

Response to the reviews – All changes are listed in the responses to the reviewers

Response to Reviewer 1

General comments

The authors have presented a study that investigates sea-surface microlayer dynamics over one seasonal cycle during 2016-2017, in a coastal area of the eastern Mediterranean Sea. Specifically, the authors investigate biogeochemical de/coupling of the surface microlayer and corresponding underlying water, with comparison to rainwater samples from the study area, and quantify DOC, CDOM, FDOM and Chl-*a*, with the addition of introducing a novel FDOM/CDOM index.

The data presented are likely to be of interest to a broad biogeochemical audience, and the study itself is within the scope of BG, but I find the data interpretation lacks cohesion. The scientific question(s) that the study aims to answer are unclear and not outlined in the manuscript, and the Discussion section does not sufficiently contextualise the findings. In my opinion, the Conclusion section also does not fully explain the importance of the study or how the findings fit within the context of other published literature. The final concluding sentence (Lines 616-618) captures the main problem; that the study does not develop an existing or present a new concept effectively. This is not to say that this study cannot present a novel concept, but the presentation falls short of making such clear and the data are not structured as a narrative.

This study has the potential to contribute meaningfully to our understanding of SML dissolved organic matter dynamics, and I commend the authors' efforts in developing the FDOM/CDOM index. However I suggest a reworking of the statistical analyses and presentation of data to ensure effectual communication of the narrative presented, which seems to get lost at the manuscript progresses. The consistent decoupling of some parameters between the SML and ULW is of particular interest, as is the different composition of rainwater to the SML. It is widely accepted that the primary source of organic matter to the SML is from the ULW, and studies such as this that demonstrate additional nuance to SML organic matter sources and dynamics are invaluable to our understanding of spatiotemporal variability in SML dynamics. If this is the authors' intended message, then it is lost in the detail.

Authors' response: We sincerely thank the reviewer for this thoughtful and constructive evaluation. We appreciate the recognition of the potential contribution of our study and the positive assessment of the novel FDOM/CDOM index. We agree that the narrative and conceptual framing of the manuscript required clarification and strengthening. In response, we have substantially revised the manuscript to improve cohesion and explicitly articulate the scientific questions and conceptual contribution of the study. Specifically:

1. *Scientific questions clarified:*

We now clearly state the main research objectives at the end of the Introduction, emphasizing our aims. The revised text has been added in the relevant specific comment

2. *Narrative restructuring:*

The Results and Discussion sections have been reorganized to better highlight the decoupling patterns between SML and ULW. We now present new statistical analyses (GLM) as advised in a more structured manner to directly support the conceptual framework.

3. Contextualisation improved:

The Discussion has been modified to better situate our aims and findings and more literature findings have been included

Conclusions strengthened:

The Conclusion section has been rewritten to explicitly articulate the conceptual contribution of the study, highlighting that CDOM enrichment in the SML is not simply a function of DOC concentration but reflects layer-specific modulation of optical quality, and that the novel FDOM/CDOM index provides a new tool in CDOM investigation. The revised conclusion section has been added in the relevant specific comment.

We believe these revisions substantially improve the clarity and cohesion of the manuscript and better communicate its conceptual significance.

Specific comments

1. References

The number of references is sufficient, but the number of recent references (i.e. within the last 10 years) is minimal (28 out of 102 citations). Considering that SML research is a very active global field and to enable relevant discussion and contextualisation of this study, I would expect to see a greater number of recent studies included in this study's literature review and discussion. Suggestions, but not an exhaustive list, of recent studies that explore CDOM (and/or FDOM or surfactants or other OM) dynamics in the SML that are missing from this study:

- Xu et al. (2025). DOI: 10.1016/j.marenvres.2025.107328
- Rickard et al. (2022). DOI: 10.1029/2021GL095469
- Barthelmeß and Engel (2022). DOI: 10.5194/bg-19-4965-2022
- Stolle et al. (2020). DOI: 10.1175/BAMS-D-17-0329.1
- Miranda et al. (2018). DOI: 10.1525/elementa.278
- Drozdowska et al. (2017). DOI: 10.5194/os-13-633-2017
- Engel et al. (2017). DOI: 10.3389/fmars.2017.00165
- Galgani and Engel (2016): DOI: 10.5194/bg-13-2453-2016
- Pereira et al. (2016). DOI: 10.5194/bg-13-3981-2016

Authors' response: We thank the reviewer for highlighting relevant recent studies. We have revised the manuscript to incorporate additional recent studies (>10) and to strengthen our interpretations.

1. Data and Statistical Analyses

A more unified approach to data analysis would benefit this study; currently there is a combination of correlation analysis, regression analysis, and Mann-Whitney U and Wilcoxon signed-rank tests, which appear to hunt for significance; with specific reliance on p-values, as these are all that are stated in text, without further scrutiny of the data. The p-values alone tell the reader nothing without f/t-statistics or the specific test used. I suggest using GLMs/GAM to include multiple variables in one model and test which have an effect on a response variable. This would streamline the narrative and ensure robustness of the suggested SML dynamics.

Authors' response: We thank the reviewer for this insightful suggestion. Performing a GLM to investigate the relationships among DOC, CDOM and FDOM in the two layers provided additional insights, which have been incorporated into the manuscript. The new findings are added in relevant specific comments

Additionally, with the current text presented, the authors negate from reporting data appropriately, for example, average values throughout the manuscript are reported without standard deviations, there are inconsistent spaces between values and units, and where p-values are stated there is no further information about the test being reported in text.

Authors' response: We thank the reviewer for identifying these inconsistencies. We corrected the spaces between values and units and added the specific statistical analysis along with the p-values. Regarding the standard deviations for the average values, since the range is reported for all the measured parameters and adequately reflects the variability of the dataset, we believe that including standard deviations would be redundant. For the sake of clarity, we therefore retained the current presentation.

