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Changes in optical characteristics of surface microlayers hint to photochemically and microbially-mediated DOM turnover in the upwelling region off Peru

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The coastal upwelling system off Peru is characterized by high biological activity and a pronounced subsurface oxygen minimum zone, as well as associated emissions of atmospheric trace gases such as N_2O , CH_4 and CO_2 . During the *Meteor* (M91) cruise to the Peruvian upwelling system in 2012, we investigated the composition of the sea-surface microlayer (SML), the oceanic uppermost boundary directly subject to high solar radiation, often enriched in specific organic compounds of biological origin like Chromophoric Dissolved Organic Matter (CDOM) and marine gels. In the SML, the continuous photochemical and microbial recycling of organic matter may strongly influence gas exchange between marine systems and the atmosphere. In order to understand organic matter cycling in surface films, we analyzed SML and underlying water samples at 38 stations determining DOC concentration, amino acid composition, marine gels, CDOM and bacterial and phytoplankton abundance as indicators of photochemical and microbial alteration processes. CDOM composition was characterized by spectral slope (S) values and Excitation-Emission Matrix fluorescence (EEMs), which allow to track changes in molecular weight (MW) of DOM, and to determine potential DOM sources and sinks. We identified five fluorescent components of the CDOM pool, of which two had excitation/emission characteristics of protein-like fluorophores and were highly enriched in the SML. CDOM composition and changes in spectral slope properties suggested a local microbial release of HMW DOM directly in the SML as a response to light exposure in this extreme environment. Our results suggest that microbial and photochemical processes play an important role for the production, alteration and loss of optically active substances in the SML.

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1 Introduction

The Peruvian Eastern Boundary Upwelling System (EBUS), extending along the coast off Peru between 4° and about 40° South, is among the most productive marine ecosystems worldwide (Capone and Hutchins, 2013; Chavez and Messié, 2009; Rosenberg et al., 1983) and it is characterized by high biological activity, involving high export rates of organic carbon both vertically and laterally (Aristegui et al., 2004; Muller-Karger et al., 2005). The high productivity is sustained by winds year-round that promote the upwelling of nutrient-rich deep waters into the euphotic zone, thus favoring phytoplankton photosynthesis and organic matter production (Chavez and Messié, 2009). High rates of organic matter production are counterbalanced by heterotrophic respiration, which provides sinks for the oxygen produced by autotrophs and leads to subsurface Oxygen Minimum Zones (OMZs) (Lachkar and Gruber, 2011). OMZs are expanding worldwide due to reduced solubility at increasing temperatures, as well as a consequence of reduced oceanic ventilation and enhanced stratification (Keeling et al., 2010; Stramma et al., 2008). OMZs become increasingly important as key marine regions for the emission of climate-relevant gases like carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O) and hydrogen sulfide (H₂S) (Paulmier et al., 2008, 2011). N₂O is a strong greenhouse gas and ozone-reactive: 30 % of its atmospheric concentration has an oceanic source (Solomon et al., 2007), of which, up to 75 % is supported by OMZs (Bange et al., 2001). Therefore, OMZs are key environments to assess the oceanic contribution to the concentration of atmospheric gases. Defining the processes that regulate gas fluxes across the water–air interface is a central objective to better understand the reciprocal relationship between changes in our climate and marine environments.

The uppermost oceanic layer in contact with the atmosphere is the sea-surface microlayer (SML), which mediates major climate-relevant processes including air–sea gas exchange and sea-spray aerosol emission (Liss and Duce, 2005). This interface between a liquid (hydrosphere) and a gas phase (atmosphere) accumulates organic

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matter of biological origin, creating a sort of “skin” of surface-active compounds able to damp capillary waves and “capping the flux” of gases across the water–air interface (GESAMP, 1995). Natural organic compounds in the SML include a vast array of photosynthesis products including carbohydrates, amino acids and lipids, as well as other carbon-rich compounds like dissolved organic matter (DOM) and marine gels (e.g. Cunliffe et al., 2013). The DOM pool represents a continuum of molecular weights and biological lability ranging from refractory to labile DOM being utilized rapidly by microorganisms (Benner, 2002; Carlson, 2002), or photochemically degraded (Kieber, 2000). These compounds, produced in the oceanic photic zone and brought to the SML through rising bubbles (Hardy, 1982), contribute to the enrichment of a natural surface biofilm and favor specific SML heterotrophic communities that are very active in recycling this organic material (Hardy, 1982; Cunliffe et al., 2011). While bulk dissolved organic carbon is not generally enriched in the SML, specific DOM fractions are present occasionally at much higher concentrations than in the underlying water (Cunliffe et al., 2013). These enriched pools of organic matter include marine gel particles (Wurl and Holmes, 2008), chromophoric dissolved organic matter (CDOM) (Zhang and Yang, 2013; Tilstone et al., 2010) and phenolic material (Carlson and Mayer, 1980).

