



1 **Selective accumulation of dissolved organic matter in the**  
2 **sea surface microlayer: Insights from CDOM and**  
3 **FDOM characterisation at a Mediterranean coastal site.**

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10  
11 **Abstract**

12 The sea surface microlayer (SML) is an extremely thin (~1 mm) boundary between the ocean and the  
13 atmosphere, forming a dynamic microenvironment that regulates air–sea gas exchange. Owing to its  
14 unique position, the SML is enriched with surface-active and hydrophobic organic compounds, typically  
15 more concentrated than in the underlying water (ULW), and can therefore modulate gas transfer across  
16 the interface. Despite its importance in ocean–atmosphere interactions, the processes governing its  
17 functioning remain insufficiently understood. This study investigates the biogeochemical coupling  
18 between the SML and ULW by examining the dynamics of dissolved organic matter (DOM)—including  
19 its chromophoric (CDOM) and fluorescent (FDOM) fractions—at a coastal Mediterranean site from 2016  
20 to 2017. Twenty-two paired SML–ULW samples and fourteen rainwater samples were analyzed for  
21 dissolved organic carbon (DOC), UV–visible (250–700 nm) absorption spectra, and 3D fluorescence  
22 excitation emission matrices (EEMs). The SML was consistently enriched in DOC, CDOM, and FDOM  
23 relative to the ULW throughout the study. Enrichment factors (EFs) for long-wavelength absorption  
24 coefficients ( $a_{300}$ ,  $a_{370}$ ) exceeded 5. Relationships between  $a_{300}$  and the spectral slope ( $S_{275-295}$ ) indicated  
25 photodegradation in both layers, though more pronounced in the ULW. In the SML, photodegradation  
26 effects appeared to be partially counterbalanced by in situ production or aggregation of hydrophobic,  
27 optically active, higher-molecular-weight material. Parallel Factor Analysis (PARAFAC) identified four  
28 FDOM components: two humic-like (A/C, A/M) and two protein-like (T, B). Terrestrial humic-like  
29 (A/C) and tryptophan-like (T) fluorophores were dominant and strongly enriched in the SML ( $EF > 4$ ).  
30 By introducing an FDOM/CDOM index, a decoupling between fluorescent and non-fluorescent  
31 chromophoric organic fractions was revealed: the SML exhibited higher fluorescence in the UV-C/UV-  
32 B regions (A, B, T peaks) but lower fluorescence in the UV-A/visible region (C peak), suggesting  
33 selective accumulation of absorbing but non-fluorescent CDOM. Potential drivers of this decoupling  
34 include biological transformations, rapid microlayer reorganization, and atmospheric inputs. Rainwater  
35 showed DOC concentrations and absorption features comparable to the SML but distinct fluorescence  
36 characteristics. PARAFAC modeling of rainwater did not resolve the tryptophan-like fluorophore and  
37 revealed blue-shifted humic-like components, consistent with photochemically aged, low molecular  
38 weight DOM of mixed marine–terrestrial origin. Overall, the results indicate that photodegradation,



39 biological activity, rapid molecular reorganization, and atmospheric deposition collectively shape the  
 40 wavelength-dependent enrichment of CDOM and FDOM in the SML, highlighting its active role in air–  
 41 sea biogeochemical exchange.

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## 43 1. Introduction

44

45 The sea surface microlayer (SML) represents the boundary interface between the ocean and the  
 46 atmosphere. Having a thickness of less than 1 mm, it ubiquitously covers the ocean surface. The  
 47 formation and persistence of the SML are generally considered to be strongly influenced by wind speed  
 48 (Liss & Duce, 1997). However, recent findings suggest that the relationship between SML stability and  
 49 wind conditions is not straightforward, as enrichment can occur even under high wind speeds  
 50 (Sabbaghzadeh et al., 2017; 2024). Beyond wind effects, other factors—including solar radiation, which  
 51 drives photochemical and microbial processes; biological activity, which produces and modifies surface-  
 52 active substances; and atmospheric deposition—play critical roles in determining the composition and  
 53 persistence of the SML (Wurl & Holmes, 2008; Cunliffe et al., 2013; Upstill-Goddard, 2006). These  
 54 physical, chemical, and biological interactions collectively define the dynamic nature of the SML and its  
 55 influence on air–sea exchange processes. Enriched with surfactants, the SML can significantly impede  
 56 the air–sea transfer of greenhouse gases such as CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O by acting as a physical barrier (Liss  
 57 & Duce, 1997; Pereira et al., 2018). Studies suggest that the presence of the SML can reduce CO<sub>2</sub> fluxes  
 58 by 15–50%. However, most gas exchange models neglect this effect, leading to potential errors of up to  
 59 20% in regions with elevated surfactant concentrations (Asher, 1997; Mustaffa et al., 2020). Integrating  
 60 SML dynamics into climate models is therefore essential for refining global gas flux estimates and  
 61 improving our understanding of ocean–atmosphere interactions (Milinković et al., 2022). The sea surface  
 62 microlayer (SML) is characterized by a high content of hydrophobic, surface-active compounds such as  
 63 carbohydrates, proteins, lipids, and humic substances, as well as particulate organic matter and a diverse  
 64 community of autotrophic and heterotrophic microorganisms (Hunter, 1981; Cunliffe et al., 2009;  
 65 Cunliffe et al., 2013). The enrichment of dissolved organic matter (DOM) in the SML is a complex  
 66 process (Mustaffa et al., 2018), primarily driven by the continuous supply of organic material from the  
 67 underlying seawater through biological activity and selective scavenging mechanisms (Liss & Duce,  
 68 2005; Obernosterer et al., 2008; Penezić et al., 2022). Additional sources of organic matter include  
 69 terrestrial and atmospheric inputs, as well as in situ production and release by primary producers and  
 70 bacteria (Hardy, 1982; Wurl & Obbard, 2005; Wurl et al., 2009; Stolle et al., 2010; Ebling & Landing,  
 71 2017). The SML often exhibits spatial heterogeneity due to the accumulation of floating particulate  
 72 material at the surface (Hunter, 1980), resulting in patchy distributions or slicks enriched in surfactants  
 73 and potentially characterized by elevated biological productivity (Ploug, 2008; Ribas-Ribas et al., 2017).  
 74 Chromophoric dissolved organic matter (CDOM) represents the fraction of DOM capable of absorbing  
 75 light in the ultraviolet (UV) and visible regions. A subset of CDOM, known as fluorescent dissolved  
 76 organic matter (FDOM), can additionally emit light upon excitation in these spectral ranges. In marine  
 77 environments, CDOM is produced in situ through processes such as primary production, bacterial



78 activity, cell metabolism and lysis, and the leakage of material from particulate organic matter. External  
 79 inputs also contribute to CDOM levels, including terrestrial sources delivered via riverine and land  
 80 runoff, sewage discharges, and atmospheric deposition through precipitation. The primary removal  
 81 mechanisms of CDOM in surface waters are photodegradation driven by UV radiation and bacterial  
 82 mineralization. Over the past decades, CDOM has received considerable attention due to its key role in  
 83 carbon cycling, the bioavailability of trace elements, and the air–sea exchange of trace gases (Mopper et  
 84 al., 1991; Zepp, 1998; Coble, 2007). Moreover, CDOM strongly influences light attenuation in the ocean  
 85 (Kirk, 1994; Siegel & Michaels, 1996; Nelson et al., 1998), thereby affecting primary productivity.  
 86 Consequently, the optical properties of CDOM at the ocean surface have significant implications for  
 87 remote sensing applications, particularly in relation to chlorophyll-a retrievals and ocean colour  
 88 observations (Tassan, 1988; Hoge et al., 1995).

89 Enrichment of CDOM in the SML relative to the underlying water (ULW) has been reported in several  
 90 studies (Obernosterer et al., 2008; Mustaffa et al., 2017, 2018). CDOM consists of large, complex  
 91 molecules rich in unsaturated bonds and aromatic moieties, structural features that impart hydrophobic  
 92 properties favouring its accumulation within the SML. In coastal regions, terrestrial inputs can contribute  
 93 substantially to the CDOM pool, while intense photochemical processes at the sea surface can  
 94 significantly modify its composition. Interaction with sunlight can lead to CDOM mineralization and  
 95 removal, accompanied by CO<sub>2</sub> and CO emissions, or to the breakdown and formation of less complex  
 96 organic compounds that are more susceptible to bacterial transformation and degradation (Gao & Zepp,  
 97 1998; Moran et al., 2000; Zhang et al., 2013; Logozzo et al., 2021). Spatially, CDOM distribution within  
 98 the SML is often patchy, with elevated concentrations occurring in slicks and other surface accumulations  
 99 (Wurl et al., 2009; Mustaffa et al., 2017). Despite its ecological and biogeochemical importance, CDOM  
 100 dynamics in the SML remain insufficiently explored, particularly under the distinct physical and  
 101 chemical conditions characteristic of this boundary layer.