1. FDOM/CDOM index

While the development of the novel FDOM/CDOM index is a strength of the paper the authors could improve the robustness of their suggested measure by including some validation steps. Given that the index is based on both modelled and transformed data (e.g. the normalisation (would also be good to know what exact transformation was used here)) the ratio of FDOM/CDOM might not vary linearly. Can the authors provide some evidence that the ratio is robust to any transformations used? You could include compare the transformed and untransformed data. It would also be useful to see a comparison of index values generated from the raw data to cross validate the smoothed modelled data. Providing these validation checks for the novel index will make this a much more robust and useful value/measure for the field and result in a more highly cited, impactful paper.

Authors' response: We sincerely thank the reviewer for acknowledging the novelty and strength of the proposed FDOM/CDOM index. We also appreciate the opportunity to clarify this point, as the original text may not have been sufficiently clear. The paragraph has now been revised accordingly. To clarify, the FDOM/CDOM index was calculated exclusively from scattering-corrected raw spectral data and not from the modelled data. The PARAFAC modelled output was used solely for peak identification and does not present the full spectrum; therefore, it was not suitable for calculating the index, which requires whole spectrum information. Furthermore, no data transformation or normalizations were applied prior to the index calculation. The revised paragraph is added in relevant specific comment.

1. Manuscript narrative flow

The manuscript as whole seems to lose steam as it progresses. The authors have evidently undertaken a considerable amount of work for this study, and as such the manuscript is lengthy, but it should be condensed. Appropriate structuring of a clear research question would help select where condensing text

will be appropriate, including which data to showcase and which to use as contextual data. For example, there is one mention of FDOM in the Introduction (Line 76), but FDOM makes up a considerable portion of the manuscript; ultimately the FDOM portion, with the novel FDOM/CDOM index, could be a standalone and potentially more impactful manuscript. Further to this, Chl-*a* data are presented, but not mentioned in the Introduction or Conclusion sections. There is a substantial portion of the Introduction that talks about surfactants and air-sea gas exchange, and while these parameters are central in SML studies they are not measured in this study. Consequently, the narrative and flow is not cohesive, and the manuscript would benefit from restructuring, with a clear focus and conclusions.

Authors' response: We thank the reviewer for the thorough assessment of the manuscript. We have revised the manuscript to more clearly present the research objectives. FDOM and Chl-a have been integrated in the Introduction while extended discussion on air-sea gas exchange has been removed.

Technical corrections / Line-by-line

L14: Some surfactants are hydrophobic yes, but some surfactants are amphiphilic; the SML is made up of a complex gelatinous matrix of particulate and dissolved surface-active organic matter.

Authors' response: We thank the reviewer for this clarification. We agree, the text has been revised accordingly.

L15-16: The typical enrichment of surface-active substances in the SML does not automatically equate to them being a control on air-sea gas transfer. More their specific physico-chemical properties that impede molecular diffusion across the interface.

Authors' response: We thank the reviewer for this comment. The text has been revised accordingly:

This enrichment, together with the specific physico-chemical properties of the SML, allows it to modulate gas transfer across the interface

L18: 'including' is misleading, as CDOM and FDOM were the only DOM fractions presented in this study.

Authors' response: The text has been revised.

L40-41: This study does not quantify any air-sea gas exchange parameter. I suggest rephrasing this sentence to be representative of what this study does highlight, such as microscale SML OM dynamics. Outlining clear research questions will help to address this.

Authors' response: This part has been removed

L45: The SML is the boundary interface between the atmosphere and ocean, it does not 'represent' the boundary.

Authors' response: Corrected in the text

L47: I would lean toward saying ‘historically’ rather than ‘generally’. The general thinking now is that the composition of the surfactant pool in the SML changes with windspeed, with in/soluble surfactants dominant at different thresholds.

Authors’ response: We thank the reviewer for this comment. The text has been revised as suggested.

L49: What are the authors classifying as ‘high wind speeds’ and how was this threshold determined?

Authors’ response: More details have been added in the text:

However, recent studies show that this relationship is not straightforward, as enrichment can occur even at wind speeds above 10 m s^{-1} , mainly due to increased bubble fluxes that return surfactants to the SML (Sabbaghzadeh et al., 2017; 2024).

L53: See *Specific Comments* re updating/expanding with recent studies.

Authors’ response: More recent studies have been added as references

L58: 15-50% reduction relative to what?

Authors’ response: Removed, Introduction has been revised to more clearly show the objectives of the study as suggested by the reviewer

L66: I advise caution with the use of ‘primarily’ here, and suggest rephrasing.

Authors’ response: The text has been revised.

L74-82: References to support these statements?

Authors’ response: References have been added

L76: This is the only mention of FDOM throughout the whole Introduction section. Given the prevalence of FDOM throughout the remainder of this study, I suggest integrating an introduction of FDOM into this section.

Authors’ response: We thank the reviewer for this comment. More details on FDOM have been added in the Introduction section

L98: Yes, but where there are slicks there is more OM overall. Have any of the studies cited found a correlation between CDOM or FDOM and surfactant concentrations in the SML?

Authors’ response: Reference has been added in the text (Rickard et al., 2022)

L99-101: Agreed, but there have been more studies within the last 10 years, which are missing from this study that have explored this (See *Specific Comments*). I suggest integrating such studies.

Authors' response: More recent studies have been added throughout the manuscript (>10)

102-107: The authors have introduced the SML and CDOM, but are yet to explain why they are undertaking this study specifically. What question(s) will it answer and/or what value will it add to the field? Outlining this clearly will help to strengthen the structure of the Discussion and Conclusion sections.

Authors' response: We appreciate the reviewer's advice and have revised the Introduction to clarify the study objectives:

Here, we introduce a new index, the FDOM/CDOM index, which links these two pools (CDOM and FDOM) and provides integrated insights into the chemical structure of optically active DOM as a whole.

The aims of this work are: i) To understand potential transformations and dynamics within the broad CDOM pool in the sea surface microlayer (SML) and the underlying water (ULW) at a Mediterranean coastal site using high-resolution (biweekly, one-year) temporal data, by applying established absorbance indices and the novel FDOM/CDOM index across multiple spectral regions. ii) To evaluate the relative contributions of in situ processes, upward flux from the ULW, and atmospheric (rainwater) inputs in the shaping of the DOM and CDOM pools in the SML.

