	Page 4, Line 104: Method section: by the Previews sentence referring to: Before begin of the time series, the surface was skimmed with a glass plate technique.	The previous version of the sentence was removed from the original version. The revised version is as follows: Page 4, Line 124-125: ..., the surface was skimmed using the glass plate technique (Harvey and Burzell, 1972) to remove residual films.
35	Page 4, Line 105: Method section: Chl- <i>a</i> measurements were used to define bloom phases. You've presented this as a Result, but you are in the methods section.	The Chl <i>a</i> data was published elsewhere in the special issue, and therefore the methods are not mentioned here. So, we clarified in the revised version as follows: Page 4, Line 128-131: We defined the three bloom phases based on chlorophyll <i>a</i> (Chl <i>a</i>) concentrations according to Bibi et al. (2025): Bibi et al. (2025): pre-bloom phase with Chl <i>a</i> concentrations averaged/below 2.2 µg L ⁻¹ (18 to 26 May), the bloom phase with average Chl <i>a</i> concentration of 7.3 µg L ⁻¹ (27 May to 05 June), and post-bloom with Chl <i>a</i> concentration below 1.8 µg L ⁻¹ (05 to 16 June).
36	Page 4, Line 105: Method section: Unless your samples were cumulatively of considerable volume, you could/should	We have quantified this. Sampled water was replaced (with filtered seawater from the Jade Bay) with

No.	Comment	Response
	neglect them. If they were, you would actually be diluting the body of water. Think it through.	625 mL d ⁻¹ . This represents ~0.13% of the 17 m ³ basin over the entire study period.
37	Page 4, Line 105: Method section: daily/hourly?? “with regular replenishment of evaporative/sample losses”.	We clarified the replenishment of sampled water as follows: Page 5, Line 149-150: The final volume removed by each sampling was replaced with the same natural pre-treated seawater after sampling.
38	Page 4, Line 107: Method section: of ~16.7.	We decided to remove the nutrient ratios , since these are not part of our results. Instead, we mentioned where to find these results. Page 4, Line 127-128: The mesocosm nutrient concentrations in SURF throughout the study are reported in Bibi et al. (2025).
39	Page 4, Line 108: Method section: How big are these silicate pulses?	We agree that the original wording was unclear and have removed it, since the silicate concentrations (not pulses) are already included in the additions. Page 4, Line 125-127: To induce a bloom, inorganic nutrients were added on 26 May (Nitrogen (N): 0 µmol L ⁻¹ , Phosphorus (P): 1.2 µmol L ⁻¹ , Silicate (Si): 19.8 µmol L ⁻¹), 30 May (N: 10 µmol L ⁻¹ , P: 0.6 µmol L ⁻¹ , Si: 10 µmol L ⁻¹) and 01 June (N: 5 µmol L ⁻¹ , P: 0.3 µmol L ⁻¹ , Si: 0 µmol L ⁻¹).
40	Page 4, Line 108: Method section: This is a Result, about how to manage a mesocosm.	They describe the shared mesocosm set-up reported by our collaborators (Bibi et al., 2025), who defined the bloom phases from ULW Chl <i>a</i> . We cite them here only as experimental context. Page 5, Line 128-129: We defined the three bloom phases based on chlorophyll <i>a</i> (Chl <i>a</i>) concentrations according to Bibi et al. (2025):
41	Page 4, Line 108: Method section: That's repetition of 'shaping'.	Corrected. The redundant restatement of "shaping" the bloom was removed. Page 4, Line 125-127: To induce a bloom, inorganic nutrients were added on 26 May (Nitrogen (N): 0 µmol L ⁻¹ , Phosphorus (P): 1.2 µmol L ⁻¹ , Silicate (Si): 19.8 µmol L ⁻¹), 30 May (N: 10 µmol L ⁻¹ , P: 0.6 µmol L ⁻¹ , Si: 10 µmol L ⁻¹) and 01 June (N: 5 µmol L ⁻¹ , P: 0.3 µmol L ⁻¹ , Si: 0 µmol L ⁻¹).
42	Page 4, Line 109: Method section: This is more a Result than a method. Consider just mentioning that you monitored the	Yes, these are results published elsewhere Page 4, Line 131-134:

No.	Comment	Response
	evolution of the bloom using microscopy and optical proxies. One can anticipate a general statement at the beginning of Results about what actually happened.	The analysis of microscopy data and optical indicators identified the coccolithophore <i>Emiliania huxleyi</i> and the diatom <i>Cylindrotheca Closterium</i> as dominant species across the study from Bibi et al. (2025) were used to infer in the organic acid-base functional groups that characterised the measured OA in this work.
43	Page 4, Line 110: Method section: I think you have mentioned Bibi because s/he studied the local aquatic flora. If so, report it like that -once again though, that's a Result.	Same as above: Page 4, Line 131-133: The analysis of microscopy data and optical indicators identified the coccolithophore <i>Emiliania huxleyi</i> and the diatom <i>Cylindrotheca Closterium</i> as dominant species across the study from Bibi et al. (2025) were used to infer the organic acid-base functional groups that characterised the measured OA in this work.
44	Page 4, Line 112: Method section: pH measurement? With a split, later, if necessary, for the two environments.	This was addressed in the revised version of the manuscript. The Method Section now follows the same order as the Results section. 2.1 Mesocosm study set-up, induced bloom and bloom phases definition 2.2 Collection of discrete SML and ULW samples 2.3 DIC and TA measurements and inference of the dominant biological processes 2.4 Measurements of OA and operational blank 2.5 Continuous pH data collection from the SML and the ULW 2.6 Organic enrichment factor, pH differences between SML and ULW and correlation 2.7 Relating OA enrichment to vertical pH differences between SML and ULW The pH measurements split description was moved to an independent, clearer paragraph in 2.5. with each sampling layer described in order, SML and then ULW [Page 8, Line 237-245].
45	Page 4, Line 113: Method section: by electrode. Cut: in both layers using electrode-based sensors.	There was confusion since two types of UNISESE microsensors were used for temperature and pH measurements. pH electrodes had a tip size of 220 µm. Page 8, Line 237: We continuously monitored pH by electrode-based sensors.
46	Page 4, Line 113: Method section: Not clear whether there were several, or just one, sensor. Describe it in principle.	We clarified that we used two of these pH microelectrodes as part of a restructuring of the 2.5. Paragraph, same as above:

No.	Comment	Response
		Page 8, Line 237-238: Two pH microelectrodes (UNISENSE, Denmark; tip diameter 220 µm).
47	Page 4, Line 116: Method section: in which - you need to describe it in principle	This one was referring to the special issue: Biogeochemical processes and Air–sea exchange in the Sea-Surface microlayer (BG/OS inter-journal SI) The sentence (Rauch et al., 2025, submitted to the current special issue) has been removed in the revised version.
48	Page 4, Line 116: Method section: that's what representative was meant to mean, earlier in the sentence!	This was addressed in the revised version of the manuscript and refers to the mean of the SML profile segment described by Rauch et al., 2026, as part of restructuring 2.5. Paragraph Page 8, Line 239-240: Following Rauch et al., (2026), linear regressions were fit across air-SML-ULW segments to resolve pH micro-profiles.
49	Page 4, Line 121: Method section: You might just state the scale you are using, and leave it at that until you come to the Results section. If you use the measurements for anything more than 'a monitor', then you would need to explain what the implications of that are.	This was addressed in the revised version of the manuscript. As part of a restructuring of the 2.5. Paragraph Page 8, Line 243-245: Both pH sensors (SML and ULW) were calibrated with buffers (pH 4.00, 7.00 and 10.00; ROTI CALIPURE, Carl Roth, Karlsruhe, Germany; nominal ± 0.02 at 20 °C); values are therefore reported on the operational NBS/IUPAC scale for relative comparison.
50	Page 4, Line 122: Method section: This section requires some sub-sectioning as there are too many individual techniques hitting the reader.	We restructured the methods section to improve reading flow, as suggested by the other reviewer. 2.1 Mesocosm study set-up, induced bloom and bloom phases definition 2.2 Collection of discrete SML and ULW samples 2.3 DIC and TA measurements and inference of the dominant biological processes 2.4 Measurements of OA and operational blank 2.5 Continuous pH data collection from the SML and the ULW 2.6 Organic enrichment factor, pH differences between SML and ULW and correlation 2.7 Relating OA enrichment to vertical pH differences between SML and ULW In the same order as they are shown in the results section.