102 The present study investigates the nature, sources, and transformation processes of CDOM/FDOM in the  
 103 SML compared to the ULW in a Mediterranean coastal site, using high-resolution temporal data obtained  
 104 from biweekly sampling over a one-year period. In addition, we examine rainwater CDOM/FDOM in  
 105 order to investigate potential linkages between the optical signatures of rainwater and those observed in  
 106 the SML. We anticipate that the results will provide new insights regarding CDOM dynamics in the  
 107 SML.

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## 109 **2. Materials and Methods**

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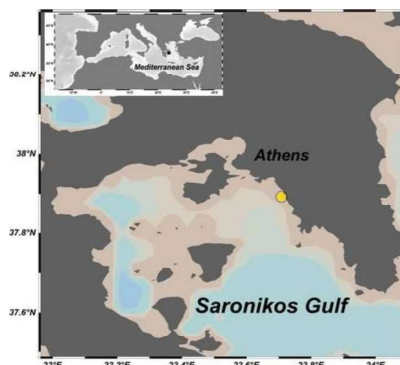
### 111 **2.1. Study area and sampling strategy**

112

113 The sampling site is located in the south-east Saronikos Gulf about 1km from the coast in the eastern  
 114 Mediterranean (Fig. 1). Due to its proximity to the coast the site is affected by urban runoff while only a  
 115 small urban stream outflows in the area. Two phytoplanktonic blooms in the spring-early summer and  
 116 autumn-early winter are characteristic for the area (Kitsiou and Karydis, 2000; Zervoudaki et al., 2022).



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**Figure 1: Study area, the yellow dot marks the sampling site in the Saronikos Gulf**

120 The study covered an annual cycle from June 2016 to June 2017. During this period data for wet  
 121 precipitation (mm), solar radiation from the National Observatory of Athens ([www.meteo.gr](http://www.meteo.gr)) and  
 122 Saharan dust episodes and deposition ( $\mu\text{g m}^{-3}$ ) from Skiron Forecasting system  
 123 (<https://forecast.uoa.gr/en/forecast-maps/skiron>) have been gathered. Saharan dust events were also  
 124 confirmed via the EOSDIS Worldview (<https://worldview.earthdata.nasa.gov/>) (Table S1).

125 Seawater samplings were performed almost twice per month under low wind speed conditions ( $< 4 \text{ ms}^{-1}$ ).  
 126 Seawater temperature (T) and salinity (S) were recorded in situ using a CTD (Seabird electronics,  
 127 Bellevue, WA, USA) instrument. Wind speed was recorded with a portable anemometer Benetech  
 128 GM816. Samples were collected from SML and from 1m depth representing the UWL, in total 22 pairs.  
 129 SML was sampled following the glass plate technique (Harvey and Burzell, 1972) yielding a microlayer  
 130 thickness of  $50 \pm 10 \mu\text{m}$  (Zhang et al., 2003) (Table S). A 30 x 30 cm glass plate sampler with a width of  
 131 4 mm was used. Samples from the ULW were collected using a Niskin sampling bottle. Samples for  
 132 DOC and CDOM/FDOM analysis were collected in amber glass containers with teflon caps while  
 133 samples for chl-a determination in HDPE containers; refrigerated and immediately transported to the  
 134 laboratory, where they were filtered through 0.22  $\mu\text{m}$  polycarbonate filters previously rinsed with Milli-  
 135 Q water. Filtered samples for DOC analysis were kept in precombusted (450°C, 12h) glass ampoules,  
 136 acidified with HCl 2N at pH~2, sealed and stored at ~4°C until analysis. Filtered samples for absorption  
 137 and fluorescence analysis were kept in amber glass bottles with teflon cups and stored at ~4°C until  
 138 analysis. The glass containers used during sampling and for the storage of CDOM/FDOM samples were  
 139 previously acid cleaned (HCl 10%, 12h) and rinsed thoroughly with Milli-Q water. Filters for chl-a  
 140 determination were preserved frozen (-20°C) in the dark until analysis.

141 For the period December 2016 to May 2017 rainwater samples were collected (14 samplings), via a  
 142 simple system made with a Nalgene bottle connected to a HDPE funnel for wet deposition (Azimi et al.,  
 143 2003) situated on the roof of a building at the coast of the study site. This was an open system, so it is  
 144 assumed it was affected by dry deposition passively collected when not raining. Details on the study site  
 145 and sampling procedure are described in Tzempelikou et al., (2025).

146



## 2.2. Chlorophyll-a (Chl-a)

Chl-a was determined according to the Holm-Hansen et al., (1965) method using fluorescence detection in a TURNER fluorometer model TD 700. An initial sample volume equal to 500mL was filtered for SML and 1.5L for ULW.

## 2.3. Dissolved Organic Carbon (DOC) analysis

The determination of DOC ( $\text{mg L}^{-1}$ ) in the samples was performed using a Shimadzu TOC-L organic carbon analyzer following the High Temperature Catalytic Oxidation, HTCO. The system was standardized prior analysis using a potassium hydrogen phthalate standard solution series. Each sample was injected 3 to 5 times and DOC concentration was estimated as the average value of three replicates that yielded standard deviation  $<2\%$ . Analytical precision and accuracy were tested daily prior and at the end of the analysis using Deep Atlantic Seawater Reference Material provided by the DOC-CRM program (University of Miami - D.A. Hansell). The certified value of the reference material is  $0.480\text{--}0.528 \text{ mg L}^{-1}$  (Batch 19 Lot 10-19) and the measured values ( $n=22$ ) during the analysis of the samples were between  $0.478\text{--}0.530 \text{ mg L}^{-1}$  indicating that no drift correction was necessary.

## 2.4. Absorption analysis

Samples for absorption determination were allowed to reach room temperature before analysis. Absorption spectra were obtained between 250 and 700nm at 1nm increments using a dual beam UV-visible spectrophotometer (Perkin Elmer, Lambda 25) equipped with 5cm quartz cells and referenced to Milli-Q water. A blank scan (Milli-Q) was measured frequently to assure the stability of the instrument and it was also subtracted from each sample spectra for baseline correction. Absorption units were converted to absorption coefficients through the relationship:

$$a(\lambda) = 2.303 \cdot A(\lambda) / l$$

where  $a(\lambda)$  is the absorption coefficient ( $\text{m}^{-1}$ ) at wavelength  $\lambda$ ,  $A(\lambda)$  is the absorbance at the certain wavelength and  $l$  is the light path length in meters.

Absorption coefficient at 300nm wavelength was used for the representation of bulk CDOM. However, 3 more wavelengths (265 nm, 280 nm, 370 nm) were used in order to investigate whether there are differences in CDOM profiles in the different regions of the spectrum between the SML and ULW. The wavelengths selected provide a good coverage of the spectrum and correspond to wavelengths of maximum fluorescence intensities of the samples (see section 2.5). Wavelength 265nm falls in the UV-C region, wavelength 280nm is the border between UV-C and UV-B region, wavelength 300nm belongs to the UV-B region while wavelength 370nm falls in the UV-A region and it is also close to the visible light preserving though high absorption values. No wavelength of the visible region ( $>400\text{nm}$ ) was chosen due to the low absorption values especially in the ULW.