CDOM is the principal light-absorbing constituent of DOM, strongly absorbing UV (100–400 nm) and visible radiation (400–700 nm), and it can comprise 20–70 % of the DOM in oceanic waters (Coble, 2007). CDOM plays a major role in the attenuation of UV wavelengths and can reduce the availability of underwater photosynthetically active radiation for primary production (Bracchini et al., 2011). Photolysis of CDOM promotes the formation of low molecular weight (LMW) compounds from the breakdown of high molecular weight DOM (HMW-DOM), facilitating the bioavailability of carbon uptake for microbial growth from biologically refractory material, and representing an important loss pathway for CDOM in the oceans (Kieber et al., 1989). Other major by-products of CDOM photolysis are carbon monoxide (CO), which often exists at supersaturated concentrations at the oceans’ surface (Van Blough, 2005, and references therein), CO₂ (Miller and Zepp, 1995) and reactive chemical species (Loiselle et al., 2012). To initiate

a photochemical reaction, light must first be absorbed and in this respect the SML is very well exposed to elevated solar radiation (Liss and Duce, 2005). CDOM photolysis may affect biological processes within the SML as well as the structure of accumulated organic matter. Optical properties and photochemical cycling of DOM have been widely investigated in the oceans (Nelson and Siegel, 2013) but processes within the SML remain poorly understood. Possible effects of photochemistry on SML chemical composition have been discussed in the past (Van Blough, 2005), but still little is known on CDOM fluorophores, sources and sinks (Tilstone et al., 2010; Zhang and Yang, 2013). To discern sources, sinks and modification of DOM in surface waters, whether microbially or photochemically-induced, we investigated optical properties of organic sea-surface microlayers and underlying water samples in the highly productive EBUS off Peru. We applied optical spectroscopy measurements combined with chemical and biological analysis to identify different compounds within the CDOM pool and their partitioning between the SML and the underlying water. The use of excitation-emission matrix fluorescence spectroscopy (EEMs) allowed us to discriminate different compound classes in the SML and underlying water based on their excitation and emission maxima (Coble, 1996).

At present, the oceans are subject to many changes in physical and chemical properties like pH, temperature, and dissolved oxygen concentration, which potentially will affect the biological cycling of carbon (Riebesell et al., 2009; Keeling et al., 2010; Bopp et al., 2002). Whether the oceans are sources or sinks of carbon depends on the production rate of organic matter with respect to its biological degradation (del Giorgio and Duarte, 2002), and high DOM degradation in the SML might represent a net source of CO₂ to the atmosphere (Garabétian, 1990). It is well known that the composition of the SML reflects biological processes of the euphotic zone (Galgani et al., 2014; Gao et al., 2012; Matrai et al., 2008; Bigg et al., 2004), and that elevated concentrations of organic matter may accumulate in the SML in highly productive regions like the Peruvian EBUS (Engel and Galgani, 2015). The enrichment of light-absorbing DOM in the SML may increase the photochemical formation and fluxes of reactive chemical

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species at the surface, with potentially important consequences for the composition of the SML itself and for the fate of compounds passing through this interface (Van Blough, 2005). Last but not least, the photochemical DOM breakdown may increase the biological availability of carbon, thus increasing heterotrophic respiration and CO₂ flux to the atmosphere.

In upwelling areas associated with OMZs, these dynamics are worth to be investigated as they may impact the exchange of gases between the ocean and the atmosphere.

2 Material and methods

2.1 Study area

The R/V *Meteor* cruise M91 was an integrated biogeochemical study in the upwelling region off Peru, with the aim to assess the importance of oxygen minimum zones (OMZs) for the air–sea exchange of gases relevant for climate and tropospheric chemistry (Bange, 2013). A total of 39 samples for SML and underlying water were collected in December 2012 between 5° S and 16° S off the Peruvian coast. Data that we report here additionally from what previously described by Engel and Galgani (2015) refer to 38 stations. We also describe “revisited stations” (Fig. 1, Table 1) where we sampled at different times of the day to monitor effects of solar radiation on the DOM composition both in the SML and underlying water.

The sampling approach for the SML was chosen as a silicate glass plate of 500 mm (length) × 250 mm (width) × 5 mm (thickness) with an effective sampling area of 2000 cm² as indicated in Engel and Galgani (2015). Briefly, the glass plate was inserted into the water perpendicular to the surface and withdrawn at a controlled rate of ~ 20 cm s⁻¹ as first suggested by Harvey and Burzell (1972). In order to minimize biases in the sampling procedure, the same person always took the samples. Sampling was performed on a rubber boat and great care was taken that the sampling procedure

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could be well standardized. The rubber boat was positioned as far upwind of the ship as possible and away from the path taken by the ship in order to avoid any potential surface contamination. The outboard motor of the rubber boat was switched off and samples were collected in upwind clean waters.

