General changes by the authors:

In response to the reviewers' valuable feedback, we have substantially revised the manuscript. The Introduction was expanded and updated with more comprehensive and recent references, particularly regarding the SML and ocean acidification. The Methods section was significantly improved, now providing detailed information on the study site, sampling strategy, instrumentation, measurement precision, and uncertainties, as well as using regionally appropriate atmospheric CO_2 data from the ICOS Lampedusa station. The Discussion was strengthened by replacing vague statements with mechanistic explanations that integrate physical, biogeochemical, and chemical processes, and by clarifying the dominant role of wind in driving CO_2 fluxes. Overall, these changes improve the clarity, accuracy, and robustness of our study.

Reviewer 1:

Comment	Response
The introduction primarily focuses on carbonate chemistry and the relevance of pCO_2 measurements, without adequately introducing the unique characteristics of the SML and its relevance to air–sea CO_2 fluxes (e.g., see the review by Cunliffe et al., 2013: https://doi.org/10.1016/j.pocean.2012.08.004). A more comprehensive and updated bibliographic foundation is needed. For example, in line 40, Cantoni et al. (2012) do not present trends in acidification but rather biogeochemical drivers of pH variability. Doney's work is a milestone, but more recent references are necessary. Similarly, in line 52, Cantoni et al. (2016) do not mention the SML.	We thank the reviewer for all the valuable suggestions. We have revised the Introduction to highlight better the unique characteristics of the sea-surface microlayer (SML) and its role in air–sea CO_2 fluxes. In particular, we have incorporated the review by Cunliffe et al. (2013) as well as more studies (Engel et al., 2017; Mustaffa et al., 2020; Wurl et al., 2017), which emphasize the biogeochemical complexity of the SML. We also updated the references on ocean acidification, replacing Cantoni et al. (2012) with more appropriate and widely cited works (Orr et al., 2005; IPCC, 2021), and clarified the scope of Cantoni et al. (2016), which does not explicitly address the SML. In addition, we included Yates et al. (2007) to support diel variability of carbonate system parameters, and Kapsenberg et al. (2017) to reflect more recent regional trends in Mediterranean acidification. These changes provide a more comprehensive and updated bibliographic framework for our study.
The methods section is unclear. It lacks essential information needed to understand what was done, where, and on how many samples the study is based. The system used for data acquisition is not described, and there is no introduction to the study site or description of where the data were collected. See detailed comments in the manuscript.	We have added information to the Methods section to address the previous lack of detail, including a description of the study site, deployment strategy, variables measured, and considerations of measurement and calculation uncertainty, as well as environmental conditions. Specific changes requested by the reviewer are addressed in more detail in the responses to the following comments.
Line 63 – please add more references	We have included additional relevant references supporting the role of nocturnal respiration in driving increases in pCO_2 and decreases in pH.
Regarding carbonate system parameters, pH was measured continuously, but no details are provided about the electrode, calibration procedures, or accuracy. DIC and TA were measured using state-of-the-art methods on a limited number of discrete samples, as reported	We note that: • pH was measured continuously using the integrated sensor of the S^3 flow-through system, reported on the total scale with a precision of ±0.005 pH units (Ribas-Ribas et al., 2017) and normalized to

in Table 1: 3–4 samples during the day and 1–2 at night. These data were then used to calculate pCO_2 and pH at 25 °C. An estimate of the uncertainty associated with these calculations is necessary before discussing the results.	25.43 °C to account for temperature variations, as already modified in the Methods section (Lines XX). • Discrete DIC and TA samples were analysed with state-of-the-art methods (coulometric titration for DIC, potentiometric titration for TA), calibrated against certified reference material, with a 1σ measurement precision of ±3 μmol kg⁻¹ for DIC and ±2 μmol kg⁻¹ for TA. These values were then used to calculate pCO_2 with the CO2SYS program, and the associated uncertainties are inherent to these calculations. We would like to clarify that pH was not calculated from DIC and TA; therefore, the uncertainty of DIC/TA does not apply. The precision and scale of the pH sensor, together with the temperature normalization, provide a reliable basis for evaluating diel and vertical differences.
Line 89 – Water depth? Distance from shore?	We have added details on water depth and distance from shore in the Methods section. Sampling was conducted in the lower estuary of the Krka River, immediately offshore from the St. Anthony Channel near Šibenik, with depths ranging from less than 2 m at the head of the estuary to about 42 m at the mouth (Cukrov, 2024; Prohic, 1989). The S^3 catamaran operated along short transects within this representative area, allowing for the accurate characterization of the SML and the underlying water while minimizing spatial variability. These details are now included in the revised Methods section (lines 91–95).
Line 90 – on total scale? NBS scale? Accuracy? These data are the backbone for carbonate chemistry characterization some details are needed	In the revised manuscript, we now clarify that pH was measured using the integrated sensor of the S^3 flow-through system, embedded in a custom-built flow cell following the original S^3 design (see Ribas-Ribas et al., 2017), and is reported on the total scale. We also specify the sensor precision (±0.005 pH units), which is now explicitly mentioned in the text (lines 135-140) and detailed in Table 1.
Line 94 - please check and rephrase, "this study" is not the correct subject	We have changed the text accordingly.
Line 96 - How does the S^3 system collect water? Is it a close system or open, in contact with atmosphere? There was somebody on board?	We have now expanded the description of the S^3 system (Ribas-Ribas *et al*., 2017) to provide a more precise explanation of how SML and ULW waters are collected. The text specifies that water is collected via rotating glass discs and transferred into a closed flow-through system, minimizing atmospheric contact. We also clarified that the S^3 was a remotely operated catamaran with no personnel on board and that