Spectral slope of the narrow region 275-295,  $S_{275-295} \text{ (nm}^{-1}\text{)}$  of the spectra was calculated using linear regression of the log-transformed spectra. This is a useful indicator of the molecular weight and source



composition of CDOM and can be determined with high precision, even in highly photobleached open-ocean environments (Helms et al., 2008). Consequently, it is often favored over other spectral slope indices. Photodegradation processes typically lead to a reduction in DOM molecular weight, resulting in elevated  $S_{275-295}$  slope values, whereas microbial transformation generally decreases this spectral slope through the production of higher-molecular-weight organic compounds that exhibit strong absorption within the 275–295 nm range. (Helms et al., 2008; Fichot and Benner, 2009; Ortega-Retuerta et al., 2009)

## 2.5. Fluorescence Analysis

Fluorescence was measured using a Horiba Aqualog-UV-800 spectrofluorometer equipped with a 150W ozone-free xenon arc-lamp and a 1cm quartz cell. Excitation-Emission Matrices (EEMs) were obtained between 240 and 450nm (5nm increments) for excitation and between 250 and 800nm (~0.6nm increments) for emission. The integration time of the measurement was adjusted according to the fluorescence intensity in the SML and ULW samples. A blank EEM (Milli-Q water) was measured daily and subtracted from each sample in order to correct Raman and Rayleigh scattering. All EEMs were corrected for inner filter effect following the Aqualog Operations Manual and were normalized to Raman Units (R.U.) using the Raman scatter emission peak of Milli-Q (Lawaetz and Stedmon, 2009) obtained after the measurement of each sample.

The collected EEMs were further analyzed using Parallel Factor Analysis (PARAFAC). PARAFAC was performed following Murphy et al. (2013) using MATLAB R2015a and the "drEEM toolbox". Prior modeling, the emission region between 550 and 800nm was removed since no significant CDOM fluorescence signal was detected. The subtraction of Milli-Q water from the EEMs did not remove sufficiently the Rayleigh and Raman scatter peaks and thus both first and second order Rayleigh and Raman scatter bands were interpolated using the "smootheem" function of the drEEM package. All EEMs were then normalized to their total signal to tackle the large concentration gradients that were observed between the SML and ULW. The model was run five times with random initial values and model validation was carried out through split half analysis using four splits yielding six different combinations and it was repeated five times ( $S_4C_6T_5$ ). The convergence criterion was  $10^{-6}$ . Visual inspection of the residuals was also implemented along with split half analysis to assure randomness (Pitta and Zeri, 2021). PARAFAC analysis was performed on the seawater EEMs (SML-ULW,  $n=22$ ). An additional PARAFAC model was conducted for the rainwater EEMs ( $n=14$ ). Spectral characteristics of the components resolved by the seawater and rain water models are given in Table S2.

For the calculation of the FDOM/CDOM index discussed in Section 4.3 we extracted the numeric values of modelled intensities of the scattering corrected EEMs derived from the 'smootheem' function of the DrEEM package. The fluorescence intensity ( $I_{ij}$ ) at each excitation wavelength ( $Ex_i$ ) was then divided by the corresponding absorption coefficient ( $a_i$ ) obtained from the absorption measurements. This was repeated for all emission wavelengths ( $Em_j$ ), thus yielding the ratio  $I_{ij}/a_i$  i.e. the FDOM/CDOM (R.U.m) index, in the form of a 3-dimensional matrix where  $Ex=250-450nm$  and  $Em=260-550nm$  (Suppl Fig. S1). We then calculated the average FDOM/CDOM index for all the samples in the SML and ULW separately. First step was the construction of 291 (number of emission wavelengths)  $n \times 41$  matrices



(where  $n$  is the number of samples in each dataset and 41 is the number of excitation wavelengths) using the FDOM/CDOM matrices of the samples in each layer. Next, we calculated the average of each column of the 291 ( $n \times 41$ ) matrices resulting into 291  $1 \times 41$  vectors. Finally, 291  $1 \times 41$  vectors i.e. the average FDOM/CDOM were illustrated in a 3-dimensional plot. This analysis was performed in MATLAB R2015a using in-house functions.

## 2.6. Enrichment factor (EF)

The Enrichment Factor, EF, of the various measured parameters in the SML is calculated as the ratio of the measured values in the SML to the measured values in the ULW:

$$EF = C_{SML} / C_{ULW}$$

where  $C_{SML}$  is the concentration of any parameter in the SML and  $C_{ULW}$  its corresponding concentration in the ULW. EF values  $> 1$  indicate enrichment in the SML, while EF values  $\leq 1$  indicate depletion.

## 2.7. Statistical analysis

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. Linear regression and Spearman correlation was applied to evaluate relationships among the measured parameters. All reported regression and correlation coefficients ( $R^2$  and  $r$  respectively) are statistically significant ( $p < 0.05$ ). All analyses were conducted using IBM SPSS Statistics, Version 20.0.

# 3. Results and discussion

## 3.1. Environmental and physicochemical conditions

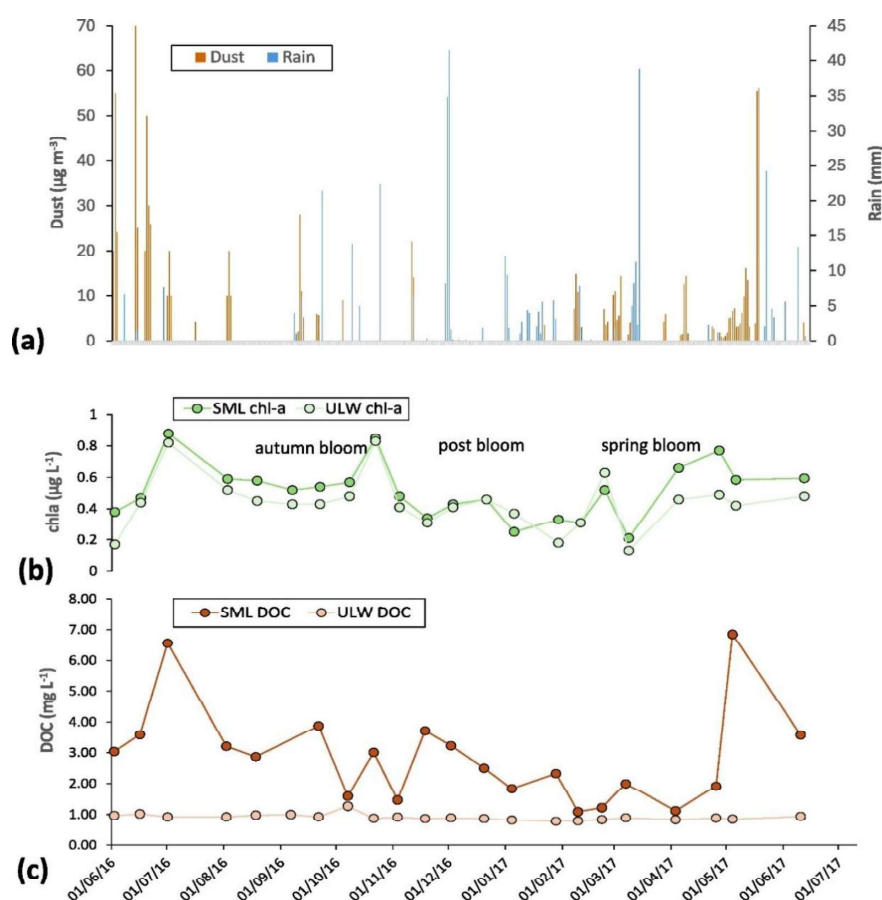
Figure 2(a) presents the timing and intensity of rain and dust events recorded between 2016 and 2017, illustrating that the study site was influenced by both wet and dry atmospheric deposition. Over the 376-day observation period, Saharan dust was detected on 103 days (27%), comprising 77 dry dust pulses and 26 dusty rain events, while dust-free rainfall occurred on 31 days (8%). Solar irradiance exhibited pronounced seasonality, peaking in summer–autumn ( $600\text{--}900 \text{ W m}^{-2}$ ) and reaching minima during winter ( $130\text{--}500 \text{ W m}^{-2}$ ). Seawater temperature (T) varied between 17 and 26 °C from June 2016 to January 2017, dropped to  $\sim 14$  °C in February–March 2017, and increased again by May. Salinity remained relatively stable (38.06–39.61 psu) throughout the study period (Table S1).

Chl-a concentrations in the SML and ULW are shown in Fig. 2(b). Values ranged from 0.21 to 0.88  $\mu\text{g L}^{-1}$  (average = 0.51  $\mu\text{g L}^{-1}$ ) in the SML and from 0.13 to 0.83  $\mu\text{g L}^{-1}$  (average = 0.44  $\mu\text{g L}^{-1}$ ) in the ULW, consistent with the region's meso-oligotrophic character. No significant difference was detected between





layers ( $p > 0.05$ ), and SML enrichment was minimal ( $EF = 1.2 \pm 0.3$ ). The annual Chl-a distribution revealed an unexpected summer peak in July 2016 followed by a secondary maximum in autumn, indicative of an autumn bloom. Thereafter, concentrations declined in winter and increased again in early spring. It should be noted that Chl-a was determined using a finer filter ( $0.22 \mu\text{m}$  instead of the standard  $\sim 0.8 \mu\text{m}$  GF/F), likely capturing smaller phytoplankton cells and yielding marginally higher values (Tzempelikou et al., 2025). Moreover, the occurrence of multiple Saharan dust pulses during our study period is expected to enhance primary production, consistent with observations in the Mediterranean ecosystem (Astrahan et al., 2016; Gallisai et al. 2014).