5 Before collecting the sample into the bottle, we let the plate drain for 20 s approximately. Then, the sample retained on both sides of the plate was removed with a Teflon wiper, and the procedure repeated about 20 times to obtain the necessary volume for analysis. The exact amount of dips per sample has been tracked. The first sample was discarded and used to rinse the collecting bottle (HCl 10 % cleaned and Milli-Q rinsed).
 10 Glass plate and wiper were acid cleaned (HCl 10 %) and Milli-Q rinsed prior use, and at sampling site they were copiously rinsed with in situ seawater to minimize any contamination with alien material during transport and handling. Underlying seawater (ULW) was collected right after SML at about ~ 20 cm depth by opening an acid cleaned (HCl 10 %) and Milli-Q rinsed glass bottle and closing it underwater. The thickness (d , cm)
 15 of our reference SML that we were able to collect was estimated as follows:

$$d = V / (A \times n) \quad (1)$$

Where V is the SML volume collected, i.e. 60–140 mL, A is the sampling area of the glass plate ($A = 2000 \text{ cm}^2$) and n is the number of dips. During this cruise, the apparent sampling thickness of the SML ranged between 45 and 60 μm (or 10^{-4} cm), with an
 20 overall mean of $49 \pm 8.9 \mu\text{m}$ (Engel and Galgani, 2015). Many factors may influence the thickness of the SML such as withdrawal rate, dipping time, and plate dimensions. With a withdrawal speed of $\sim 20 \text{ cm s}^{-1}$, the apparent SML thickness was in accordance with previous findings at similar withdrawal rate reporting 60–100 μm (Harvey and Burzell, 1972) and 50–60 μm (Zhang et al., 1998). The sampling thickness was very well com-
 25 parable among all stations, indicating that no major biases due to sampling procedure may have occurred.

After sampling, bottles were stored in the dark and the samples immediately processes in the laboratory onboard, within maximum 30 min from sampling.

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2.2 Chemical and biological analyses

2.2.1 Dissolved organic matter (DOM)

20 mL samples for dissolved organic carbon (DOC) were filtered through combusted GF/F filters (8 h, 500 °C), collected in combusted glass ampoules (8 h, 500 °C), acidified (80 µL of H₃PO₄ 85 %), heat sealed immediately, and stored at 4 °C in the dark until analysis. DOC samples were analyzed high-temperature catalytic oxidation method (TOC-VCSH, Shimadzu). Calibration and analysis procedure has been described in details by Engel (2015).

Samples for chromophoric and fluorescent DOM (CDOM and FDOM) were filtered through 0.45 µm PES syringe filters and collected into 40 mL pre-combusted (8 h, 500 °C) amber glass vials. Samples were stored in the dark at 4 °C with no other treatment than pre-filtering. Since storage procedures may affect the absorbance and fluorescence properties of DOM, absorbance and fluorescence readings were performed directly on-board within a few hours from sampling or the next day according to Schneider-Zapp and colleagues (2013). Prior to measurements, samples were stored in the dark and acclimatized at room temperature. For CDOM, triplicate absorbance measurements were made on a Shimadzu 1800 UV-Visible Spectrophotometer in the range 220 to 700 nm with 0.5 nm increments, in a 10 cm path-length quartz cuvette against Milli-Q water as a reference. For FDOM, 3-D fluorescence spectroscopy was performed with a Varian Cary Eclipse Fluorescence Spectrophotometer equipped with a xenon flash lamp and data assembled into Excitation/Emission matrices (EEMs) which enable to individuate single DOM fluorophores (Coble, 1996) and to perform parallel factor analysis PARAFAC (Stedmon and Bro, 2008). Samples have been acclimatized and scanned at a fixed 20 °C temperature (Cary Single Cell Peltier Accessory, VARIAN) in 1 cm path length quartz cuvette. Scans were performed at 600 nm min⁻¹ using an excitation range (Ex) of 240–450 nm with 5 nm increments and recorded emission (Em) in the range 242–600 nm with 2 nm increments. Samples were run in a mode of 5 nm slit for both excitation and emission and 0.1 s integration time.