L117-119: Figure 1: The map area is very large relative to the study area. I suggest zooming in further to the study area so that it is more obvious to the reader, so that individual sampling sites can be marked. Also, use a colour that is easier to see clearly than yellow.

Authors' response: Corrected, there is only one sampling point

L123: Suggest 'were' instead of 'have been'.

Authors' response: The text has been revised.

L128: Should be 'ULW'.

Authors' response: We thank the reviewer for pointing out, corrected

L130: Table S?

Authors' response: We thank the reviewer for noticing, corrected

L133: This is the first mention of Chl-*a* so far in the manuscript. Please also integrate into Introduction.

*Authors' response: We appreciate the reviewer's comment. Although chlorophyll-*a* was measured as a complementary parameter and showed limited influence on the main variables, we have now briefly introduced it in the Introduction to improve context:*

Chlorophyll-*a* (Chl-*a*) is widely used as a proxy for phytoplankton biomass and primary productivity and is closely linked to the production and transformation of DOM in surface waters. Phytoplankton blooms have been identified as important drivers of DOM enrichment in SML, with phytoplankton-derived organic matter fueling microbial activity and influencing biogeochemical cycling at the air–sea interface (Wurl et al., 2016; Bibi et al., 2025)

L134-135: Were only the Chl-*a* samples 0.22 µm filtered, or where all DOC, CDOM, FDOM and Chl-*a* filtered? This reads like only the Chl-*a*. Rephrase for clarity. If the DOC, CDOM and FDOM were not filtered then the parameters measured are of the total, not the dissolved phase.

Authors' response: All samples were filtered, the text has been revised.

L137: Should be 'caps' not 'cups'.

Authors' response: We thank the reviewer for pointing out

L139: Is the 10% HCl stated by volume or concentration? Molar concentration would be clearer.

Authors' response: It is dilution by volume, added to the text

L150-151: Why was a lower volume filtered for the SML than the ULW? Is this an established or tested technique? Please outline which here, and cite accordingly.

*Authors' response: The lower filtration volumes used for the SML were due to sampling constraints associated with the glass plate technique. Laboratories tests evaluating different filtration volumes showed no significant differences in Chl-*a* concentrations. We have added this clarification in the text*

L167-175: No backscatter correction done? See Kitidis et al. (2006); DOI: 10.1016/j.dsr2.2006.05.009

Authors' response: Kitidis et al., refer to unfiltered samples. Samples for CDOM analysis were filtered through 0.22µm polycarbonate filters right after the sampling (clarification has been added in the text) and thus no backscatter correction was needed beside the subtraction of the average absorbance between 680-700nm from each sample. We follow the IOCCG protocol which has been added in the text as references along with more details in the method section.

L176: The absorption coefficient in marine waters is often calculated using 300 nm (see references already cited and those listed above in *Specific Comments*) but also often using 350 nm. Can you justify further why you selected 300 nm for this study area?

Authors' response: The justification has been added in the text:

Absorption coefficient at 300 nm wavelength or 350 nm is commonly used for the representation of bulk CDOM quantity. In this study, absorption coefficient at 300 nm was selected as a more reliable proxy, since absorption at 350 nm was strongly attenuated, particularly in ULW samples.

L185: Should be '275-295' not '275-275'.

Authors' response: We thank the reviewer for pointing out

L218: I suggest a stand-alone section for the FDOM/CDOM Index method description.

Authors' response: We thank the reviewer for the suggestion. The method section has been revised accordingly:

2.6. FDOM/CDOM index

For the calculation of the FDOM/CDOM index discussed in Section 3.4 numerical fluorescence intensity values were extracted from scattering corrected EEMs using the 'smootheem' function of the drEEM package. Fluorescence intensity (I_{ij}) at each excitation wavelength (E_{x_i}) was normalized by the corresponding absorption coefficient (a_i) derived from absorption measurements. This normalization was applied across all emission wavelengths (E_{m_j}), yielding the ratio I_{ij}/a_i i.e., the FDOM/CDOM (R.U.m) index, in the form of a 3-dimensional matrix spanning excitation wavelengths of 250-450 nm and emission wavelengths of 260-550 nm (Suppl Fig. S1). To obtain mean FDOM/CDOM index for each layer, the FDOM/CDOM matrices of all samples were grouped separately for the SML and ULW. For each dataset the average ($n=22$) ratio matrix was calculated and plotted. All analyses were conducted in MATLAB R2015a using in-house functions (Pitta and Zeri, 2021).

L239: EF = 1 does not indicate depletion; EF < 1 indicates depletion.

Authors' response: We thank the reviewer for pointing out

L241-249: See above in *Specific Comments* section.

Authors' response: We thank again the reviewer for the advice. The paragraph has been revised to include GLMs statistics:

The variability of the measured parameters between SML and ULW was evaluated using the Mann–Whitney U test, as the data did not meet the assumptions required for parametric analysis. For the same reason, deviations of enrichment factors from unity were assessed using the one-sample Wilcoxon signed-rank test. Generalized linear models (GLMs) were applied to examine relationships

between the response variables (a_{300} , spectral slope and PARAFAC component intensities) and predictors (DOC, a_{300} and layer). A Gamma error distribution with a log link function was selected because the response variables were continuous, positive and exhibited right-skewed distributions, making this framework more appropriate than Gaussian linear models. GLMs were preferred over simple linear regression because they allow the simultaneous evaluation of continuous predictors (e.g., DOC, a_{300}) and a categorical factor (layer), as well as their interaction terms, thereby explicitly testing whether the strength or direction of relationships differed between layers. Spearman rank correlation analysis was additionally applied to assess monotonic relationships among variables. All analyses were conducted using IBM SPSS Statistics, Version 20.0.

L260-261: End of sentence trails off, can you also be quantitative for the April-May period?

Authors' response: The temperature has been added

L266: An EF of 1.2 is not typically considered minimal. This would be an excellent opportunity to contextualise this with other literature.