**Figure 2: Monthly variation of (a) Saharan dust ( $\mu\text{g m}^{-3}$ ) and rain (mm) deposition, (b) chl-a ( $\mu\text{g L}^{-1}$ ) and (c) DOC ( $\text{mg L}^{-1}$ ) during the sampling period. (a) Dust is given in orange and rain in blue (b,c) dark dots correspond to SML concentrations and light colored to ULW ones.**

The environmental conditions during our study period (low wind speed, relatively elevated dust particles and chl-a) favored pronounced SML formation, as evidenced macroscopically by apparent surface slicks in 12 of the 22 samplings (Table S1). These gel-like surface slicks are formed primarily by surfactants,



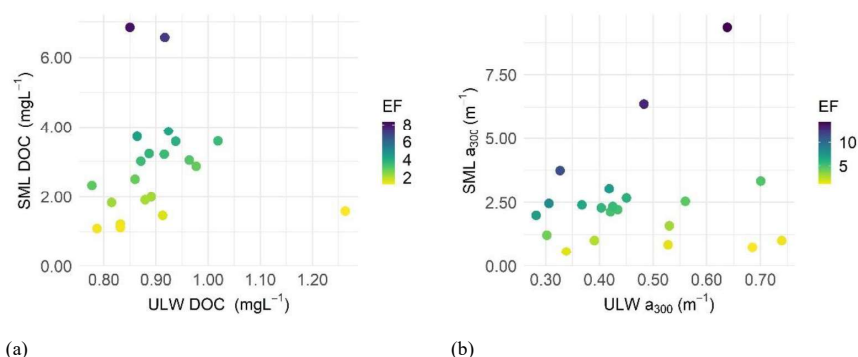


are rich in hydrophobic organic matter and can host microorganisms and particles forming a distinct ecosystem in the SML compared to the ULW (Zancker et al., 2017; Wurl et al., 2016). Indeed, accumulation of phytoplankton exudates such as gel-like transparent exopolymer particles (TEPs) has been recorded for the area during the same period (Tzempelikou et al., 2025).

### 3.2. Dissolved organic carbon in the SML and ULW

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<sup>-1</sup>, with an average concentration of 3.13 mg L<sup>-1</sup>, significantly higher than that in the ULW (average: 0.93 mg L<sup>-1</sup>; range: 0.78–1.23 mg L<sup>-1</sup>; p = 0.001). Two exceptionally high DOC values observed in the SML (01 July 2016 and 04 May 2017) were not reflected in the ULW, suggesting episodic enrichment events. DOC dynamics in the SML tracked those in the ULW during winter but diverged substantially during summer and autumn (Table S1). Consequently, DOC concentrations between the two layers were weakly but significantly correlated (r = 0.463; p = 0.046, excluding the two extreme values) indicating that apart from upward transport of DOM other processes affect the DOC pool in the SML.

Significant correlation of several DOM compounds between the SML and ULW is a common feature across studies indicating that upward transport of material plays a dominant role in the composition of the SML in DOM (Chen et al., 2013; 2016; Engel and Galgani, 2016). Furthermore, the DOC enrichment factor (EF = 2.7 ± 1; p = 0.001; Fig. 3(a)) confirms substantial accumulation of DOM components in the SML.



**Figure 3: Correlation graphs between the SML (y axis) and ULW (x axis) of (a) DOC (mg L<sup>-1</sup>); (b) absorption coefficient  $a_{300}$  (m<sup>-1</sup>). The z axis illustrates the enrichment factors**

### 3.3. CDOM dynamics within the DOM pool in SML and ULW

The distribution of the absorption coefficients at 300nm,  $a_{300}$ (m<sup>-1</sup>) in the SML and ULW is presented in Fig. 3 (b), (see Table S3 for wavelengths 265, 280, 370 nm). In the SML,  $a_{300}$  ranged from 0.569 to 9.347



307  $\text{m}^{-1}$ , with an average of  $2.565 \text{ m}^{-1}$ . The distribution of  $a_{300} (\text{m}^{-1})$  closely mirrored the one of DOC,  
308 displaying maxima on 01 July 2016 and 04 May 2017. As observed in the case of DOC,  $a_{300}$  values in  
309 the ULW were significantly lower ( $p = 0.001$ ), and the high SML peaks were not reflected in the ULW.  
310 The lack of correlation between  $a_{300}$  in the two layers (Fig. 3(b)) suggests that CDOM originates from  
311 different sources and undergoes distinct processes rather than being influenced primarily by upward flux,  
312 highlighting the additional roles of in situ photochemical or biological transformations and/or direct  
313 atmospheric inputs to the optically active DOM pool.

314 In the SML, DOC was strongly correlated with  $a_{300}$  indicating that the variations in CDOM are largely  
315 driven (by 77%) by those in the bulk DOM. In contrast, no significant correlation between DOC and  
316 CDOM was observed in the ULW (Table 1). The overall strong coupling between the optically active  
317 fraction of DOM and bulk DOM in the SML suggests shared sources and transformation dynamics,  
318 whereas their decoupling in the ULW implies that DOM and CDOM respond differently to  
319 biogeochemical and photochemical processes taking place in the ULW.

320 Enrichment factors (EFs) of  $a(\lambda)$  were consistently and significantly greater than unity ( $p < 0.05$ ),  
321 confirming systematic enrichment of CDOM in the SML as observed in previous works (Obenosterer  
322 et al., 2008; Wurl et al., 2009; Lechtenfeld et al., 2014; Mustaffa et al., 2017). Moreover, EFs increased  
323 progressively from the UV-C ( $a_{265}$ ) (EF=3.6) to the UV-A/near-visible regions ( $a_{370}$ ) (EF=7.4) (Table  
324 S4), indicating wavelength-dependent accumulation of chromophoric material at the surface. Yang et al.,  
325 2022 also reported higher EFs in longer wavelengths in the eastern marginal seas of China. UV-A/near-  
326 visible chromophores are disproportionately enriched at the surface, highlighting a decoupling of CDOM  
327 constituents in the SML relative to the underlying water.

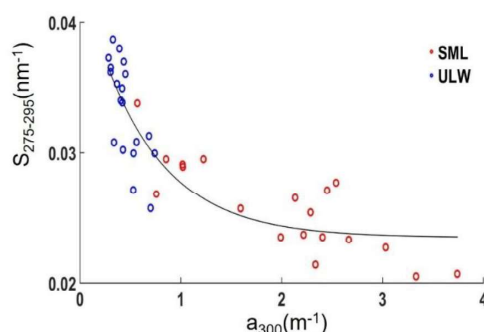
328 **Table 1.** Linear regression analysis of DOC vs absorption coefficients in SML, ULW and rain waters  
329 (excluding the outlier values of 01 July 206 and 04 May 2017).

|                     | <i>equation</i>  | $R^2$ | $p$   |
|---------------------|------------------|-------|-------|
| <b>SML (n=22)</b>   |                  |       |       |
| DOC vs $a_{300}$    | $y=0.844x-0.094$ | 0.774 | 0     |
| <b>ULW (n=22)</b>   |                  |       |       |
| DOC vs $a_{300}$    | -                | 0.073 | 0.224 |
| <b>Rain (n= 14)</b> |                  |       |       |
| DOC vs $a_{300}$    | $y=1.225x+0.534$ | 0.878 | 0     |

330  
331 Spectral slope values  $S_{275-295}$  in the SML ranged from  $0.015$  to  $0.034 \text{ nm}^{-1}$  with an average of  $0.025 \text{ nm}^{-1}$   
332 <sup>1</sup>. In the ULW  $S_{275-295}$  values were considerably ( $p=0.001$ ) higher than those in the SML fluctuating  
333 between  $0.029$ - $0.039 \text{ nm}^{-1}$  with an average of  $0.034 \text{ nm}^{-1}$ . The increase in spectral slope  $S_{275-295} (\text{nm}^{-1})$   
334 i.e. a steeper absorption spectra, usually reflects a decrease in molecular weight, and when plotted against  
335 the absorption coefficients  $a_{300} (\text{m}^{-1})$ , typically exhibits a negative trend (Chin et al., 1994; Weishaar et  
336 al., 2003; Helms et al., 2008; Tzortziou et al., 2011). This relationship is commonly used to interpret  
337 changes in CDOM resulting from photodegradation processes in surface waters (Helms et al., 2008;  
338 Fichot and Benner, 2012). The relationship tends to be linear within a compositionally uniform DOM