	discrete DIC and TA samples were collected separately from its outlets by approaching the catamaran with the support Zodiac. (lines 103-105).
Line 98- Every 30 seconds you collected a seawater sample, for 30-45 min (2x30 samples?)? Or this is for instruments? Please expline better	We did not collect discrete seawater samples every 30 seconds. Instead, the S^3 system continuously pumped SML and ULW water through a flow-through system, and the sensors recorded temperature, conductivity, and pH at 30-second intervals during each 30–45-minute deployment. Discrete samples were not collected at 30-second intervals. Instead, DIC and TA samples were taken separately in small bottles directly from the S^3 outlets by approaching the catamaran with a support zodiac and immediately sealed to minimize atmospheric contamination. This clarification has been added in the revised text (lines 115–117).
Line 99 - please find another way to define this, "noticeable" is not a scientific definition.	We have changed the text accordingly.
Line 134 - Use data from the ICOS station at Lampedusa or other interpolated pCO₂ product, Mauna Loa is in a tropical area, it is not possible to use these data for atmospheric xCO₂ in the Mediterranean area.	In the revised manuscript, atmospheric pCO_2 data are now obtained from the ICOS atmospheric station at Lampedusa (8 m height), which provides quality-controlled dry-air CO_2 mole fraction measurements representative of Mediterranean conditions (di Sarra et al., 2025). Specifically, we used the monthly mean for August 2020, corresponding to our sampling period. This ensures that the ΔpCO_2 values used in the flux calculations are regionally appropriate. The Methods section (Lines 160–166) has been updated accordingly, and the results have been recalculated; however, the revised results are very similar to the previous ones.
Line 135-137 - please explain better, it is not clear.	In the revised Methods, we now provide a detailed explanation of how the percentage error was determined. Specifically, we clarify that we computed mean fluxes for each diel cycle, including all available data (day and night), and compared them with mean fluxes derived from daytime measurements only. The relative difference was expressed as $\left(\frac{F_{daytime}-F_{diel}}{F_{diel}}\right) \times 100$. We also note that both means were simple arithmetic averages of the available deployments. This revision (Lines 166–170) clarifies the procedure and explicitly highlights the rationale for quantifying the bias introduced by excluding nocturnal fluxes.
Line 148 - divide salinity-density correction and discussion from the carbonate chemistry section and move it above.	To improve clarity, we have introduced a new subsection heading for the salinity-density correction.
Line 195 (Figure 3) - check the units of salinity; Please explain better, how long are these timesteps?	The salinity units in Figure 3 are expressed in grams per kilogram (g kg^{-1}), consistent with the values reported in the Results. We have also