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2.2.2 Dissolved amino acids

For dissolved hydrolysable amino acids (DHAA), 5 mL of sample previously filtered through 0.45 µm Millipore Acrodisc[®] syringe filters were filled into pre-combusted glass vials (8 h, 500 °C) and stored at −20 °C until analysis. Analysis was performed according to Lindroth & Mopper (1979). Duplicate samples were analyzed with a detection limit of 2 nM on a HPLC system (1260, Agilent). Thirteen different amino acids were separated with a C18 column (Phenomenex Kinetex, 2.6 µm, 150 mm × 4.6 mm) after in-line derivatization with o-phthalaldehyde and mercaptoethanol. Additionally, to track DOM diagenetic state and bioavailability, we used the carbon-normalized yields of dissolved amino acids to DOC, expressed as DHAA%-DOC (Amon and Fitznar, 2001; Benner, 2002; Kaiser and Benner, 2009; Davis and Benner, 2007). A value of ~ 2 % of DHAA%-DOC may indicate the threshold between labile and semi-labile and refractory DOM (Davis and Benner, 2007).

2.2.3 Gel particles

Total numbers of gel particles were determined by microscopy after Engel (2009). Therefore, 20 to 30 mL were filtered onto 0.4 µm Nuclepore membranes (Whatmann) and stained with 1 mL prefiltered (< 0.2 µm) Alcian Blue solution for polysaccharidic gels, i.e. transparent exopolymer particles (TEP), and 1 mL prefiltered (< 0.2 µm) Coomassie Brilliant Blue G (CBBG) working solution for proteinaceous gels, i.e. Coomassie Stainable Particles (CSP). Filters were mounted onto Cytoclear[®] slides and stored at −20 °C until microscopy analysis.

2.2.4 Heterotrophic bacteria

For bacterial cell numbers, 4 mL samples were fixed with 200 µL glutaraldehyde (25 % final concentration) and stored at −20 °C until enumeration. Samples were stained with SYBR Green I (Molecular Probes). Heterotrophic bacteria were enumerated using

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a flow cytometer (Becton & Dickinson FACScalibur) equipped with a laser emitting at 488 nm and detected by their signature in a plot of side scatter (SSC) vs. green fluorescence (FL1). Yellow-green latex beads (Polysciences, 0.5 μm) were used as internal standard.

2.2.5 Phytoplankton

For autotrophic cell numbers, 4 mL samples were fixed with 20 μL glutaraldehyde (25 % final concentration), and stored at -80°C until enumeration. Phytoplankton counts were performed with a FACScalibur flow-cytometer (Becton Dickinson) equipped with an air-cooled laser providing 15 mW at 488 nm and with a standard filter set-up. The cells were analyzed from fresh samples at high flow rate ($\sim 39\text{--}41 \mu\text{L min}^{-1}$) with the addition of 1 μm -fluorescent beads (Trucount, BD). Autotrophic groups were discriminated on the basis of their forward or right angle light scatter (FALS, RALS) as well as from chlorophyll and phycoerythrin (for cyanobacterial, mainly *Synechococcus* populations) fluorescence. Cell counts were analysed using BD CellQuest Pro-Software.

2.3 Data analysis

2.3.1 CDOM

The measured absorbance at every wavelength λ was converted to absorption coefficient a (m^{-1}) according to the following equation (Bricaud et al., 1981):

$$a = 2.303A_\lambda/L \quad (2)$$

where A_λ is the absorbance and L is the path-length of the cuvette (here 0.10 m). CDOM concentration was quantified by its absorption coefficient at 325 nm as often used for the open ocean (Swan et al., 2009; Nelson and Siegel, 2013). The dependence of a on the wavelength was determined by analyzing the spectral slope parameter S (nm^{-1}) in the discrete wavelength ranges of 275–295 nm and 350–400 nm, de-

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terminated by linear regression of log-transformed absorption spectra against the wavelength (Bricaud et al., 1981; Helms et al., 2008):

$$a(\lambda) = a(\lambda_0)e^{-S(\lambda - \lambda_0)} \quad (3)$$

where $a(\lambda_0)$ is the absorption coefficient at a reference wavelength λ_0 . S measured in the wavelength range 275–295 nm ($S(275\text{--}295)$, nm^{-1}) and 350–400 nm ($S(350\text{--}400)$, nm^{-1}) as well as slope ratio (SR) defined as $S(275\text{--}295) : S(350\text{--}400)$ are good indicators to characterize CDOM (Helms et al., 2008). SR is characterized by lower values for terrestrial DOM with respect to DOM produced by autochthonous marine sources and instead of S alone, could be a more sensitive indicator of photochemically induced changes in the molecular weight of the DOM pool as an increase in SR suggests photodegradation processes, while a decrease is often related to microbially altered CDOM (Helms et al., 2008). Both $S(275\text{--}295)$ and SR increase with (a) irradiation (photobleaching), (b) with decreasing DOM molecular weight, and (c) with increasing salinity. As such they are useful as tracers to determine mixing and coastal inputs. We also determined the SUVA_{254} index, that is, the specific ultraviolet absorption at 254 nm normalized to DOC concentration. This index was shown to correlate significantly with increasing aromaticity of DOM (Weishaar et al., 2003):

$$\text{SUVA}_{254}(\text{mg CL}^{-1} \text{ m}^{-1}) = a(254)(\text{m}^{-1})/\text{DOC}(\text{mg L}^{-1}) \quad (4)$$