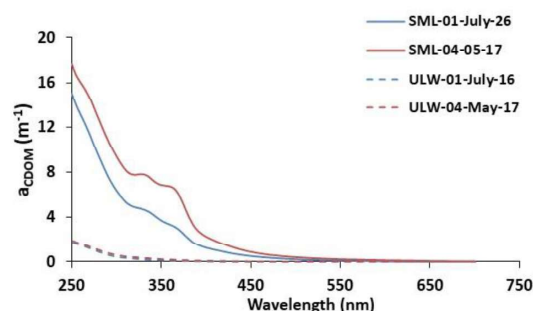


source (Helms et al., 2008; Twardowski and Donaghay, 2001) while it becomes nonlinear (often exponential) across natural gradients encompassing a wide range of CDOM concentrations or mixed sources (e.g., riverine and marine), due to the coexistence of DOM with differing molecular compositions and reactivities (Fichot and Benner, 2012; Nelson and Siegel, 2013). In Fig. 4, this relationship is presented against  $a_{300}$  ( $\text{m}^{-1}$ ). It is evident that for the ULW, the relationship between the two parameters exhibits a steeper slope compared to the SML. Furthermore, for both layers 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 different CDOM composition in the two layers. These observations indicate photodegradation of CDOM in both the SML and ULW. Yet, the less steep/moderate slopes found for the  $a_{300}$  vs  $S_{275-295}$  relationship in the SML suggest that other processes taking place in the SML probably compensate the effect of photodegradation. Possible explanations are the continuous reorganization of the hydrophobic DOM in the SML, (Wurl et al., 2009; Lechtenfeld et al., 2014; Mustaffa et al., 2017; Penezic et al., 2022) and/or the in-situ production of optically active material in the UV-A -near visible region in the SML. 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.



**Figure 4: Relationship between  $a_{300}(\text{m}^{-1})$  and  $S_{275-295}(\text{nm}^{-1})$  in the SML (red circles) and ULW (blue circles). When both layers are combined the relationship is well approximated by an exponential decay equation denoting multiple chemical structures of CDOM compounds**

As previously noted, absorption was noticeably higher in the SML on 01 July 2016 and 04 May 2017, following the trends observed in DOC concentrations. Alongside these elevated absorption values, the SML spectra exhibited two distinct shoulders at approximately 330 nm and 360 nm, features that were absent in the respective spectra in the ULW (Fig. 5).



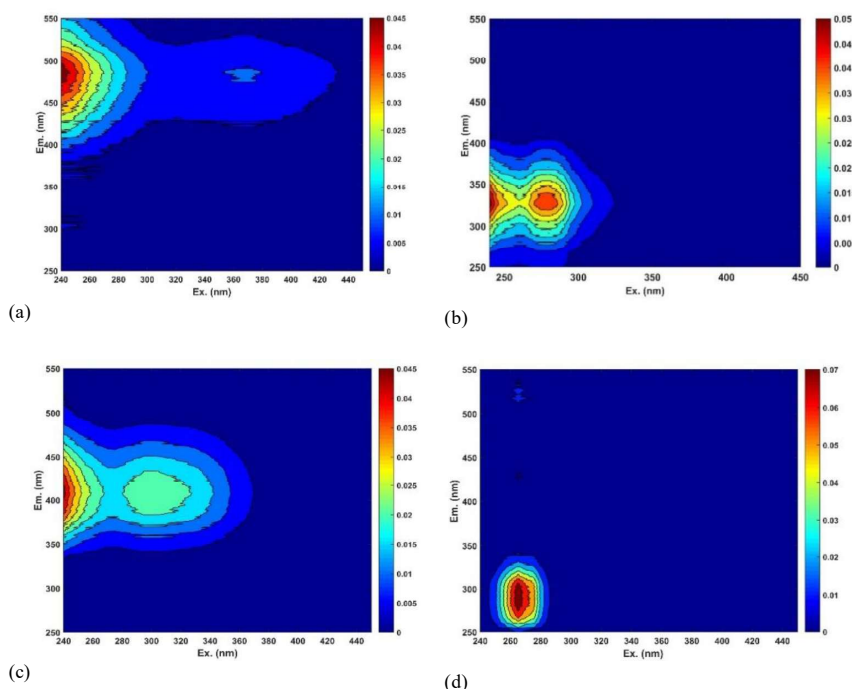
**Figure 5: Absorption spectra in the SML (solid lines) and ULW (dashed lines) on 01 July 2016 (blue) and 04 May 2017 (red). Spectra shoulders at 330 nm, 360 nm are indicative of MAA absorption**

362  
 363 Tilstone et al. (2010) reported pronounced UV absorption shoulders at 300–340 nm, coinciding with  
 364 elevated concentrations of mycosporine-like amino acids (MAAs), particularly during surface slicks.  
 365 These high MAAs levels were linked to coastal phytoplankton blooms and associated exudation, which  
 366 protect cells from solar irradiance and tend to accumulate in the SML. Similarly, Sabbaghzadeh et al.  
 367 (2024) observed sporadic UV absorption shoulders across an Atlantic-wide survey, attributing them also  
 368 to in situ MAAs production by phytoplankton and bacteria in high-UV environments. During both  
 369 sampling events (01 July 2016 and 04 May 2017), surface slicks were clearly observed. Solar irradiance  
 370 reached some of its annual maximum values (approximately 800 and 750 W m<sup>-2</sup>, respectively), while  
 371 consecutive Saharan dust episodes (30 and 40 µg m<sup>-3</sup>, of dust flux respectively) occurred concurrently.  
 372 These conditions favoured intense phytoplankton activity as reflected by the elevated chlorophyll-a  
 373 concentrations (0.88 and 0.58 µg L<sup>-1</sup>, respectively) and corroborate to the release of MAAs into the  
 374 consolidated SML, contributing to the UV absorption features observed in the CDOM spectra of Fig. 5.  
 375 Although distinct spectral signatures of MAAs were not discernible during the remaining samplings,  
 376 their occurrence provides clear evidence of biological processes within the SML that influence CDOM  
 377 dynamics.

### 378 3.3. FDOM composition in the SML and ULW resolved by PARAFAC modelling

379  
 380 In Fig. 6 the components resolved by the PARAFAC model on SML and ULW EEMs are shown.  
 381 Hereafter C1, C2, C3 and C4 will refer to the components and I<sub>1</sub>, I<sub>2</sub>, I<sub>3</sub> and I<sub>4</sub> to the intensities of the  
 382 respective components in the SML and ULW samples.

383



**Figure 6: The four components resolved in the SML and ULW by the seawater PARAFAC model, (a) Component C1, peaks A/C, (b) Component C2, peak T, (c) Component C3, peaks A/M, (d) Component C4, peak B**

384

385 Component C1 presented two excitation maxima at 240 nm and 375 nm and a single emission maximum  
 386 at 486 nm that resembles peaks A and C described by Coble et al. (1990; 1998). Peak A (ex/em 240/486  
 387 nm) has been associated with aromatic highly conjugated humic material origin (McKnight et al., 2001),  
 388 while peak C (ex/em 375/486 nm) reflects more mature, condensed aromatic humics also of terrestrial  
 389 origin. The fact that peak C presents longer excitation wavelength compared to peak A implies that the  
 390 organic substances that fluoresce in the region of peak C are of relatively higher molecular weight and  
 391 aromaticity compared to the substances that fluoresce in the region of peak A (McKnight et al, 2001).  
 392 Component C2 presented excitation maxima at 240 nm and 280 nm and maximum at 338 nm and is  
 393 associated with peak T (Coble et al., 1998). The spectral characteristics of component C2 indicate  
 394 proteinaceous material that resembles tryptophan amino acid (Coble, 1996; Coble et al., 1998), indicative  
 395 of autochthonous biological production in aquatic systems. The third component, C3 showed two  
 396 excitation maxima at 240 nm and 295 nm and a single emission maximum at 408 nm. These two peaks  
 397 resemble peaks A and M respectively. In this case peak A (ex/em 240/408 nm) is resolved in shorter  
 398 wavelengths. Peak M (ex/em 295/408 nm) is indicative of lower molecular weight less aromatic humic  
 399 substances predominately associated with in situ bacterial humification processes, while there are also  
 400 references attributing to peak M terrestrial or riverine origin especially in estuaries and coastal