	clarified in the figure caption that each timestep corresponds to a 30–45 minute deployment (with data collected at 30-second intervals), with four daytime and two nighttime deployments per cycle.
Line 215 (Figure 4) - of the anomaly of temperature...	We have changed the text accordingly.
Line 286 - please add an explanation on how the temperature change affect the change in pH_{T25}.	We have clarified in the Discussion that, although pH values were normalized to 25 °C to ensure comparability, the carbonate system speciation and CO_2 solubility remain intrinsically temperature-dependent. Thus, short-term cooling of the SML still leads to detectable changes in pH_{T25}
The data discussion is weak. Various hypotheses are proposed to explain the observed variability, but these are not supported by further analysis or robust conclusions. For instance, in line 285 and following, the effect of evaporation on SML cooling is introduced, but the conclusion simply states that this affects pH_{t25}, without explaining whether it increases or decreases, and by which mechanisms. Other processes are mentioned without clarification. The overall conclusion is that "it is complicated, with an interplay of several factors," but this does not advance the current understanding.	In the revised Discussion (lines 327–330), we expanded the explanation of how physical processes affect pH_{T25}. We now specify that carbonate speciation itself is temperature-dependent (Zeebe & Wolf-Gladrow, 2001), so short-term thermal fluctuations directly influence pH_{T25}, even after normalization. In addition, we clarify that while evaporation tends to increase salinity and alkalinity, and thus pH_{T25}, vertical mixing can counteract this effect by introducing water with lower pH_{T25} and higher pCO_2. These revisions replace the previous vague statement of "an interplay of several factors" with a mechanistic interpretation that links temperature, evaporation, and mixing to carbonate system variability, thereby strengthening the conclusions.
One of the main conclusions is the importance of including nighttime in the study of air–sea CO_2 fluxes. Wind speed and ΔpCO_2 are the primary variables controlling these fluxes, with wind dependence incorporated into the parameterization of "k" (line 131; Wanninkhof, 2014). Wind speeds were lower during the night (line 174), which would be expected to result in lower fluxes. However, the authors do not consider this aspect, and the relevance of diel ΔpCO_2 variability is not adequately discussed.	We agree that wind speed, via its effect on the gas transfer velocity (k), is the dominant factor controlling the magnitude of the fluxes in our dataset, consistent with the Wanninkhof (2014) parameterisation. This explains the clear contrast observed between daytime fluxes, when wind speeds increased, and nighttime fluxes, when calm conditions reduced the exchange to near zero. In our results, the diel variability of pCO_2 was not statistically significant (Table S2), suggesting that its role was secondary compared to wind forcing. Nevertheless, our observations also indicate that buoyancy fluxes linked to evaporation and density instabilities may have modulated daytime exchange, amplifying the effect of wind. In the revised Discussion,we have clarified these points: (i) wind is the primary driver of the diel variability in fluxes, and (ii) the inclusion of nighttime data is essential to avoid overestimation of daily means, since omitting the nocturnal period led to differences of 33–50% in our cycles.
Line 298-299 - You have already discussed the relevance of this process a few lines above, so	In the revised discussion, we have expanded our explanation of negative diurnal anomalies. We

you should elaborate more on the causes of the observed trends.	now clarify that, under the conditions of strong stratification and weak winds observed during the study, localized evaporative cooling and convection could have offset the expected surface warming, as described in previous studies on surface layer instabilities (Cronin and Sprintall, 2001; Soloviev and Lukas, 2014).
Line 303 - all this processes would change the salinity both in the SML and ULM and cannot be used to explain the anomalies.	We agree that external processes such as evaporation, river discharge, precipitation, or tides cannot explain the negative salinity anomalies between SML and ULW. In the revised Discussion (lines 338–344), we clarify that while evaporation tends to increase salinity, the consistently negative anomalies observed indicate that vertical mixing processes dominate over evaporation. External inputs (river, precipitation, groundwater, and tides) were negligible during the study period and would, in any case, affect both layers simultaneously. Therefore, we attribute the anomalies specifically to localized near-surface mixing.
Line 314 – 319 - the discussion is very weak, you should say more than just "is complex and there are several factors". e.g.: normalize pCO_2 at a constant temperature and discuss the effect of biology on this parameter.	In the revised Discussion (lines 372–377), we strengthened the interpretation of Cycle 3. We now emphasize that the observed daytime increase in pCO_2 and pH_{T25} is best explained by biological and physical processes, rather than leaving it as a generic statement. Specifically, we discuss the likely contributions of enhanced respiration and CO_2 accumulation due to limited mixing, together with potential photoinhibition under high irradiance (Platt et al., 1980), which would reduce photosynthetic uptake. These additions provide a more precise mechanistic explanation for the observed pattern.
Line 331 – 334 - the main driver of this difference is wind, this has to be taken into account in the discussion.	We agree with the reviewer. The Discussion has been revised to state that wind is clearly the primary driver of the observed diel differences in CO_2 fluxes, in line with Wanninkhof's (2014) parameterization of k. We also add that the absence of wind at night helps explain why fluxes were nearly zero. This has been incorporated into the last paragraph of the Discussion (Lines 389–404).
Line 340 – 342 - In all the studyes wind variability at night is always considered, pCO_2 variability is neglected if pCO_2 is not measured by authonomous instruments. Here the main difference between day and night is the wind velocity.	We appreciate the reviewer's remark and agree that wind variability is the key difference between day and night in our dataset. Our intention was not to downplay this, but to emphasize that, since nocturnal fluxes were nearly zero, excluding them can lead to an overestimation of daily means. In the revised Discussion (Lines XX–XX), we have rephrased this point to make it more straightforward: wind remains the dominant driver, but our results illustrate that considering both day and night

	periods provides a more balanced estimate of diel air–sea CO_2 exchange.