Authors' response: We agree that an enrichment factor of 1.2 does not necessarily indicate minimal enrichment per se. Our interpretation was based on the relatively high variability ($SD = 0.3$), resulting in a substantial fraction of samples with $EF \leq 1$, as well as the contrast with the other measured parameters, which consistently exhibited much higher enrichment factors (>2). To avoid ambiguity, we have revised the text to describe chlorophyll-a enrichment as weak or modest, and we now explicitly refer to its variability and relative magnitude:

No significant difference was detected between layers ($p > 0.05$), and SML enrichment was weak ($EF = 1.2 \pm 0.3$) with considerable variability and several samples showing no enrichment ($EF < 1$).

L267: Is this unexpected considering that two phytoplankton blooms are expected per year, as outlined earlier in the manuscript?

Authors' response: We thank the reviewer for the opportunity to clarify this point. The two blooms are expected in the spring and autumn, not in summer. We have revised the text in the study area.

L274: Figure 2c: The decoupling of DOC between the SML and ULW is very interesting and certainly worth further exploration in the text.

Authors' response: We thank the reviewer for pointing out. We added a discussion of DOC decoupling in section 3.2. (please see also the answer at comment L280-291)

L275: How have you categorised a 'low' windspeed? And dust particles were elevated 'relative' to what? Were these parameters measured throughout the whole 'study period' or just on sampling days? Please be clear with this.

Authors' response: Windspeed during samplings was $<3.5 \text{ m s}^{-1}$, consistently below the threshold recommended for SML collection. The mention to the dust particle has been removed. Rain and dust data were retrieved from observatory data sources throughout the whole study period while chl-a was measured only during the samplings. The certain lines as well as the caption of figure 2 have been revised for clarity.

L283: Should be 'ULW' not 'UWL'.

Authors' response: We thank the reviewer for pointing out

L287-289: This is where enrichment factors are useful. I suggest reporting DOC EFs in parallel to DOC concentrations.

Authors' response: We thank the reviewer for the suggestion, the text has been revised accordingly:

Annual variability of DOC concentrations in the SML and ULW is shown in Fig. 2(c). In the SML, DOC ranged from 1.09 to 8.33 mg L^{-1} , with an average concentration of 3.13 mg L^{-1} , significantly higher than that in the ULW (average: 0.93 mg L^{-1} ; range: 0.78–1.23 mg L^{-1} ; Mann Whitney U test $p = 0.001$) while the enrichment factor ($EF = 2.7 \pm 1$; Wilcoxon signed-rank test $p = 0.001$; Fig. 3(a)) confirms substantial accumulation of DOM components in the SML.

L280-291: I disagree, there is clear decoupling evident from the seasonal cycle shown in Figure 2c, and from the immediately previous sentences in this paragraph.

Authors' response: We thank the reviewer for the insight. We replaced the correlation analysis with regression analysis to better show the decoupling of DOC in the two layers:

Moreover, no significant relationship was observed between DOC in the two layers ($r^2=0.028$, $p=0.492$), indicating a clear decoupling and suggesting that DOC in the ULW does not exert a measurable influence on DOC in the SML (Fig. 3(a)). This observation contrasts with previous studies in which a strong correlation was reported between the DOC in the SML and the ULW indicating that upward transport of material plays a dominant role in the composition of the SML in DOM (Chen et al., 2013; 2016; 2022; Engel and Galgani, 2016; Engel et al., 2018).

L290-293: The decoupling is evident from Figure 2c, and of much more interest and inherent value to the narrative of this study than it is given here. I suggest a more thorough review of the SML DOC literature.

Authors' response: We thank the reviewer for the insight. See our answer above on decoupling. We further discuss findings in relation to literature.

L297: What statistical test was applied here?

Authors' response: The statistical test has been added:

(EF = 2.7 ± 1 ; Wilcoxon signed-rank test $p = 0.001$; Fig. 3(a))

L299-301: Figure 3: The colour bar would be more informative to show seasonality of samples, while a 1:1 EF line can be plotted on each figure (above shows SML accumulation and below show depletion). Otherwise the two EF colour bars should be of the same scale.

Authors' response: We appreciate the reviewer's suggestion. However, as no significant seasonal patterns were observed in any of the measured parameters, we believe that modifying the colour bar to reflect seasonality would not enhance the interpretation of the figure or provide additional insight. Seasonality is depicted in Figure 2. Instead, keeping the colour bar in Figure 3 as is, clearly shows the variation in EFs. Also, since all the enrichment factors were well above 2 we believe that adding the 1:1 EF line on the figure would not enhance the reading of the figure since there will not be any points below the line. Lastly, we kept the EF colour bars on different scales since there is no direct comparison between EFs of DOC and a_{300} and changing the scale would diminish visual resolution.

L307: Is the correlation between DOC and a_{300} shown?

Authors' response: We replaced the correlation with GLM after the reviewer's suggestion. A table (Table 1) has been added summarizing the results of all the GLMs.

Table 1: Results of Generalized Linear Model analysis assessing the influence of DOC, a_{300} and water layer on CDOM optical properties and PARAFAC intensities.

		B	Std. Error	Wald χ^2
Response	Predictor			
a_{300}	DOC	0.682	0.537	4.791
Layer (SML vs ULW)	0.761	0.522	2.125	0.145
DOC x Layer	-0.179	0.542	0.109	0.741
$S_{275-295}$	DOC	-0.070	0.242	0.467
Layer (SML vs ULW)	-0.079	0.231	0.119	0.730
DOC x Layer	-0.027	0.234	0.012	0.912
$S_{275-295}$	a_{300}	-0.618	0.129	32.62
Layer	-0.286	0.075	14.65	<0.001

(SML vs ULW)				
$a_{300} \times \text{Layer}$	0.493	0.130	14.37	<0.001
I1	a_{300}	1.006	0.383	11.89
Layer (SML vs ULW)	1.064	0.224	22.52	<0.001
$a_{300} \times \text{Layer}$	-0.676	0.388	3.041	0.081
I2	a_{300}	0.606	0.456	3.205
Layer (SML vs ULW)	1.277	0.270	22.49	<0.001
$a_{300} \times \text{Layer}$	-0.386	0.462	0.698	0.403
I3	a_{300}	1.105	0.494	7.924
Layer (SML vs ULW)	0.987	0.295	11.21	0.001
$a_{300} \times \text{Layer}$	-0.801	0.501	2.559	0.110
I4	a_{300}	0.691	1.186	0.961
Layer (SML vs ULW)	0.278	0.780	0.127	0.721
$a_{300} \times \text{Layer}$	-0.193	1.213	0.025	0.874

L310-313: This has been found in other studies – some already cited in this manuscript and some listed above in *Specific Comments*.