environments (Stedmon and Markager, 2005; Fellman et al., 2010; Catala et al., 2013). A common feature for PARAFAC modelling of FDOM in aquatic systems is that peak A may be deconvoluted in several components. This likely reflects the fact that the fluorescence associated with the humic-like peaks A, C, and M originates from aromatic chromophores that differ in their degree of conjugation, oxidation state, and source. Moreover, in coastal environments, dissolved organic matter is often enriched in lignin-derived compounds, originating from terrestrial plant material. Lignin exhibits strong UV absorption around 280 nm, which closely aligns with the excitation wavelength of fluorescence peak A, and fluoresces in the 420–470 nm range, overlapping with the emission regions of both fluorescence peaks A and C (Del Vecchio and Blough, 2004). Component C4 shows a single excitation and emission maximum at ex/em 270/290 nm similar to the maximum of peak B (Coble et al. 1998). Peak B is representative of proteinaceous material that resembles tyrosine amino acids. This organic material is associated to bacterial degradation processes in contrast to the proteinaceous peak T which is associated with primary production processes. All four components have been previously reported in the SML in the Mediterranean Sea and the global ocean (Galgani and Engel 2016; Pitta et al., 2017; Martinez-Perez et al., 2019; Drozdowska et al., 2018). In marine environments, humic-like fluorescent components are generally more susceptible to photodegradation than protein-like components. Several studies have shown that exposure to solar radiation leads to a marked decrease in the intensity of humic-like peaks (A, C, M), while the protein-like peaks (T, B) are comparatively less affected (Retelletti Brogi et al., 2020; Romera-Castillo et al., 2011; Zhang et al., 2013). Among the humic-like components, peak C typically exhibits the greatest sensitivity to photobleaching, followed by peak A (Helms et al., 2003; Retelletti Brogi et al., 2020).

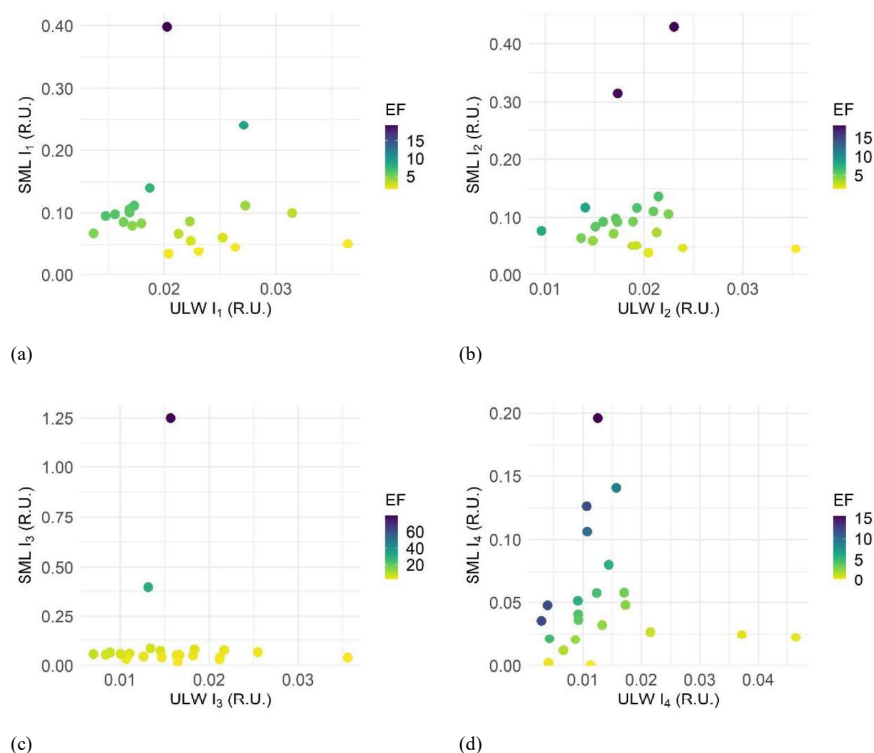
422

### 423 3.4. FDOM dynamics within the CDOM pool in the SML and ULW

424

As illustrated from Y-axes in Fig. 7, in the SML during most months, components C1 (peak A–C) and C2 (peak T) exhibited higher 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, intensities show roughly equal contributions of the humic-like C1 and tryptophan-like C2 to the FDOM pool. Component C3 (peak A–M) had the highest average 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. Component C4 (peak B) displayed the lowest values but higher variability (70.4%) with highest values during summer 2016 and lowest occurred from late winter (February) to mid-spring 2017 (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. In the ULW, components C1, C2, and C3 showed minimal variation overall, peaking during autumn bloom on 07 October 2016. In contrast, component C4 was more variable, with higher intensities from June to October 2016 (Table S5).

439



**Figure 7: Correlation graphs between the SML (y axis) and ULW (x axis) of PARAFAC maximum fluorescence intensities (R.U.) of (a)  $I_1$ ; (b)  $I_2$ ; (c)  $I_3$ ; (d)  $I_4$ . The z axis illustrates the enrichment factors**

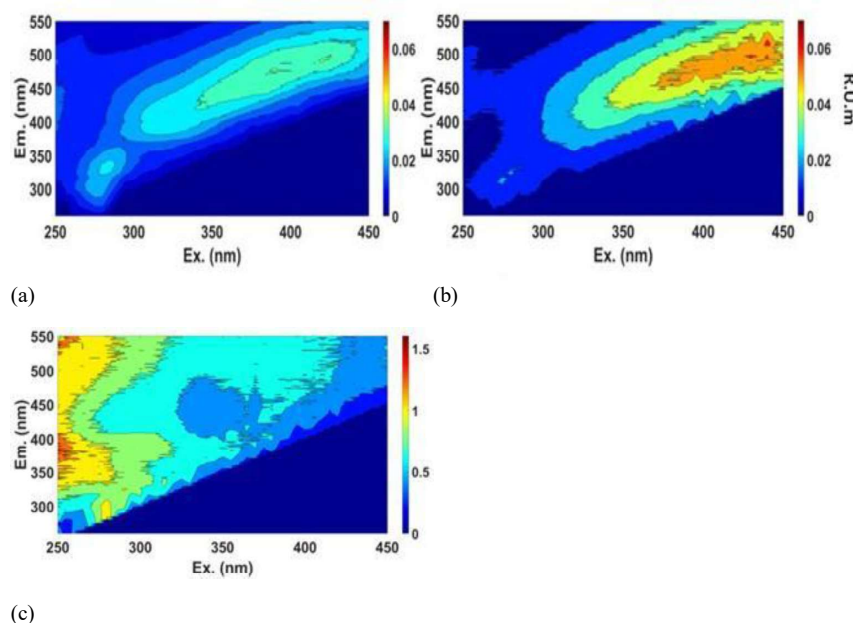
The lack of correlation of the PARAFAC intensities  $I_{1,4}$  between the SML and ULW ( $p > 0.05$ ), denotes a decoupling of processes acting upon FDOM in the two water layers (Fig. 7). As with DOC and CDOM, the SML is found enriched in FDOM with most of the EFs fluctuating well above 1 ( $p < 0.05$  in all cases) (Fig. 7, Table S4). In particular, the humic like fluorophores (peak A/C) and the tryptophan like one (peak T) appear the most enriched in the SML (average EF: 4.2 and 4.5 respectively). Yang et al. 2022, reported clearly higher EFs of the tryptophan-like peak in the SML compared the humic-like and tyrosine-like peaks, indicating a greater contribution of marine autochthonous DOM in the SML relative to the ULW. In our study, the FDOM enrichment within the SML appears to be more evenly distributed between humic (terrestrial) DOM and protein (autochthonous) DOM.

As described previously, PARAFAC modelling resolved the terrestrial humic-like fluorophores (peak A) into two components—C1 (peak A/C) and C2 (peak A/M)—reflecting overlapping emission regions typical of marine samples. However, this separation makes it difficult to directly assess the relationship between FDOM and CDOM compounds across the full spectral range. To investigate the relative contribution of FDOM to the bulk CDOM, we calculated the FDOM to CDOM index (FDOM/CDOM, R.U.·m) by dividing the full excitation–emission matrix (EEM) of each sample by the corresponding absorption coefficients at the respective excitation wavelengths, as described in Section 2.6 (Fig. S1). The average ratios for all SML and ULW samples are presented in the plots of Fig. 8. This approach





459 provides qualitative insight on the relative importance of the fluorescent to absorbing chromophores  
 460 present in the two water layers.