2.3.2 FDOM

The 3-D recorded spectra were corrected for the instrumental biases both for excitation and emission using correction curves provided by the manufacturer (Stedmon and Bro, 2008). Additionally, spectra were corrected against a Milli-Q water blank run every day before the samples to remove water Raman peaks. No correction for inner filter effects was applied to our data as for each sample the relative $a(\lambda)$ value was below 10 m^{-1} (Lawaetz and Stedmon, 2009; Stedmon and Bro, 2008). As an example, $a(254)$ was on average $2 \pm 2 \text{ m}^{-1}$ for SML and $1.6 \pm 1.3 \text{ m}^{-1}$ for underlying water (ULW) samples.

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3.1 CDOM optical absorption properties

In the upwelling region off Peru, values for $a(325)$ ranged from 0.09 to 1.47 m^{-1} in the SML and from 0.07 to 1.47 m^{-1} in ULW. Highest values were observed at stations S10_1 to S10_4 along the coast for both SML and ULW, probably due to an input of terrestrial material from urban and agricultural activities at the coast and from inland (Fig. 2), or to the upwelling of colder, nutrient-rich waters as also indicated by lower salinity (Engel and Galgani, 2015). Generally CDOM was enriched in the SML (Fig. 3), with median EF for $a(325) = 1.2$ in a range varying between 0.4 and 2.8. Besides the southern transect, higher EF values were observed at the northern stations S2 and S2_2, and in the southern coastal upwelling stations S15_1 to S15_3 (Fig. 4).

The spectral slope parameter between 275 and 295 nm ($S(275-295)$, nm^{-1}) is a good indicator for DOM molecular weight as an increase of this parameter indicates decreasing molecular weight, thus revealing accumulation or degradation processes of bioavailable DOM (Helms et al., 2008). In our samples, $S(275-295)$ ranged from 0.012 to 0.038 nm^{-1} in the SML and from 0.017 to 0.043 nm^{-1} in ULW. In general, $S(275-295)$ was quite similar between SML and ULW. Higher values were observed in the ULW of the southern stations below 15° S (S19, S19_2, S20, S20_2, S1778). In the coastal stations S10_1 to S10_4 and S14_1 to S15_3 lower $S(275-295)$ values were determined for both SML and ULW. Median enrichment factor (EF) for $S(275-295)$ was 1 (Fig. 3), thus indicating similar molecular weight of DOM compounds in the SML and ULW. Lower EFs were observed in the northernmost and southernmost stations and along the coast, thus implying a higher accumulation of HMW DOM in the SML of those sites.

The SUVA_{254} index and HIX are related to the degree of DOM aromaticity and to its humic content, respectively. In our study, SUVA_{254} ranged from 1.13 to 4 $\text{mg CL}^{-1} \text{m}^{-1}$ in the SML, with highest values at coastal southern stations S10_1 to S10_4 and S14_1 to S17_2. Similar values were recorded for ULW, ranging from 1.05 to 2.79 $\text{mg CL}^{-1} \text{m}^{-1}$. Generally, SUVA_{254} values in our samples were high for the Pacific

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Ocean with a typical SUVA_{254} of $0.6 \text{ mg CL}^{-1} \text{ m}^{-1}$ and comparable to riverine waters (Helms et al., 2008; Weishaar et al., 2003). Median EF for SUVA_{254} was 1.1, with higher values in correspondence of northern stations and coastal southern stations (S2, S2_2, S15_1 to S15_3 and S19 to S1778) where the higher EF for $a(325)$ were also observed (Figs. 3 and 4). HIX ranged from -1.33 to 2.05 for SML and from -0.1 to 3.03 for ULW, with highest values in ULW. Enrichment factors showed an overall depletion of high-humic acid containing DOM in the SML (Fig. 3), with median EF = 0.8. Higher humic acid enrichment in the SML was observed on the southern transect S19 to S1778 (Fig. 4), where we recorded the highest enrichment of CDOM (as $a(325)$) as well.

The carbon-normalized yields of dissolved amino acids (DHAA%-DOC) as indicator of DOM diagenetic state, ranged from 1.4 to 8.1 % in SML samples and from 0.9 to 3.6 % in ULW samples, indicating relatively more labile DOM in the SML. This observation was supported by the enrichment factors (EF), which showed a general enrichment of more labile DOM in the SML (Fig. 3), with median EF values for DHAA%-DOC of 1.5. Highest EFs were recorded in the northernmost stations S1 to S3, and on the southernmost transect S19 to S1778.