Authors' response: The text has been revised referencing previous studies as suggested:

The lack of any significant relationship between a_{300} in the two layers (Fig. 3(b)) suggests that CDOM either originates from different sources and/or undergoes distinct processes, highlighting the additional roles of in situ photochemical or biological transformations and/or direct atmospheric inputs to the optically active DOM pool. Penezic et al., (2022) reported lack of CDOM correlation between the SML and ULW even with similar absorption coefficient values in the two layers. Contrary, other studies (Galgani and Engel, 2016; Yang et al., 2022) reported strong correlation of CDOM between the SML and ULW implying a connection of CDOM in the two layers.

L314-315: Correlation does not indicate that one variable influences another variable, only that they covary.

Authors' response: This part has been changed according to GLM analysis:

To investigate potential drivers on CDOM dynamics, generalized linear models were applied as described in Table 1. The relationship between DOC and CDOM was first examined using a GLM with a_{300} as the response variable and DOC and layer as predictors. DOC concentrations significantly explained variation in CDOM absorption at 300 nm across both layers (Wald $\chi^2=4.79$, $p=0.029$). The effect of layers was not significant ($p=0.145$) and there was not significant interaction between DOC and layer ($p=0.741$) indicating that the DOC vs a_{300} relationship did not differ between layers. These results suggest that the significantly higher a_{300} values in the SML are primarily attributed to DOC enrichment rather than a layer specific change in CDOM bulk quantity.

L315-316 and Table 1: The text refers to correlation analysis while the Table caption refers to regression analysis. Which is it?

Authors' response: Table 1 has been modified since the regression analysis has been replaced with GLMs, please see also the answer comment L307.

L317 and L318: DOC is not bulk DOM.

Authors' response: The text has been revised

L318-319: Again, referring to recently published studies here would be useful and informative. It could also be that the processes in the SML and ULW are different, or that the DOC and CDOM pools are compositionally different in the two layers to begin with.

Authors' response: We have revised this paragraph based on the new findings of the GLM, please see also the answer in comment L314-315

L326: Please explain how they are 'disproportionately' enriched? In context of other studies?

Authors' response: The text has been revised for clarity:

UV-A/near-visible chromophores are disproportionately enriched at the surface relative to UV-B and UV-C, highlighting a compositional differentiation of CDOM in the SML with higher contribution of HMW DOM compared to the underlying water.

L343-346: I don't understand what these sentences are saying, please clarify.

Authors' response: The text has been revised based on the new findings of GLM with slope as response variable. Please see also the answer at comment L347-349

L346-347: Studies have looked at CDOM photodegradation in the SML specifically, or shown data that suggest a difference between the SML and ULW: e.g. Rickard et al., 2022; Sabbaghzadeh et al., 2017.

Authors' response: We thank the reviewer, suggested references are added among others. Please see also the answer in the next comment.

L347-349: There is considerable overlap between the SML and ULW (i.e. $S_{275-295} > \sim 0.025$ on Figure 4). Can you provide evidence to support that they are in fact different, to support your suggestion of 'other processes'? The fact that you have fit one exponential decay equation to both depths together is also contradictory to this statement.

Authors' response: There are actually only two points that overlap. The text has been revised accordingly. We report the slopes for each relationship separately, showing that the relationships between absorption coefficients and slope differ markedly between the two layers. We have also performed GLM that shows different relationships between slope and a_{300} in the SML and ULW. The findings of GLM have been added in the text and Table 1:

In contrast, when a_{300} and layer were included as predictors and slope as response variable, the GLM revealed significant effects of layer ($p < 0.001$), a_{300} ($p < 0.001$) and the layer – a_{300} interaction ($p < 0.001$). Particularly, slope values were significantly lower in the SML (Wald $\chi^2 = 14.65$, $p < 0.001$), slope decreased with increasing a_{300} in the ULW (Wald $\chi^2 = 32.62$, $p < 0.001$) while the slope – a_{300} relationship differed between layers (Wald $\chi^2 = 14.37$, $p < 0.001$). These results indicate that spectral slope is modulated by CDOM quantity in a layer specific manner, with the SML showing a weaker negative relationship between slope and a_{300} than the underlying water. Thus, the GLM analysis of spectral slope suggest that specific processes in the SML, rather than DOC concentration alone, control the optical quality of DOM. Overall, the combined GLM results for DOC and CDOM indices indicate that CDOM enrichment in the SML is not layer specific in terms of quantity, but is layer specific with respect to optical quality. The negative relationship between spectral slope and absorption coefficients revealed by GLM has been previously reported (Chin et al., 1994; Weishaar et al., 2003; Helms et al., 2008; Tzortziou et al., 2011). This relationship is commonly used to interpret changes in CDOM resulting from photodegradation processes in surface waters (Helms et al., 2008; Fichot and Benner, 2012). The relationship tends to be linear within a compositionally uniform DOM source (Helms et al., 2008; Twardowski and Donaghay, 2001) while it becomes nonlinear (often exponential) across natural gradients encompassing a wide range of CDOM concentrations or mixed sources (e.g., riverine and marine), due to the coexistence of DOM with differing molecular compositions and reactivities (Fichot and Benner, 2012; Nelson and Siegel, 2013). In Fig. 4, this relationship is presented against a_{300} (m^{-1}). When both layers are combined, the a_{300} vs $S_{275-295}$ relationship is well described by an exponential decay equation $R^2 = 0.791$ ($y = 0.020 \cdot e^{-1.572 \cdot x} + 0.023$) indicating photodegradation of CDOM in the two layers. However, it is obvious that the relationship in the ULW presents steeper slope (slope = -0.02 , $R^2 = 0.533$, $p = 0.000$) than in the SML (slope = -0.003 , $R^2 = 0.699$, $p = 0.000$) indicating more intense photodegradation in the ULW. The less steep slope in the SML suggests that other processes taking place there probably compensate the effect of photodegradation; in accordance with the GLM outcome revealing layer specific dependency of spectral slope. Previous studies have also reported persistent CDOM concentrations in the SML hindering photodegradation effect (Obernosterer et al., 2008; Wurl et al., 2009; Xu et al., 2025). Particularly, Xu et al., (2025) reported 16% loss in a_{350} in the SML compared to 30% loss in a_{350} in surface waters. Possible explanations for the less profound