No.	Comment	Response
51	Page 4, Line 124: Method section: Suggest you write this sentence in two parts as there are rather too many acronyms to cope with, all at once!	This paragraph has been restructured, starting from the general discrete sample – SML sampling – ULW sampling – Poisoning of both sampling – and SML and ULW paired data. 2.2 Collection of discrete SML and ULW samples Page 5, Line 136-150: Discrete samples for the parameters DIC, TA, and OA were collected from both layers as part of the multidisciplinary BASS collaboration under alternating natural-light (~1300 hrs UTC) and dark (~0300 hrs UTC) conditions. The SML samples were collected using a pre-cleaned glass plate (Harvey & Burzel, 1972) that was immersed through the SML, moved away from the perturbed immersing area, and withdrawn vertically. Manually controlled ~at a rate of 5 to 6 cm s⁻¹ as suggested by Carlson (1982); at such speed the glass plate can collect a microlayer of 52 ± 1.8 µm thickness (mean ± 95 % CI, and multiple dips were combined to reach the required sample volume. Immediately thereafter, the sample was wiped from both sides of the glass plate into the sample bottle using a squeegee recommended by (Cunliffe et al., 2013). A 30 mL borosilicate bottle was filled for DIC and a 100 mL bottle from which TA and OA were measured. The SML was sampled every third day: the collected volume was limited and shared among several BASS subprojects to let the SML re-establish between samplings. The ULW was sampled daily from 40 cm depth through a 10 mm tube by gentle suction created with a syringe, once a constant flow was created the sample was collected in a 250 mL borosilicate glass bottle from where DIC, TA and OA were measured. The SML and ULW samples were immediately poisoned with a saturated mercuric chloride (HgCl₂) solution (0.02% of the bottle volume, Dickson, 2007), sealed, and stored in the dark at room temperature until analysis. On each SML day, the ULW was sampled simultaneously, yielding ten paired SML–ULW data points across the time series. The final volume removed by each sampling was replaced with the same natural pre-treated seawater after sampling.
52	Page 4, Line 126: Method section: join these two sentences with, 'in which'. Oh, maybe not! You see, you have already described the plate method, so the second part is possibly redundant.	Page 5, Line 137-139: The SML samples were collected using a pre-cleaned glass plate (Harvey & Burzel, 1972) that was immersed through the SML, moved away from the perturbed immersing area, and withdrawn vertically.

No.	Comment	Response
53	Page 5, Line 127: Method section: How did you control it?	Page 5, Line 139-141: Manually controlled ~at a rate of 5 to 6 cm s ⁻¹ as suggested by Carlson (1982); at this speed, the glass plate can collect a microlayer of $52 \pm 1.8 \mu\text{m}$ thickness (mean $\pm$ 95% CI), and multiple dips were combined to reach the required sample volume.
54	Page 5, Line 128: Method section: How did you wipe it?	Page 5, Line 141-142: Immediately thereafter, the sample was wiped from both sides of the glass plate into the sample bottle using a squeegee recommended by (Cunliffe et al., 2013).
55	Page 5, Line 128: Method section: Not clear what you mean by 'together with OA.	We meant that TA and OA were measured from a single 100mL sample bottle. However, we revised the sentence for clarification. Page 5, Line 142-143: A 30 mL borosilicate bottle was filled for DIC and a 100 mL bottle from which TA and OA were measured.
56	Page 5, Line 130: Method section: what is this assembly; probably a Buchner funnel plus inlet tube?	The sentence was unclear. We addressed it as follows: Page 5, Line 145-146: The ULW was sampled daily from 40 cm depth through a 10 mm tube by gentle suction created with a syringe, once a constant flow was created the sample was collected in a 250 mL borosilicate glass bottle from where DIC, TA and OA were measured.
57	Page 5, Line 131: Method section: Cut: To prevent biological alteration in the samples, and just state that it was poisoned.	Page 5, Line 147-148: SML and ULW samples were immediately poisoned with a saturated mercuric chloride (HgCl ₂) solution (0.02% of the bottle volume, Dickson, 2007), sealed, and stored in the dark at room temperature until analysis.
58	Page 5, Line 133: Method section: by the method described by Dickson 007 - need to say basically what type of method that is.	We agree and revised accordingly. Page 5, Line 147-148: (0.02% of the bottle volume, Dickson, 2007).
59	Page 5, Line 134: Method section: to standards of	We corrected these two comments in the same sentence. Page 5, Line 154-155: Our protocol was based on the method described by Johnson et al. (1985) and the procedures according to the standards of best practices in ocean CO ₂ measurements (Dickson et al., 2007).
60	Page 5, Line 135: Method section: according to	