Reviewer 2:

Specific comments:

Comments	Response
My primary concerns have to do with a lack of methodological details and a failure to consider explanations for patterns observed in the data. Specifically, the authors need to address the potential effects of tidal mixing on their data.	We thank the reviewer for all the valuable suggestions. The Methods section has been revised to provide additional detail on the study site, deployment strategy, variables measured, and environmental conditions. We also included a general explanation of why tidal effects were not considered in the study. Specific details and clarifications are provided in the responses to the following, more specific comments.
what are the uncertainties in the temperature, pH and salinity measurements collected using the S3 sampler? The differences being discussed between night and day, SML and ULW, and over short timescales are quite small. Similarly, what is the propagated uncertainty in the sigma-T, pH-T25, and pCO_2 calculations. One must know the uncertainties in the measurements to understand whether the fluctuations displayed in figures 5 and 6 (as just two examples of many) are relevant.	We appreciate the reviewer's attention to the uncertainties associated with the S^3 measurements and their impact on the interpretation of diel variability. First, regarding the uncertainties of the sensors, the precision of the temperature, salinity, and pH measurements is now explicitly provided in the Methods section and in Table 1. The pH sensor is reported on the total scale with an accuracy of ±0.005 pH units. In contrast, the precision of the temperature and salinity sensors is ±0.1 °C and ±0.2%, respectively. Second, concerning the propagated uncertainties in derived variables (σ-t, pH_{T25}, and pCO_2), we have now added a description in the Methods section indicating that these uncertainties were estimated based on the sensor precisions and the measurement errors of DIC and TA. Importantly, the observed diel fluctuations in temperature, salinity, and pH_{T25} (e.g., changes of ~0.28 °C, 0.30 g kg^{-1}, and 0.016 pH_{T25} units over 3–5 min intervals) are substantially larger than the associated measurement uncertainties. Therefore, the reported differences between day and night, SML and ULW, and over short timescales are robust and exceed the detection limits of the instrumentation. These clarifications directly address the reviewer's concern regarding whether the fluctuations displayed in Figures 5 and 6 are relevant relative to measurement uncertainty.
pCO_2 data from the Mauna Loa observatory does not seem relevant for the calculation of fluxes in the Mediterranean.	We appreciate the reviewer's remark. We agree that the Mauna Loa data are not suitable for flux calculations in a Mediterranean context. To address this, we now use atmospheric pCO_2 data from the ICOS Lampedusa station (di Sarra et al., 2025), which provides representative values for the region. The monthly mean for August 2020

	was used to calculate ΔpCO_2 during the campaign. This substitution improves the accuracy and regional relevance of our flux estimates. The corresponding changes have been implemented in the Methods section (Lines 160–166) and applied consistently throughout the results and figures.
More information is needed on the sampling location and environmental conditions at the time of sampling. Did the S3 move? Was it deployed in exactly the same location the entire 6 days? A better description of deployment details is needed. What is the water depth at the sampling location? Was there rainfall preceding or during the sampling event? What is the tidal range in the sampling location? What is the typical salinity range at the site (and how does this vary daily due to tides?)?	We appreciate the reviewer's request for additional information. The Methods section has been revised to clarify the deployment strategy. The S^3 was deployed six times per diel cycle, moving along short transects but treating the sampling location as a single point due to minimal spatial variability. Each deployment lasted 30–45 minutes, during which sensors recorded temperature, conductivity, and pH from both SML and ULW every 30 seconds. The catamaran was remotely piloted and carried an automated water sampler for collecting discrete samples of ~15 L for inorganic carbon analysis. Environmental conditions were typical for the region during the summer season, as reported in previous studies in nearby areas (cited in lines 94-102). Furthermore, precipitation averaged 1.4 mm during the first 15 days of August, and there was none during the campaign (Croatian Meteorological and Hydrological Service, 2020). (Croatian Meteorological and Hydrological Service, 2020). Tidal ranges were also small, ranging from 0.2 to 0.5 m (Cukrov, 2024), resulting in minimal currents and stable stratification. This environment provided ideal stable conditions for assessing the daily variability of SML and ULW parameters with minimal interference from precipitation or tides (discussed in more detail in the following comment).
Tides: I was surprised that the potential influence of tides on the diurnal parameter variations was never discussed, given that the sampling location is described as being on the Croatian coast and appears to be at the mouth of the Krka River estuary, where even microtidal tides could influence the salinity, CO_2, temperature, and pH parameters the authors are measuring. The authors should provide text and/or analysis demonstrating the degree to which tidal mixing of water masses does or does not contribute to the observed variations. To what extent could variations in tides influence the data in Figures 3 and 4, for example? Overlaying the tidal cycle on the graphs in Figure 3 could be very instructive and useful for providing support for or against diurnal-nocturnal versus tidal controls.	We thank the reviewer for bringing this issue to our attention. The Krka River estuary is micro-tidal, with tidal ranges of only 0.2–0.5 m (Cukrov, 2024), resulting in minimal tidal currentsDuring the sampling period, mean precipitation amounted to 1.4 mm for the period preceding the campaign (Croatian Meteorological and Hydrological Service, 2020), resulting in limited variation in river flow. Additionally, groundwater inflows during dry periods, such as summer, are minimal, ranging from 0.19 to 0.31 m^3/s (Liu et al., 2019). Consequently, tidal mixing and precipitation-driven river flow are expected to have a negligible influence on the observed diurnal variability of temperature, salinity, pH, and pCO_2. Therefore, these day–night variations primarily reflect local near-surface processes, including surface heating, evaporation, and