photodegradation of CDOM in the SML compared to the ULW are the continuous reorganization of the amphiphilic DOM in the SML (Wurl et al., 2009; Mustaffa et al., 2017, Penezic et al., 2022). Rickard et al. 2022, suggested the production of relatively low molecular weight surfactants through CDOM photodegradation in surface waters. On the other hand, biological in-situ production of optically active material in the UV-A/ near-visible region in the SML is also possible. Galgani and Engel (2016) have observed a decrease in spectral slope in the SML due to the abundance of bacterial and phytoplankton cells in parallel to elevated gelatinous material (Coomassie particles and TEPs), thus corroborating to SML specific processes leading to the production of higher molecular weight CDOM.

L369: Slicks were only observed? Or actually sampled from? It would be informative to mark these samples of the figures presented in the manuscript, and highlight if any of the extreme EFs reported were (or were not) from slick sampling.

Authors' response: Whenever slicks were present, SML samples were collected directly from the slicks. This clarification has been added in section 3.1. Two extreme EFs are reported and both were from slick sampling. However, the rest slick samplings did not show extreme EFs. All samples with slicks are marked on Table S1 in the supplementary data.

L425: There is no temporal component presented in Fig. 7, so 'during most months' cannot be ascertained by the reader. As with Fig. 3, a seasonal colour bar would be more informative than an EF colour bar. There can be no direct comparison between specific samples/components if the temporal component is not presented.

Authors' response: We appreciate the reviewer's suggestion. Same as comment L299-301, no significant seasonal patterns were observed in PARAFAC components and thus the results are not discussed in terms of seasonality. We removed 'during most months' for clarity. Furthermore, we believe that modifying the colour bar to reflect seasonality would not enhance the interpretation of the figure or provide additional insight.

L425-438: The language in this paragraph is imprecise, with frequent use of non-specific words, such as 'high', 'considerably lower', 'exceptionally strong', without the in-text data to illustrate the narrative. Suggest condensing this paragraph, and/or including respective data to strengthen the text throughout (i.e. state value of outlier as well as sample date: L431).

Authors' response: We thank the reviewer for the suggestions. We have revised this paragraph:

As illustrated from Y-axes in Fig. 7, in the SML, components C1 (peak A–C) and C2 (peak T) exhibited higher fluorescence intensities (I1: 0.033–0.398 R.U. and I2: 0.038–0.429 R.U.,) than components C3 (peak A–M) (I3: 0.016–1.249 R.U.) and C4 (peak B) (I4: 0–0.196 R.U.) consistent with their order of deconvolution by the PARAFAC model. Moreover, fluorescence intensities show roughly equal contributions of the humic-like C1 (average 30.6 %) and tryptophan- like C2 (average 31.7 %) to the FDOM pool. Component C3 (peak A–M) had the highest average fluorescence intensity (0.122 R.U.) and the widest range; however, this was largely due to an outlier recorded on 01 July 2016 (Fig. 7(c)). Excluding this outlier, C3 intensities remained considerably lower than those of C1 and C2

contributing on average 21.1 % to the total FDOM. Component C4 (peak B) displayed the lowest values with only 14.8 % contribution to total FDOM (Table S5). The two samplings on 01 July 2016 and 04 May 2017, which exhibited high DOC and $a(\lambda)$ absorption values in the SML, also demonstrated exceptionally strong fluorescence intensities across all four PARAFAC components (2.5, 4.6, 18 and 2.8 times higher than the average of I1, I2, I3 and I4 respectively). Other than that, no clear seasonal trend was observed in any of the four PARAFAC components in the SML. Likewise, in the ULW, the four components showed little seasonal variation, peaking during autumn bloom on 07 October 2016. (Table S5).

L446: ‘Appear’ most enriched? They either are or they aren’t.

Authors’ response: Corrected in the text

L449-450: So what does this suggest?

Authors’ response: We added some interpretations in the text:

In our study, the FDOM enrichment within the SML appears to be more evenly distributed between humic DOM and proteinaceous DOM indicating a relatively balanced influence of terrestrial and autochthonous inputs. Miranda et al. (2018) reported enrichment of the humic-like C fraction in the SML, which followed the pattern of solar radiation. This enrichment was attributed to photolysis of DOM compounds and enhanced microbial activity, leading to reprocessing of photodegraded DOM into FDOM and thus suggesting that humic-like FDOM can be produced in-situ in the SML under the influence of solar radiation.

L454-457: Already described in Methods section.

Authors’ response: We thank the reviewer for pointing out, has been removed

Lines 467 and 470: Use of ‘appears’ – ditto above comment (L446).

Authors’ response: Corrected in the text

L591-618: Conclusion section: The authors frequently refer to DOM instead of DOC; yes, DOC is a dominant component of DOM but the two are not interchangeable terms, and DOC was measured in this study. Please correct the terminology. Additionally, for this section as a whole the text does not indicate why any of the findings matter in the broader context; the final sentence is very general and does not indicate anything new (it is already widely accepted that the SML is an important and dynamic environmental compartment).