No.	Comment	Response
61	Page 5, Line 135: Method section: In principle, a 25 mL ...	Page 5, Line 155-156: A 25 mL aliquot was extracted from the borosilicate bottles and introduced into an acidification module.
62	Page 5, Line 139: Method section: Break here ; I'm out of breath!	We have split this long sentence into shorter ones, making it easier to follow step by step, and allowing the reader to follow the content more easily. Page 5, 156-160: The sample was acidified with 2 mL of H ₃ PO ₄ (0.1 M) to transform the DIC into the CO ₂ gas phase. The evolved CO ₂ gas was carried by a high-purity N ₂ stream (99.999%, Alphagaz, Air Liquide, Düsseldorf, Germany) at 100 mL min ⁻¹ into a closed coulometric cell. Two chambers in the cell contain separate cathode and anode solutions for the titration. The CO ₂ was quantitatively absorbed into the cathode solution and quantified.
63	Page 5, Line 142: Method section: Don't think these are the right nouns - international comparability?	This is described more clearly in the revised version. Page 5, Line 160-162: Certified Reference Materials (CRMs; batches 191, 198 and 209) supplied by Andrew Dickson's laboratory (Scripps Institution of Oceanography, CA, USA) were routinely analysed to verify the true value for measurement accuracy of TA and DIC.
64	Page 5, Line 143: Method section: Be more specific: Internal standards were performed ..	Page 6, Line 162-163: Quality-control measurement checks were performed routinely with analytical uncertainty within $\pm 3 \mu\text{mol kg}^{-1}$ (Dickson et al., 2007) by using a secondary standard.
65	Page 5, Line 145: Method section: measured directly	This grammatical error was removed in the revised version. Page 6, Line 164: The TA was determined by high-precision closed-cell potentiometric titration using ...
66	Page 5, Line 146: Method section: under	This issue was resolved in the revised version. Page 5, Line 165: according to the standards of best practices in ocean CO ₂ measurements (Dickson et al., 2007).
67	Page 5, Line 147: Method section: split this sentence	This issue was resolved in the revised version. Page 6, Line 164-176: The TA was measured directly by high-precision closed-cell potentiometric titration using a 916 Ti-Touch (Metrohm, Switzerland), according to the

No.	Comment	Response
		standards of best practices in ocean CO₂ measurements (Dickson et al., 2007). Titrations were performed with an Aquatrode Plus electrode equipped with a Pt1000 temperature sensor (Metrohm AG, Herisau, Switzerland). Samples were maintained at 25 °C in a thermostatic water bath throughout the analysis. Certified HCl (0.1 M) in NaCl (0.6 M) was dispensed automatically in successive increments using a monotone equivalent-point routine (5 µL steps) to a potential of +225 mV (approximately pH 3 at 24.6 – 25.0 °C). During the titration, samples were continuously purged with a high-purity N₂ stream (99.999%), which removed CO₂ released from DIC during HCl addition and maintained a CO₂-free headspace within the closed cell. Gentle stirring ensured homogeneous mixing and prevented bubble accumulation near the electrode caused by the incoming N₂ stream. Total alkalinity was calculated from the electromotive force-volume data using the Gran function, which linearises the titration data to determine the equivalence point (Dickson et al., 2007). Certified Reference Materials (CRMs; batches 191, 198 and 209) supplied by Andrew Dickson's laboratory (Scripps Institution of Oceanography, CA, USA) were routinely analysed to verify the true value for measurement accuracy. Quality-control measurements were performed routinely with analytical uncertainty within $\pm 3 \mu\text{mol kg}^{-1}$ (Dickson et al., 2007) by using a secondary standard.
68	Page 5, Line 149: Method section: was, or were?	It was resolved in the revised version as follows: Page 6, Line 167-169: Certified HCl (0.1 M) in NaCl (0.6 M) was dispensed automatically in successive increments using a monotone equivalent-point routine (5 µL steps) to a potential of +225 mV (approximately pH 3 at 24.6 – 25.0 °C).
69	Page 5, Line 151: Method section: I think you are going back on yourself?	This issue was removed in the revised version to avoid repetition and clarify it at the end of the paragraph as follows: Page 6, Line 175-176: Quality-control measurements were performed routinely with analytical uncertainty within $\pm 3 \mu\text{mol kg}^{-1}$ (Dickson et al., 2007) by using a secondary standard.