3.2 PARAFAC analysis for CDOM fluorophores

Five optically active components were identified by PARAFAC analysis with the DrEEM toolbox in Matlab (Murphy et al., 2013), hereafter named F1, F2, F3, F4 and F5 (Fig. 5). The spectral characteristics of the five identified components were compared to previous studies as described in Table 2. F1 had an excitation range of 250–290 nm with emission peaks between 320 and 350 nm, which corresponds to peak T of the protein-like fluorescence of tryptophan, derived by in situ primary production. This component (F1) was generally enriched in the SML (Figs. 6 and 7) with a median EF = 1.5, between a minimum EF of 0.5 and a maximum EF of 3.3. Potential loss processes of this compound are its destruction by UV light and microbial degradation (Stedmon and Markager, 2005b). F1 has also been related to protein-like fluorescence of extracellular

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polymeric substances (Liu and Fang, 2002). Based on its excitation/emission maxima and fluorescence intensities, and its relationship to other parameters in this study (Table 3), we can assume F1 as a tryptophan-like fluorophore, originating by in situ primary production, relatively labile and included in the formation of gel particles. Its negative correlation to SR may hint to a loss of F1 during microbial processing, as a decrease in SR suggests microbially reworked CDOM (Helms et al., 2008). Fluorescence intensities of F1 were the lowest compared to the other fluorophores, but significantly higher in the SML compared to the ULW (Mann–Whitney Rank Sum Test, $p < 0.001$, $n = 38$). Both in SML and ULW, fluorescence intensities of F1 were positively correlated to components F3, F4 and F5 (Spearman Rank Order Correlation coefficient $C = 0.37$, $p < 0.001$, $n = 76$ with F3; $C = 0.41$, $p = 0.001$, $n = 57$ with F4; $C = 0.38$, $p < 0.001$, $n = 76$ with F5).

Component F2 had a short wavelength excitation range (250–260 nm) with emission at longer wavelengths (500–520 nm), corresponding to peak A of fulvic acids and humic acids (Stedmon and Markager, 2005a; Singh et al., 2010; Yamashita and Jaffé, 2008; Coble, 2007; Santín et al., 2009). Component F2 has been characterized as of terrestrial origin, allochthonous in marine environments, and was found in bays, rivers and coastal waters. It is assumed to reflect small-sized molecules, being resistant to photodegradation, biologically not available, and mainly derived from photobleached terrestrial humic acids in marine waters with highest concentrations near the surface (Ishii and Boyer, 2012). F2 did not show a clear enrichment in the SML (Figs. 6 and 7), with median EF = 1, ranging from a minimum EF = 0.5 and a maximum EF = 3.6. Highest SML concentrations of F2 were observed at the northernmost stations S2 to S3 (Fig. 7). F2 positively correlated with bacterial abundance and temperature (Table 3), potentially hinting to a refractory DOM component of terrestrial origin, characterized by small molecules completely degraded either photochemically or microbially and therefore of low bioavailability. F2 strongly correlated to F3 and F5 components, further suggesting its origin from larger organic molecules (Spearman Rank Order Correlation

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was also negatively correlated to HIX, suggesting a low humic-acid content of this fluorophore material. Interestingly, F4 showed the highest fluorescence intensities among all samples.

Component F5 was quite difficult to identify, as we found no comparable spectra in the literature. It showed typical characteristics of allochthonous humic-like material with excitation/emission ranges in the peak A and C regions, which have been observed in bay and offshore waters (Mostofa et al., 2013). F5 had the highest fluorescence intensities both in the SML and ULW but was not clearly enriched in one or the other compartment (Fig. 7). EF ranged from a minimum of 0.5 and a maximum of 3, with median value = 1.1. Highest enrichments in the SML were observed at northern stations S4 and S4_2, at stations S10_1 to S10_4, and in the southern stations S20 to S1778 (Fig. 6). F5 was similar in characteristics to component F3, and positively correlated to bacterial abundance and proteinaceous CSP particles (Table 3). Component F5 was also positively correlated to all other fluorophores F1, F2, F3 as described, and to F4 (Spearman Rank Order Correlation coefficient $C = 0.34$, $p = 0.009$, $n = 57$).