	small-scale turbulence, rather than vertical mixing induced by tides or river discharge. It is essential to note that the variability we observed follows a diurnal cycle (24 hours) rather than a semi-diurnal cycle (12 hours), further supporting the notion that the observed patterns are driven by surface forcing processes rather than tides. Our approach is also consistent with studies conducted before our experiment on the Croatian coast. Specifically, Stolle et al. (2020) conducted a similar diurnal study in Jade Bay, Germany, where the influence of tides was strong; therefore, the research group decided to replicate the study in a Mediterranean region (characterized by microtidal conditions) to minimize tidal interference. This supports our interpretation that the diurnal patterns we report arise from local environmental processes, rather than tidal forcing.
Lines 303-307 - the authors note that the Krka River normally has low discharge in summer months, but what were the discharge conditions during the time of sampling? Presumably, there are at least precipitation data for that time period, if not discharge data for the river. Those data will be effective for justifying their argument.	We appreciate the reviewer's suggestion. We have now clarified in the revised manuscript that discharge from the Krka River is generally reduced during the summer months, which is consistent with previous observations in this estuary (Frka et al., 2009; Marcinek et al., 2020). During our sampling period (10–15 August 2020), precipitation was minimal (1.4 mm),as reported by the Croatian Meteorological and Hydrological Service (2020), resulting in negligible short-term fluctuations in river discharge. Moreover, submarine groundwater discharge in the area is known to contribute only a minimal volume (0.19–0.31 m^3 s^{-1}) compared to the annual mean river discharge (Bužančić et al., 2016; Marcinek et al., 2020). Together, these hydrological conditions confirm that river inputs and precipitation-driven variability had no significant effect on the salinity and carbonate system parameters observed during our study. The updated manuscript text now includes this clarification.
Lines 335-336 - why does the lack of wind which forces CO2 fluxes to near 0 demonstrate the need for gas transfer parameterizations with an intercept? While this may be true, the justification is not clear in the argument being made here.	We thank the reviewer for this remark. We agree that our dataset alone cannot demonstrate the need for an intercept in parameterisations of k. To clarify this, we have revised the sentence in the Discussion to indicate that our observations are consistent with previous suggestions in the literature (Ribas-Ribas et al., 2019), rather than presenting it as a conclusion from our data.
Lines 340-342 - can the authors determine the degree to which the physical and biogeochemical differences in the SML contribute to the differences in the estimated CO_2 fluxes (as opposed simply to the wind speed differences)? It seems this could be calculated using a sensitivity	While a sensitivity analysis would indeed be the ideal approach to disentangle the relative contributions of physical and biogeochemical differences in the SML from those driven by wind speed, our dataset does not provide sufficient resolution to support such an analysis in a

analysis, which would demonstrate which parameters control these differences in CO_2 fluxes between day and night. That type of analysis would place the importance of the diurnal-nocturnal differences in the physical and biogeochemical parameters into proper context.	statistically robust way. The primary objective of this study is rather to illustrate the observed variability and, most importantly, to highlight the bias introduced when nocturnal data are excluded. We agree that a more detailed quantification of parameter control would be valuable, and we plan to address this in future studies with larger datasets. In the revised Discussion (lines 395–4040), we now also emphasize that SML properties, such as enhanced CO_2 solubility under slightly cooler and fresher conditions and reduced turbulence at night, contribute to the observed differences in fluxes.
Note that 'night' is spelled incorrectly in tables 1 and S2	We have changed the text accordingly.