No.	Comment	Response
70	Page 5, Line 155: Method section: is this a statistical remark, or an accuracy remark; if the latter, how about using the word: true?	This is an accuracy (trueness) statement for good practices in measuring alkalinity (Dickson et al., 2007), not a statistical one. Page 6, Line 173-176: Certified Reference Materials (CRMs; batches 191, 198 and 209) supplied by Andrew Dickson's laboratory (Scripps Institution of Oceanography, CA, USA) were routinely analysed to verify the true value for measurement accuracy. Quality-control measurements were performed routinely with analytical uncertainty within $\pm 3 \mu\text{mol kg}^{-1}$ (Dickson et al., 2007) by using a secondary standard.
71	Page 5, Line 157: Method section: It's not clear how you did this - did you sub-sample the original sample twice, or use the residue from the TA titration, in a second titration? If the latter, try: upon the residue from the TA determination ...	A more descriptive method was phrased for clarification Page 7, Line 209-210: Using the residual sample from the TA determination, a second potentiometric titration was then performed to the same endpoint ($\text{pH} < 3$; $+225 \text{ mV}$ at 25.0°C).
72	Page 5, Line 157: Method section: Cut: The OA concentration and simply use: OA.	The term "concentration" was removed throughout the manuscript; leave it only when necessary. But keep it to a minimum.
73	Page 5, Line 157: Method section: by back-titration even: by what amounts to back-titration.	We changed the term back-titration throughout the manuscript to second titration, as it is more explicit.
74	Page 5, Line 158: Method section: Start sentence here - no need for, By then"? Incidentally, is it one aliquot, or aliquots?	This was revised as follows: Page 7, Line 207-208: a single $80 \mu\text{L}$ aliquot of NaOH (35 g of solid NaOH per litre of 0.6 M NaCl) was added to restore the sample pH to approximately 8.1.
75	Page 5, Line 158: Method section: remove back titration from here.	The term back-titration was changed throughout the manuscript to second titration, as it is more explicit.
76	Page 5, Line 159: Method section: Cut: prepared by dissolving NaOH (35 g) and remove brackets.	This was resolved in a revised version of the manuscript Page 8, Line 228-229: We prepared the ASW by dissolving 38 g of Tropic Marin Pro Reef Salt in 1 L of ultrapure water.
77	Page 5, Line 160: Method section: cut this 'and', but put a comma in.	This was resolved in a revised version of the manuscript Page 7, Line 206-208: Once the CO_2 was completely removed with a continuous N_2 stream, maintaining a CO_2-free

No.	Comment	Response
		headspace, a single 80 µL aliquot of NaOH (35 g of solid NaOH per litre of 0.6 M NaCl) was added to restore the sample pH to approximately 8.1.
78	Page 6, Line 162: Method section: I'm left thinking that Gran evaluation has suddenly entered! Make the link clearer.	This was resolved by adding a brief description of what the method gran function implies. But it was positioned in the TA measurement paragraph since it is mentioned there for the first time. Page 6, Line 172-173: Total alkalinity was calculated from the electromotive force-volume data using the Gran function, which linearises the titration data to determine the equivalence point (Dickson et al., 2007).
79	Page 6, Line 163: Method section: There seems to be a complex, mixed nomenclature here with both concentrations and special acronyms. Why not rationalise to [OH-] to [S2-] AND [H+], and kick out your own arbitrary inventions?	Nomenclature was unified. We introduced the term “inorganic alkalinity” in the introduction section so we can refer to these species (in the equation) more briefly. Page 2, Line 52-53: Introduction section: The seawater buffer capacity to resist pH changes is maintained primarily by bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) species, which account for most of the TA as inorganic alkalinity (Dickson, 1981; Millero et al., 1993). And we added more detail on the method section Page 7, Line 215-225: Method section: Following Dickson's (1981) explicit parameterisation, the operational equation for OA can be grouped by its inorganic components expressed as: $\text{OA} = \text{NCA} - (\text{A}_\text{B} + \text{A}_\text{W} + \text{A}_\text{P} + \text{A}_\text{Si} + \text{A}_\text{minor}) \quad (3)$ Where the inorganic non-carbonate alkalinity components are defined as the contributions from borate (A_B), water dissociation and sulphate/fluoride (A_W), phosphate (A_P), silicate (A_Si), and other minor inorganic species (A_minor, e.g., NH_3, HS). The nitrogen, phosphate and silicate concentrations required to correct TA for their inorganic contributions in Eq. 1 were taken from the daily ambient nutrient measurements of Bibi et al., (2025). To solve Equation (2), the theoretical components (A_B, A_W, A_P, and A_Si) were calculated using the CO2SYS program. The software estimates the exact speciation based on the sample's practical salinity