461 **Figure 8: The FDOM/CDOM index ( $R.U.\cdot m$ ) in the (a) SML, (b) ULW, (c) the ratio  $(FDOM/CDOM)_{SML} /$   
 462  $(FDOM/CDOM)_{ULW}$ . (a,b) Depletion of UV-a/near visible fluorescence is apparent in the SML relative to the  
 463 ULW. (c) Higher contribution of short wavelength (UV-C/UV-B) FDOM to CDOM is apparent in the SML**

464 Figure 8 (a, b) show that FDOM/CDOM index values are elevated at longer excitation wavelengths ( $>350$   
 465 nm) relative to shorter wavelengths in both the SML and ULW, indicating a relatively higher contribution  
 466 of UV-A/near-visible FDOM to bulk CDOM compared to UV-B and UV-C FDOM. Between layers, the  
 467 SML appears less enriched in UV-A–near-visible FDOM compared to CDOM, likely reflecting the  
 468 higher bulk CDOM content in the SML at these wavelengths, as discussed previously based on CDOM  
 469 indices. CDOM enrichment factors (EFs) increased more than threefold from the UV-C to the UV-A  
 470 region, consistent with selective enrichment of UV-A near visible chromophores. It appears that the  
 471 humic-like FDOM fraction of CDOM is more susceptible to photodegradation than the corresponding  
 472 humic CDOM fraction, and/or that humic CDOM is produced at a higher rate than humic FDOM within  
 473 the SML. Photodegradation of terrigenous DOM, leads to the formation of lower molecular weight, less  
 474 complex DOM with altered optical characteristics (Opsahl & Benner, 1998; Opsahl & Zepp, 2001;  
 475 Obernosterer & Benner, 2004), while contrary plankton-derived DOM (mostly protein-like and low  
 476 molecular weight substances) presents minimal photochemical alteration (Obernosterer and Benner,  
 477 2004). Previous studies have also demonstrated that FDOM exhibits stronger photodegradation at longer  
 478 excitation wavelengths than at shorter ones (Helms et al., 2013; Gonsior et al., 2013). Particularly, Helms  
 479 et al. (2013) observed that irradiation caused the emission maxima of humic-like peaks A and C to shift  
 480 toward shorter wavelengths, with the greater shift occurring for peak C, while its excitation maximum



shifted toward longer wavelengths. At the same time, the SML may be influenced by atmospheric inputs of water-soluble organic carbon (WSOC) with distinct optical signatures. For example, nitro-aromatic compounds present in atmospheric WSOC exhibit strong absorption at 300-500 nm (Huang et al., 2021, Lin et al., 2017) but show minimal fluorescence likely due to the significant reduction in the electron density of the benzene ring by the nitro group (Chen et al., 2020, Cao et al. 2023). Because of the hydrophobic nature of these aromatic compounds, they are expected to preferentially accumulate in the SML. Overall, the various sources and complex DOM transformation processes occurring in the SML appear to promote a more pronounced accumulation of absorbing but not fluorescent CDOM at longer wavelengths.

In the UV-B and UV-C regions, where humic-like peak A and protein-like peaks T and B are observed in the EEMs ( $\text{Ex/Em} = 250/485 \text{ nm}$ ), the FDOM/CDOM index is relatively low in both layers, suggesting that highly absorbing material dominates over fluorescent material in this spectral range in both layers. To examine differences between the SML and ULW in the low-wavelength region, we calculated the ratio  $(\text{FDOM/CDOM})_{\text{sml}} / (\text{FDOM/CDOM})_{\text{ulw}}$  (Fig. 8(c)). This analysis revealed that the SML has a relatively higher FDOM fraction at UV-C and UV-B wavelengths, indicating that the proportion of highly aromatic, terrestrial humic material and freshly produced protein-like material is greater in the SML than in the ULW. Terrestrial humics and lignin degradation products absorbing at the short UV-B and UV-C regions can be small sized allochthonous molecules, resistant to photodegradation and are expected to enter the coastal environments either via land runoff or via the atmosphere. (Hernes and Benner, 2003; Jaffe et al., 2014)

The preferential enrichment of nitrogen organic compounds, mostly amino-acids, in the SML is documented for diverse coastal and open waters (Liss and Duce, 1997; Kuznetsova and Lee, 2002; Kuznetsova et al., 2004; van Pixteren et al., 2012; Cunliffe et al., 2013; Chen et al., 2022). It is documented that amino acid enrichment in the SML is likely facilitated by other factors rather than excess in situ production (Kuznetsova and Lee, 2002; Kuznetsova et al., 2004). Within the FDOM pool in particular, the accumulation of amino acid like fluorophores (peaks T and B) has been attributed to microbial release by photoprotection mechanisms and/or cell lysis (Galgani and Engel, 2016; Yang et al., 2022). Our study provides indication of episodic MAAs production in the SML. Increased bacterial production in the SML compared to the ULW has been reported in the Mediterranean Sea under the influence of dry atmospheric deposition (Astrahan et al., 2016). As already stated, several dust events occurred during the sampling period, likely stimulating bacterial activity and the subsequent production of humic-like compounds in the SML.

Overall, the SML and ULW display distinct FDOM to CDOM profiles. The SML exhibits a higher fluorescent fraction relative to bulk CDOM in the UV-C and UV-B regions (protein-like peaks and peak A) but a lower fraction in the UV-A/near-visible range (peak C) compared to the ULW. Based on CDOM and FDOM indices, the SML appears enriched in high molecular weight, non-fluorescent organic compounds, together with low molecular weight fluorescent material of terrestrial and amino acid-like origin. This pattern suggests that the SML acts as a selective accumulation layer, concentrating photoreactive and surface-active DOM fractions, while bulk UV-A fluorescent material is comparatively



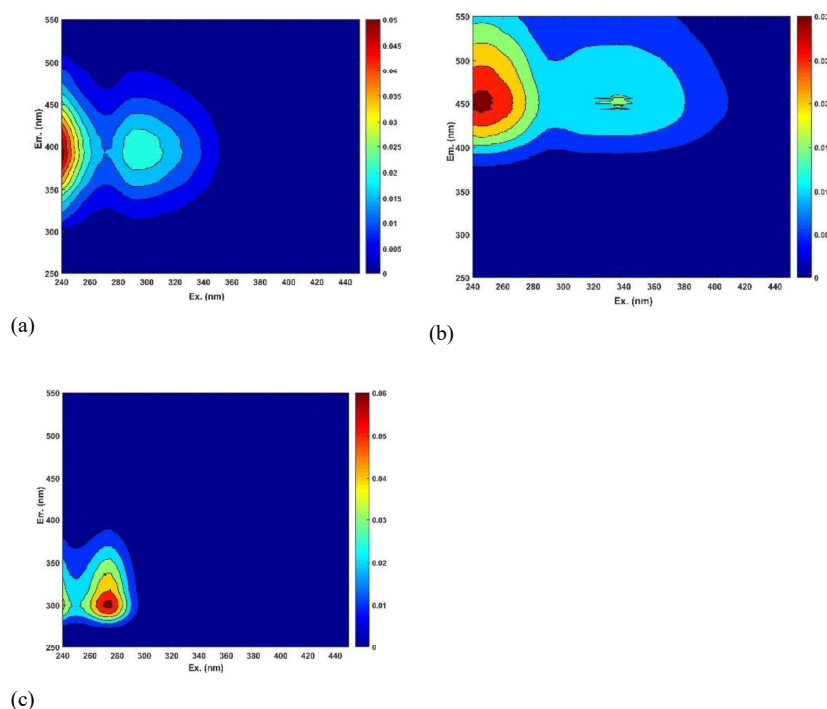
diluted, reflecting differential contributions of in situ production, atmospheric deposition, and selective photochemical or biological transformations.