3.3 “Revisited stations”

During R/V *Meteor* cruise leg M91, we sampled four stations within a time frame of 24 h for SML and ULW, as described in Table 1. Exact latitude and longitude were not always possible to retrieve after a certain time, but were similar for the stations sampled in a few hours time lag. We were interested in monitoring the spectral characteristics of CDOM in the SML and ULW at different times of the day depending on the solar irradiation and therefore in the evolution of the optical properties. Whenever possible, we sampled at sunrise, midday and sunset. For security reasons, it was not possible to sample later than sunset, as the zodiac operations were not allowed out at dark. On the revisited stations only component F1 showed a direct dependency on light exposure, decreasing in fluorescence – thus concentration – with increasing levels of solar radiation (Fig. 8). As previously observed, F1 was characterized by higher aromaticity (measured as SUVA₂₅₄), which also decreased at higher solar radiation (Fig. 8), imply-

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$S(275-295)$ increased with increasing temperature (Fig. 10d) both in the SML and in the ULW. Moreover, temperature increment was inversely correlated to DOM lability, and therefore bioavailability, expressed as DHAA%-DOC, suggesting a higher degree of DOM degradation (Spearman Rank Order Correlation coefficient $C = -0.64$, $p < 0.001$, $n = 38$ in the SML and $C = -0.68$, $p < 0.001$, $n = 38$ in the ULW). As for $S(275-295)$, we observed similar trends in SR (data not shown): SR was negatively correlated to DOM lability as DHAA%-DOC (Spearman Rank Order correlation coefficient $C = -0.50$, $p < 0.001$, $n = 75$) and to both gel particles abundance (Spearman Rank Order correlation coefficient $C = -0.37$, $p < 0.001$, $n = 75$ for TEP and $C = -0.33$, $p = 0.004$, $n = 75$ for CSP). SR did not show any significant correlation to total bacteria or phytoplankton abundance, but was significantly lower in the SML, with a median EF = 0.9 (Mann–Whitney Rank Sum Test, $p = 0.013$, $n = 38$). Furthermore, DHAA%-DOC was significantly higher in the SML (Mann–Whitney Rank Sum Test, $p = 0.036$, $n = 38$).

4 Discussion

4.1 CDOM enrichment and production in the top surface layer of the ocean

The enrichment of organic material in the SML has been mainly related to biological processes in the euphotic zone below the surface (Hardy, 1982; Liss and Duce, 2005). EBUS are among the most productive regions in the ocean and therefore interesting systems to investigate the relationship between organic matter accumulation and SML biogeochemical properties. The Peruvian EBUS is associated with an extensive OMZ and a key region for the study of gas fluxes from the ocean (Paulmier et al., 2008; Paulmier and Ruiz-Pino, 2009; Keeling et al., 2010). The presence of an organics-enriched surface layer may strongly affect gas exchange between the marine and the atmospheric systems (Engel and Galgani, 2015). The characterization of CDOM via its optical properties adds relevant information to the organic matter composition in the

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SML, as it allows discriminating between terrestrial and marine sources of DOM that may be equally enriched at the surface. Moreover, it helps tracking changes in DOM “quality” deriving from the exposure of SML to solar radiation more than any other marine environment. As such, microbial and photochemical DOM turnover in the SML may contribute to the atmospheric emission of gases and chemical reactive species, and interfere with the microbial carbon loop in the ocean.

In the Peruvian EBUS, we observed a general enrichment of CDOM in the SML with respect to the ULW, based on values of the specific absorption coefficient $a(\lambda)$ measured at 325 nm. Higher CDOM concentrations were observed in the coastal upwelling stations characterized by lowest salinity, temperature and highest enrichment of organic components, both in the particulate and dissolved fraction (Engel and Galgani, 2015). DOC concentrations in the SML were related to DOC concentrations in the ULW (Engel and Galgani, 2015), and the same was true for CDOM concentrations (Spearman Rank Order Correlation coefficient $C = 0.82$, $p < 0.001$, $n = 38$), implying a direct dependency of SML CDOM on the organic matter in the ULW (Zhang and Yang, 2013). CDOM concentration as well as its spectral slope $S(275\text{--}295)$ did not show any correlation to changes in DOC concentrations neither in the SML, nor in the ULW, but were significantly related to DOM diagenesis (DHAA%-DOC), suggesting a recent production of labile or semi-labile substrates driven by in situ microbial or photochemical processes in the nutrient-rich euphotic zone. However, a closer look on CDOM spectral properties revealed significant differences between SML and ULW in CDOM source and lability as evidenced by spectral slope ratio SR and DHAA%-DOC. This observation suggested a microbial production of relatively recent and labile DOM directly in the SML due to lysis or exudation, which has been previously proposed (Tilstone et al., 2010).