No.	Comment	Response
		(which dictates total boron), laboratory temperature, and the specific pH of the second titration. Equilibrium constants followed the recommended best-practice sets: $K_{B(HO)_4}^*$ (Dickson, 1990), $K_{PO_4^{3-}}^*$ (Dickson, 2007), K_{HF}^* (Perez & Fraga, 1987), F from (Riley, 1965).
80	Page 6, Line 163: Method section: conventionally as: kick out: 'the following equation'	We have chosen the following wording: Page 7, Line 216: expressed as:
81	Page 6, Line 165: Method section: recommended best-practice sets	These two comments were solved in the same sentence as follows: Page 7, Line 224: Equilibrium constants followed the recommended best-practice sets.
82	Page 6, Line 165: Method section: Equilibrium	
83	Page 6, Line 166: Method section: nutrient concentrations should have been mentioned already, somewhere above all of this TA, OA stuff.	Nutrient data used was mentioned in the in 2.1 Mesocosm study set-up, induced bloom and bloom phases definition. Page 4, Line 125-128: To induce a bloom, inorganic nutrients were added on 26 May (Nitrogen (N): 0 $\mu\text{mol L}^{-1}$, Phosphorus (P): 1.2 $\mu\text{mol L}^{-1}$, Silicate (Si): 19.8 $\mu\text{mol L}^{-1}$), 30 May (N: 10 $\mu\text{mol L}^{-1}$, P: 0.6 $\mu\text{mol L}^{-1}$, Si: 10 $\mu\text{mol L}^{-1}$) and 01 June (N: 5 $\mu\text{mol L}^{-1}$, P: 0.3 $\mu\text{mol L}^{-1}$, Si: 0 $\mu\text{mol L}^{-1}$). The mesocosm nutrient concentrations in SURF throughout the study are reported in Bibi et al. (2025).
84	Page 6, Line 168: Method section: Ha, ha! as written, the substandard refers to the titration!! No serious scientist knowingly conducts sub-standard titrations! Complicated language, isn't it!	These issues were solved as follows: Page 7, Line 233-234: Quality-control measurements were performed routinely and assessed by measuring a secondary standard, with analytical uncertainty within $\pm 3 \mu\text{mol kg}^{-1}$.
85	Page 6, Line 168: Method section: Try instead: duplicate titrations of a secondary, rolling standard	
86	Page 6, Line 168: Method section: which, throughout the study, remained within	
87	Page 6, Line 168: Method section: Then why mention it??!!	The content was removed in the revised version of the manuscript.
88	Page 6, Line 169: Method section: Ah, I see: you are wandering around again, not being direct, and saying things ONCE!	We have revised the methods section to be more concise.

No.	Comment	Response
89	Page 6, Line 171: Method section: I'm NOT sure that rationalisation makes sense like this. Are you suggesting that if you hadn't run the mesocosm at 35 S (or S _{ref}) that you could have calculated the value at 35S, from it?	This point was clarified as follows: Page 6, Line 177-187: The dominant biological processes from each layer were inferred from the direction of the resultant vector in the paired data of a Deffeyes-type diagram of salinity-normalised DIC vs TA. The change produced by a given process appears as a vector whose direction is set by the stoichiometry of that process (Deffeyes, 1965; Middelburg et al., 2020). We therefore interpreted the direction of these vectors, rather than the absolute DIC and TA values, to identify the process controlling each layer. Due to evaporation, salinity in the mesocosm rose from 29.3 to 32.0 over the study; DIC and TA were therefore normalised to a reference salinity following Friis et al. (2003) to separate this physical concentration effect from biogeochemical change in DIC and TA: $NX = X \times \left(\frac{S_{ref}}{S_i}\right) \quad (1)$ where NX represents the normalised parameter (NDIC, NTA); X is the measured concentration in $\mu\text{mol kg}^{-1}$; S_i refers to the salinity measured on each discrete sampling day (i); and $S_{ref} = 29.243 \pm 0.412$ represents here the study's initial salinity as a reference.
90	Page 6, Line 171: Method section: Here's another 'wandering about - Matlab has already been mentioned a sentence above!	This issue has been removed from the revised version.
91	Page 6, Line 172: Method section: What is visualisation? Do you mean interpretation? Well, even if you did, interrpetaion goes on in your brain, not in Matlab! Be careful!	This confusing sentence has been removed in the revised version of the manuscript, since it didn't add relevant content to the manuscript.
92	Page 7, Line 201: Method section: 'Due to' implies a reason. I think you might try: Finding a negative correl...	The causal "due to" was removed. Due to a relocation of the analysis of the data in 2.7 Relating OA enrichment to vertical pH difference between SML and ULW. Page 9, Line 265-268: As normality was not met, we used a two-tailed Spearman rank correlation ($n = 10$ paired SML and ULW days). Spearman's rho (ρ) gives the strength and direction of the monotonic relationship between OA EF and ΔpH (-1 to $+1$, 0 = none), and the p-value < 0.05 ($\alpha = 0.05$) its scientific significance.
93	Page 7, Line 204: Method section: deming?	Deming regression is a linear fit that accounts for measurement error in two variables (x and y), rather