Authors’ response: We thank the reviewer for pointing this out. The conclusion section has been revised accordingly to address the DOC/DOM corrections and to better highlight the findings of the study

1. Conclusion

This study demonstrates that the sea surface microlayer (SML) functions as a highly dynamic biogeochemical boundary characterized by the selective accumulation and transformation of dissolved organic matter. Although the SML was consistently enriched in DOC, CDOM, and FDOM relative to the ULW, the absence of clear coupling between the two layers indicates that upward transport alone cannot explain DOM enrichment in the SML. Instead, the optical and compositional signatures point to the dominance of in situ processes and atmospheric inputs in shaping microlayer DOM.

The strong relationship between DOC and CDOM absorption suggests that bulk carbon availability controls chromophoric material in respect of quantity; however, the layer-dependent behavior of spectral slope reveals that the optical quality of DOM is further modified by processes specific to the SML. Additionally, the investigation of absorption coefficients in various wavelengths covering the UV-C, UV-B, UV-A and near-visible regions of the spectrum, revealed information that could not be discerned through the investigation of absorption at a single wavelength, i.e., 300nm. The preferential enrichment of higher-molecular-weight, aromatic compounds was revealed which coupled with the weaker photodegradation signal compared to the ULW, support the view that photochemical alteration is partially counterbalanced by rapid biological production, aggregation, and molecular reorganization at the air–sea interface.

Fluorescence analyses further indicate that the accumulated DOM reflects mixed sources. The concurrent enrichment of humic-like and protein-like components suggests a balanced contribution from terrestrial inputs and marine autochthonous production, while the distinct relationships between fluorescent fractions and CDOM highlight compositional differentiation within the microlayer. The application of the novel FDOM/CDOM index which covers the whole absorption/emission spectrum provided an additional dimension for resolving compositional variability, offering a sensitive optical metric for detecting shifts in bulk CDOM quality and transformation processes at the air–sea interface. Overall, the CDOM and FDOM analyses highlight that integrating optical indices spanning different spectral regions—such as absorption coefficients at multiple wavelengths, spectral slope, and the FDOM/CDOM index—provides comprehensive insights into CDOM–FDOM dynamics and interactions.

Rainwater signatures reinforce the importance of atmospheric deposition as an additional pathway supplying optically altered, humic-like material to the SML, emphasizing the tight connectivity between atmospheric processes and surface ocean biogeochemistry.

Overall, these findings underscore that the SML is not merely an enriched extension of the underlying water but a distinct reactive environment where photochemical, biological, and atmospheric processes interact to regulate DOM composition. Given the central role of surface-active organic matter in air–sea exchange, such transformations may have important implications for carbon cycling and climate-relevant processes.

L686-688: Reference incomplete. 2018 paper?

Authors' response: We thank the reviewer for pointing out, has been corrected

Response to Reviewer 2

1. Scientific significance:

The results presented in the manuscript “Selective accumulation...” have significant innovative and scientific value. The authors 1) proposed a new index for estimating the selective enrichment of specific DOM molecules in the surface microlayer (SML) in relation to the underlying water (ULW), which is 2) supported by the careful discussion with the other classical parameters' results. The SML was consistently enriched in DOC, CDOM, and FDOM relative to the ULW throughout the study. Rainwater samples (analysed in the same way as the marine ones) showed DOC and CDOM features comparable to those of the SML, while PARAFAC analysis did not reveal the T component and showed a blue-shift in the emission of the FDOM bands, consistent with the processes reported in the literature. The authors introduced an FDOM/CDOM index to test for decoupling between fluorescent and non-fluorescent chromophoric organic components and for their selective accumulation in the SML. The results and discussion of the applied index were particularly interesting, revealing wavelength-dependent enrichment patterns. This parameter will not facilitate a faster assessment of the impact of SML on gas exchange, but may help understand the course of processes occurring in the sea surface layers under different environmental conditions.

2. Scientific quality:

The results are well presented and explained; in particular: 1) chl-a results are discussed with rain and Sahara dust events, 2) upward transport of DOC and evidence on other processes affected the DOC pool in the SML and ULW discussed based on the relations between a_{300} and DOC; DOC in the SML and ULW), 3) valuable discussion on the relationship between a_{300} and $S_{275-295}$, which reflects changes in CDOM resulting from photodegradation processes in surface waters that reveals different CDOM dynamics in the SML and ULW, 4) detailed and comprehensive description of the PARAFAC model results, 5) comprehensive introduction and explaining the meaning of FDOM/CDOM index variability.

3. Presentation quality:

The scientific results and conclusions presented in the manuscript are clear, concise, and well-structured. Figures present the most important results and have clear, informative captions. The

number of equations, figures and tables (in a text and in supplement materials) is appropriate and sufficient.

Authors' response: We thank the reviewer for the careful evaluation and positive feedback on the scientific significance, quality, and presentation of our manuscript. We appreciate the reviewer's supportive comments.

I found typos and minor lapses that the authors themselves would surely have caught during the final technical editing of the text. Here they are:

L. 58. These numbers '15-50 %' (~14-51%) were reported in: Pereira R, Schneider-Zapp K, Upstill-Goddard RC. Surfactant control of gas transfer velocity along an offshore coastal transect: results from a laboratory gas exchange tank. Biogeosciences 2016, 13(13): 3981-3989.

Authors' response: We thank the reviewer for pointing out, however upon the suggestion of Reviewer 1 the Introduction section was condensed to better highlight the objectives and findings of the study and thus this part was removed.

L.119 Choosing yellow to mark the site's location on the map was not a good choice

Authors' response: We have changed the color to red

L.128 It should be ULW (not UWL)

Authors' response: We thank the reviewer for pointing out

L.150-152 Why did you filter 500mL water from the SML but 1500 mL from the ULW – for chl-a determination?

Authors' response: The lower filtration volumes used for the SML were due to sampling constraints associated with the glass plate technique. Laboratories tests evaluating different filtration volumes showed no significant differences in Chl-a concentrations. We have added this clarification in the text

L. 179 Instead of 'to wavelengths of' – 'to excitation wavelengths inducing'

Authors' response: We thank the reviewer for this helpful suggestion, the text has been revised accordingly.