### 3.4. Influence of Wet Deposition on SML Enrichment

Rain events are significant sources of dissolved organic carbon in surface seawater as it was estimated that they contribute about  $90 \times 10^{12} \text{ g C yr}^{-1}$  (Willey et al., 2000). Rainwater can be exceptionally rich in CDOM (Kieber et al., 2006) while increased DOM concentrations in the SML during rain events have been reported (Wurl and Obbard 2005; Lim et al., 2007; Ribas-Ribas et al. 2017). Several sources contribute to water soluble organic carbon (WSOC) forms in the atmosphere, such as biomass burning, fossil fuel combustion, wind driven soil particulates, including Saharan dust, volatile organic compounds over urban areas, and sea spray over coastal and marine sites (Mladenov et al., 2011; Miyazaki et al., 2018). Studies on the optical properties of WSOC in the atmosphere have shown an overall similarity with the fluorophores found in the marine environment, i.e., humic-like and protein-like substances, yet with distinct differences in their spectral position (Wu et al., 2021 and references therein). Given the coastal location of the rainwater sampler near an urban area and the prevailing meteorological conditions, the collected samples are expected to reflect contributions from multiple sources. The objective of the CDOM/FDOM analysis in rainwater was to investigate potential linkages between the optical signatures of rainwater and those observed in the SML. DOC ranged from 0.60 to 6.26  $\text{mg L}^{-1}$  (average 2.49  $\text{mg L}^{-1}$ ). Absorption coefficients at 300 nm ( $a_{300}$ ) varied between 0.931 and 8.070  $\text{m}^{-1}$  (average 3.395  $\text{m}^{-1}$ ), while the spectral slope  $S_{275-295}$  exhibited a narrow range 0.021–0.030  $\text{nm}^{-1}$  (average 0.024  $\text{nm}^{-1}$ ) (Table S6). Rainwater DOM was highly enriched in optically active material, with a strong coupling observed between DOC and  $a(\lambda)$  (Table 1). Compared to the SML, rainwater exhibited comparable DOC concentrations, slightly higher  $a_{300}$  values, and similar average spectral slope  $S_{275-295}$ , though with a narrower range. PARAFAC analysis of the rainwater EEMs resolved three fluorescent components (R1, R2, and R3) (Table S6, Fig. 9). Component R1, with excitation maxima at 240 and 290 nm and an emission maximum at 394 nm, corresponds to peaks A and M and is analogous to seawater component C3, albeit slightly blue-shifted, suggesting a smaller molecular weight. This component was dominant with fluorescence intensities  $I_1$  ranging from 0.108 R.U. to 1.09 R.U. Component R2 exhibited excitation maxima at 245 and 335 nm and an emission maximum at 456 nm, representing peaks A and C, and was similarly blue-shifted relative to seawater component C1. These spectral shifts indicate differences in the composition of aromatic, high-molecular-weight humic substances between seawater and rainwater. Intensities of component R2 ranged from 0.025 R.U. to 0.389 R.U. Component R3, with excitation maxima at 240 and 270 nm and an emission maximum at 299 nm, corresponds to peak B, whose spectral characteristics closely match those observed in seawater.  $I_3$  fluorescence intensities fluctuated in levels comparable to those of  $I_2$ , from 0.056 R.U. to 0.457 R.U., indicating an equal contribution of components R2 (peak A/C) and R3 (peak B) in rainwater FDOM. All identified rainwater components have been previously reported in studies of CDOM in precipitation (Müller et al., 2008; Santos et al., 2012; Yang et al., 2019). Notably, peak T, resolved in seawater, was not resolved in the rainwater PARAFAC model.



560



561 **Figure 9: The three components resolved by the rainwater PARAFAC model, (a) Component R1, peaks A/M,**  
 562 **(b) Component R2, peaks A/C, (c) Component R3, peak B**

563 The predominance of humic-like fluorophores over protein-like ones in marine aerosols has been  
 564 reported by Miyazaki et al. (2019), particularly within the spectral range of peak M fluorophores (Ex/Em  
 565 = 300/400). These authors suggest that during the transfer of DOC to the atmosphere, protein-like  
 566 compounds undergo substantial decomposition and/or there is preferential formation of humic-like  
 567 substances in atmospheric aerosols. They also propose that the absence of protein-like fluorophores in  
 568 sea spray may result from the strong association of these molecules with gel-like exopolymer colloids.  
 569 Based on laboratory oxidation studies of atmospheric organic carbon, Fan et al. (2019) reported that  
 570 various oxidation pathways—beyond simple photodegradation—affect atmospheric WSOC, including  
 571 reactions with hydroxyl radicals ( $\cdot\text{OH}$ ), ozone ( $\text{O}_3$ ), and nitrogen oxides ( $\text{NO}_x$ ). In particular, tryptophan-  
 572 like fluorophores were found to be highly susceptible to  $\cdot\text{OH}$  oxidation, leading to their transformation  
 573 into humic-like and tyrosine-like compounds. Moreover, several works on atmospheric humic-like  
 574 substances provide evidence that during atmospheric transport degradation processes (photo- and  
 575 oxidative ones) generate low molecular weight molecules, and of more aliphatic nature (Wu et al., 2021  
 576 and references therein).

577 Consistent with these findings, our data show a clear predominance of humic-like peaks A and M  
 578 (component R1) in rainwater samples, the absence of tryptophan-like fluorophores among the



PARAFAC components, and blue shifted FDOM components R1 (peak A/M) and R2 (peak A/C). These features suggest: (i) a significant contribution of marine aerosols to rainwater over our study area, and (ii) effective photodegradation and oxidation processes leading to the depletion of tryptophan-like fluorophores and the formation of relatively low-molecular-weight, humic-like compounds. The optical signatures of the rainwater samples further indicate that wet deposition contributes to the CDOM/FDOM pool in the SML primarily through degraded, humic-like components of terrestrial origin (peaks A and C) and tyrosine-like amino acids. At the same time, the prevalence of marine humic-like fluorescence (peak M) points to an efficient recirculation of marine FDOM through sea spray derived marine aerosols. In parallel, the similarities in  $a_{300}$  and spectral slope values  $S_{275-295}$  with the SML suggest that high molecular weight, light-absorbing but non-fluorescent compounds are present in both rainwater and the SML.

#### 4. Conclusion

The SML exhibited consistent enrichment in DOM, CDOM and FDOM relative to the ULW. Upward transport from the ULW to the SML was found more important for bulk DOM while different processes seem to act upon the CDOM and FDOM pools within each layer. Although bulk CDOM was closely coupled to DOM in the SML, based on CDOM and FDOM indices we were able to discriminate variable accumulation patterns of the optically active organic material. Surprisingly the impact of photodegradation processes on the  $S_{275-295}$  vs  $a_{300}$  relationship was less evident in the SML relatively to the ULW. This was attributed to the selective enrichment of high molecular weight optically active material in the UV-A/near visible region, as evidenced by the increase in  $a(\lambda)$  EFs for longer wavelengths, and the lower  $S_{275-295}$  values relatively to the ULW. By introducing the FDOM/CDOM ratio we further revealed wavelength-dependent enrichment patterns: SML exhibited lower fraction of the more conjugated fluorophores at the UV-A/near visible range relatively to the ULW and higher fractions of low molecular weight terrestrial humics and protein like fluorophores in the UV-C, UV-B regions. In combination with CDOM indices, these observations suggest that the SML favors the selective accumulation of high molecular weight, non-fluorescent organic compounds alongside low molecular weight fluorescent material of terrestrial and amino-acid-like origin. Several parallel processes may contribute to these patterns including: i) biological transformation of DOM within the SML generating molecules of variable molecular weight, ii) fast reorganisation of the SML macromolecular structure, iii) atmospheric inputs of optically active DOM. For the latter our analysis in rainwater provided evidence of the presence of relatively low molecular weight fluorescent humic-like material (blue shifted peaks) while at the same time low spectral slopes point to the presence of non-fluorescent high molecular weight CDOM in wet deposition. In contrast, CDOM in the ULW exhibited weaker coupling with DOC, higher spectral slopes, and clear evidence of photodegradation, emphasizing the distinct processes governing DOM dynamics between the two layers.



Collectively, these findings highlight the SML as a dynamic, selectively enriched interface where specific DOM fractions accumulate relative to the underlying water, underscoring its chemical and biological significance in marine ecosystems.

619

**Data availability:** Detailed data are provided in the Supplementary material of this work.

621

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624

**Author contribution:** Writing (original draft preparation) EP, CZ; Investigation ET, EP; Formal Analysis EP, CZ; Writing (review and editing) EP, CZ, ET; Conceptualization CZ, ET, EP.

627

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631

**Competing interests:** The authors declare that they have no conflict of interest.

633

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