No.	Comment	Response
		than in y alone as in ordinary least squares. It was popularised by W. E. Deming (1943), after whom it is named. Deming, W. E. (1943), <i>Statistical Adjustment of Data</i>, Wiley Page 9, Line 268-270: Additionally, we quantified this relationship using Deming regression (Deming, 1943), an errors-in-variables linear fit that accounts for measurement uncertainty in OA EF against ΔpH, unlike ordinary least-squares regression, which assumes the predictor is error-free.
94	Page 7, Line 210: Method section: I suspect you have a serious problem here in your entire strategy - see the list of main points.	We have therefore rephrased the strategy: the Methods now state only that the Spearman correlation and the linear regression quantify the strength, significance and rate of the relationship between OA EF and ΔpH Page 9, Line 263-272. Paragraph 2.7 Relating OA enrichment to vertical pH differences between SML and ULW To test whether SML OA enrichment covaries with the vertical pH difference between layers, we related the OA enrichment factor values to the ΔpH across the study. We assessed the normality of OA EF and ΔpH with histograms, Q-Q plots and the Shapiro-Wilk test, and homoscedasticity across bloom phases with Levene's test. As normality was not met, we used a two-tailed Spearman rank correlation ($n = 10$ paired SML and ULW days). Spearman's rho (ρ) gives the strength and direction of the monotonic relationship between OA EF and ΔpH (-1 to $+1$, $0 = \text{none}$), and the $p\text{-value} < 0.05$ ($\alpha = 0.05$) its scientific significance. Additionally, we quantified this relationship using Deming regression (Deming, 1943), an errors-in-variables linear fit that accounts for measurement uncertainty in OA EF against ΔpH, unlike ordinary least-squares regression, which assumes the predictor is error-free. The paired OA EF and ΔpH values from the sampling days were plotted together as a single scatter plot, identifying which group of data belongs to each bloom phase. This scatter plot represents the co-variation of OA enrichment in the SML and the vertical pH difference between layers over the study period.