L. 185 It should be: 275-295

Authors' response: We thank the reviewer for pointing out

L. 192 Instead of '275-295 nm' it should be rather 'longer wavelength, $\lambda > 300\text{nm}$ '

Authors' response: We thank the reviewer for the suggestion, the text has been revised accordingly.

L.216 I propose ('pairs of samples from the SML and ULW', n=22)

Authors' response: We thank the reviewer for the suggestion, the text has been revised accordingly.

L.219 There is no Section 4.3 (probably 2.5)

Authors' response: We thank the reviewer for pointing out, has been corrected to Section 3.4

L.221 consequently with a small letter: 'drEEM package'

Authors' response: We thank the reviewer for pointing out

L.229 I propose the parentheses: 291 (1×41) vectors

Authors' response: We thank the reviewer for the suggestion, the whole paragraph has been revised for clarity

L.244-255 You don't have to put this information: ', as the data did not meet the assumptions required for parametric analysis'. Thus, the next sentence may start with: 'Deviations...'

Authors' response: We thank the reviewer for this suggestion. However, we have retained this information to clarify the reasoning for applying a non-parametric test and to ensure methodological transparency. Indicating that the data did not meet the assumptions required for parametric analysis helps justify the statistical approach used.

L.263 on Fig.2(b) on Y axis it should be 'chl-a ($\mu\text{g L}^{-1}$)', not 'chla...'

Authors' response: We thank the reviewer for pointing out

L.266 and 269 Consequently, you should write ‘chl-a’ with a small letter

Authors’ response: We thank the reviewer for pointing out

L.270 the standard GF/F filter is ‘~0.7 μm ’, not ‘~0.8 μm ’

Authors’ response: We thank the reviewer for pointing out

L.349 ‘amphiphilic’ instead of ‘hydrophobic’

Authors’ response: Corrected as suggested

L.359, 363 and 367 I propose ‘maxima’ or ‘bands’ instead of ‘shoulders’.

Authors’ response: We thank the reviewer for the suggestion, we have revised accordingly

L.361-362 In the caption of Fig. 5: ‘CDOM absorption spectra...’ instead of ‘Absorption spectra...’

‘Spectral’ instead of ‘Spectra’; ‘... bands with maxima at’ instead of ‘... shoulders at’

Authors’ response: We thank the reviewer for the suggestions, we have revised accordingly

L.368 I propose: ‘in environments exposed to high UV radiation’ instead of ‘in high-UV environments’

Authors’ response: We thank the reviewer for the suggestions, we have revised accordingly

L.381 ‘the fluorescence intensities’ instead of ‘the intensities’

Authors’ response: We thank the reviewer for pointing out

L.382 ‘fluorescent components’ instead of ‘components’

Authors’ response: We thank the reviewer for pointing out

L.398 ‘low...low’ instead of ‘lower...less’ – because it is only in the following sentences that you write about other components related to humic substances with which the M fraction can be compared.

Authors’ response: We thank the reviewer for the suggestion

L.426, 428, 430, 431 and 438 ‘fluorescence intensities’ instead of ‘intensities’

Authors’ response: Corrected in the text

L.452 It should be ‘C1 and C3’, not ‘C1 and C2’.

Authors’ response: We thank the reviewer for pointing out, corrected in the text

L.457 It should be ‘2.5’ instead of ‘2.6’

Authors’ response: We thank the reviewer for pointing out, following the suggestion of the other reviewer we moved the FDOM/CDOM Index method description in a stand-alone section, Section 2.6

L.462 and 463 I propose: ‘Depletion of the fluorescence intensity excited in the UV-A/near-visible range’ instead of ‘Depletion of UV-a/near visible fluorescence’; and similar: ‘Higher contribution of FDOM excited at short wavelengths (UV-C/UV-B)’

Authors’ response: We thank the reviewer for the suggestion, we have revised accordingly

L.470 I propose: ‘chromophores absorbing at the UV-A and near visible light’ instead of ‘UV-A near visible chromophores’

Authors’ response: We thank the reviewer for the suggestion, we have revised accordingly

L.481 I propose: ‘Moreover’ instead of ‘At the same time’

Authors’ response: Corrected in the text

L.485-487 I propose: ‘Due to the hydrophobic nature of these aromatic compounds forming amphiphilic organic molecules, they are expected to preferentially accumulate in SML.’ Instead of ‘Because of the hydrophobic nature of these aromatic compounds, they are expected to preferentially accumulate in the SML.’

Authors’ response: We thank the reviewer for the suggestion, we have revised accordingly

L.490, 493, 514, 515 and 604 I propose: ‘excitation regions’ instead of ‘regions’

Authors’ response: Corrected in the text

L.495 I propose: ‘excitation wavelengths’ instead of ‘wavelengths’

Authors’ response: Corrected in the text

L.526 It should be 90×10^{12} (ten to the power of twelve) instead of ‘ 90×10^{12} ’

Authors’ response: We thank the reviewer for pointing out, corrected

L.533 I propose: ‘the fluorophores of organic molecules’ instead of ‘the fluorophores’

Authors’ response: Corrected in the text

L.547, 550, and 611 I propose: ‘blue shifted in emission’ instead of ‘blue shifted’

Authors’ response: Corrected in the text

L.565 To add 'nm' in '300/400'

Authors' response: We thank the reviewer for pointing out

Generally, in the text, shorthand notations are often used (CDOM/FDOM instead of CDOM and FDOM; peaks A/M and peaks A/C instead of peaks A and M, peaks A and C; the UV-A/near-visible range instead of the UV-A and near-visible range). I suggest considering whether to retain this notation in every instance, or, for example, when mentioning “CDOM and FDOM” for the first time, to add (CDOM/FDOM) in brackets, and similarly (peaks A/C) when mentioning “two peaks A and C” for the first time.

Authors' response: We thank the reviewer for the suggestion, the text has been revised accordingly