No.	Comment	Response
95	Page 7, Line 213: Result section: Try: This mesocosm study considered the co-variation of OA and pH in the SML and the ULW over an X month period. Note that you should present the Results so that they are understood by the reader, in their simplest form. You will want to manhandle 'the Results' but the reader needs to know that you have done this 'properly. As Salinity variation is likely to have been fairly high I think you should comment upon that early on. Indeed, I suspect that you have normalised data because of that - however, I see no mention of it!	Page 9, Line 274-285: This mesocosm study examined the covariation of OA and pH in the SML and the ULW over a 35-day phytoplankton bloom. The bloom dynamics of three phases were inferred from Chl-<i>a</i> measurements. An 8-day pre-bloom phase was followed by a sharp increase of Chl-<i>a</i> over 11 days, and a rapid decline over the final 11 days (Supplementary S3, Fig. 1). Microscopy and optical proxies identified a mixed haptophyte and diatom bloom dominated by the coccolithophore <i>Emiliania huxleyi</i> at bloom onset and the diatom <i>Cylindrotheca closterium</i> afterwards (Bibi et al., 2025). Across the study period, evaporation raised salinity from ~29.2 to ~32.3, a change large enough to alter DIC and TA through physical concentration alone. Therefore, DIC and TA are reported throughout as salinity-normalised values (NDIC, NTA). The Deffeyes-type diagram NDIC vs NTA shows vector trajectories associated with dominant biological processes, which differed between the SML and ULW across all bloom phases (Sect. 3.1). The information provided the basis for inferring the organic acids and bases that defined the OA reported here. OA accumulated persistently in the SML, accompanied by opposing pH trends in both layers (Sect. 3.2). OA EF and the vertical ΔpH quantify the difference between the SML and ULW across bloom phases (Sect. 3.3). OA EF and ΔpH are negatively and significantly correlated (Sect. 3.4).
96	Page 7, Line 214: Result section: Bloom dynamics of three phases were inferred from chlorophyll-<i>a</i> (Chl-<i>a</i>) measurements. A pre-bloom phase of 8 days was followed by a sharp increase over 11 days, and a rapid decline over the final 11 days. Now the species.	Page 9, Line 275-278: The bloom dynamics of three phases were inferred from Chl-<i>a</i> measurements. An 8-day pre-bloom phase was followed by a sharp increase of Chl-<i>a</i> over 11 days, and a rapid decline over the final 11 days (Supplementary S3, Fig. 1). Microscopy and optical proxies identified a mixed haptophyte and diatom bloom dominated by the coccolithophore <i>Emiliania huxleyi</i> at bloom onset and the diatom <i>Cylindrotheca closterium</i> afterward (Bibi et al., 2025).
97	Page 7, Line 217: Result section: Does this history provide anything for the reader? I suspect not. Why not follow on instead with a statement about what you saw, and a diagram.	Yes, because the biological processes helped us to infer in the characterisation of the OA Page 9, Line 279-283: DIC and TA are therefore reported throughout as salinity-normalised values (NDIC, NTA). The Deffeyes-type diagram NDIC vs NTA shows vector trajectories associated with dominant biological processes, which differed between the SML and ULW

No.	Comment	Response
		across all bloom phases (Sect. 3.1). The information provided the basis for inferring the organic acids and bases that defined the OA reported here. OA accumulated persistently in the SML, accompanied by opposing pH trends in both layers (Sect. 3.2).
98	Page 7, Line 219: Result section: You will appreciate, I think, that it is better to remove the time element in your discovery, e.g., we then ..., and simply report the findings unemotionally, as it were; factually, against figs.	We were aware of this time element, so the revised version treats this more carefully.
99	Page 8, Line 227: Result section: why is this section 3.1? That ought to have been the material immediately below 3.	Section 3 has been restructured to reduce to the basic general description needed for the main findings overview.
100	Page 8, Line 228: Result section: No! Go for the jugular, and start talking about the biology, with graphs if available.	Section 3.1 now opens directly with the biology: the dominant processes inferred for each bloom phase.
101	Page 8, Line 234: Result section: Too sophisticated a term! Think of co-variation, and talk about that. This could be much, much shorter.	Section 3.1 is now written in a plainer language.
102	Page 13, Line 346: Result section: If the Results were good enough, this last sentence would have been appropriate in the Discussion. But, the point would be made something like: The Results provide a basis for discussion of mechanisms and implication. Unfortunately, I am not persuaded that they do!	The closing sentence that anticipated the Discussion has been removed; Sect. 3.4 now ends with the observed association. Mechanistic interpretation and implications are now developed in the Discussion. Page 14, Line 398-399: Strong SML OA enrichment was therefore associated with a decrease in the vertical pH difference between the layers.
103	Page 13, Line 352: Discussion section: This is more 'Results stuff', which is bleeding out into the Discussion. The change is one of going from evidence, to implications.	This issue was addressed in a completely revised version of the discussion section, based on the reviewer's comment.
104	Page 15, Line 420: Conclusion section: corresponds with	This issue was removed for clarity. Page 18, Line 519-520: which reduced the vertical pH differences between the two layers.
105	Page 15, Line 424: Discussion section: You are introducing something new, when you ought to be closing down. If you want to do some modelling, the Discussion would have been the place.	We discussed this three-layer model issue in the revised version of the manuscript. The conclusion sentence was changed for clarity: Page 18, Line 520-523:

No.	Comment	Response
		Conceptually, the traditional two-layer air-sea CO₂ exchange might be ignoring important buffer changes in the SML; we posit that a three-layer view is a more accurate representation of this important ecohydrological interface. An air-SML-ULW CO₂ exchange model locates where changes in pH arise from organic-rich waters and helps avoid attributing pH variability solely to the low OA in the ULW.