4.2 CDOM composition

The analysis of EEMs allowed the identification of five fluorescent components both in the SML and ULW, of which two (F1 and F4) showed a protein-like fluorescence of

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autochthonous material, and three (F2, F3 and F5) had the characteristics of terrestrially derived fulvic-acid like or humic-acid like DOM (Table 2). These classes of fluorophores are commonly found in marine environments (Coble, 2007; Mostofa et al., 2013), but EEMs analyses of SML samples are scarce and up to now revealed the enrichment in humic-acid like fluorophores (Zhang and Yang, 2013). Phenolic materials deriving from humic and fulvic acids transported by river drainage, and from macroalgae polyphe-
nols, are often enriched in the SML, and indicate the presence of surface slicks (Carlson, 1982; Carlson and Mayer, 1980). Here, we observed a significant enrichment of protein-like fluorophores F1 and F4 with respect to ULW, in good accordance with previous reports on amino acids enrichment in the SML (Kuznetsova et al., 2004; Cunliffe et al., 2013; Tilstone et al., 2010), and with our own observations for the Peruvian EBUS (Engel and Galgani, 2015). Moreover, F4 was among the most abundant components, as, when present, it showed higher fluorescence intensities compared to F1, F2 and F3. Component F4 was characterized as a tyrosine or phenylalanine-like fluo-
rophore, and both amino acids were enriched in the SML of the Peruvian upwelling (Engel and Galgani, 2015). A recent study reported that the greenhouse gas N_2O can bind to aromatic groups in phenylalanine and tyrosine (Cao et al., 2014), thus suggesting an interaction with biological processes and with the exchange of N_2O between the ocean and the atmosphere in the Peruvian EBUS (Engel and Galgani, 2015). The enrichment of protein-like fluorophores in the SML could be related to the upwelling of colder nutrient-rich waters that boost primary production in the euphotic zone (as indicated by an inverse correlation of F1 to salinity and temperature, Table 2). However, a local microbial production as response to high solar radiation may be another source for protein-like fluorophores in the SML. Major losses of autochthonous protein-like fluorophores in the SML were related to photochemical and microbial degradation, as evidenced during the revisited stations.

The fulvic acid or humic acid-like components F2, F3 and F5 were ubiquitous in SML and ULW, with no significant differences in fluorescence intensities between the two compartments. F2 and F3 have been previously observed in coastal marine environ-

ments (e.g. Jørgensen et al., 2011; Ishii and Boyer, 2012). F2 fluorescence appears to be related to DOM exposure to sunlight, although we did not find a significant correlation to global radiation in this study, but instead a positive correlation to temperature (Table 2). This kind of fluorophores has been shown having highest intensities near the surface, decreasing with depth (Yamashita et al., 2008). The positive correlation to bacterial abundance might suggest F2 as the ultimate product of microbial degradation in the surface ocean. F3-like fluorophores have been identified as an intermediate product of terrestrially-derived DOM, still subject to further photochemical degradation (Stedmon et al., 2007). Moreover, F3 appearance has been related to apparent oxygen utilization (Yamashita et al., 2010), suggesting a microbial source of this material (Jørgensen et al., 2011). In this study, F3 showed a slight enrichment in the SML and was related to heterotrophic bacteria as well as to CSP particles, indicating an origin related to microbial reworking of larger organic material. F5 showed characteristics of allochthonous humic acid fluorophores, with fluorescence maximum ranges to the lower end of F3 emission indicating a more pronounced DOM alteration with respect to F3. Showing similar correlations to heterotrophic bacteria and CSP, F5 may as well derive from an indirect microbial in situ reworking of starting terrestrial material both in the SML and ULW that contribute to the gel particles pool in surface waters. In fact, a net production and accumulation of humic-like CDOM in surface waters may occur in upwelling regions (Nieto-Cid et al., 2005; Jørgensen et al., 2011), whereas photochemical loss is thought to be the major removal mechanism of this material (e.g. Mopper and Schultz, 1993).

Based on CDOM absorption and fluorescence characteristics, in Fig. 11 we summarized potential DOM production and losses in the SML and ULW that relate to microbial and photochemical processes. We hypothesize that the accumulation of HMW DOM in the SML is the result of (a) the biological production of HMW DOM in the ULW and deeper water column, stimulated by the upwelling of nutrient-rich waters to the sunlit surface and (b) the local microbial release of DOM as a response to elevated solar radiation. Mycosporine-like amino acids (MAAs) are well known as microbial sunscreen

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in aquatic environments (Bhatia et al., 2011; Shick and Dunlap, 2002), and were observed in higher concentrations in the SML during surface slicks development (Tilstone et al., 2010). In our study, the enrichment of specific amino-acid fluorophores (F1, F4), as well as the enrichment of CSP and amino acids described elsewhere (Engel and Galgani, 2015) may suggest bacterial release of fresh DOM directly within the SML, as a consequence of light exposure.

Both in the SML and ULW, microbial and photochemical processes would lead to a loss of amino-acid like fluorophores (F1, F4) and to the accumulation of more refractory and humic-like components completely degraded (F2) or still subject to further photochemical degradation (F3, F5).

4.3 Implications for surface ocean dynamics and future perspectives

Optical properties of DOM in the Peruvian EBUS revealed a SML characterized by protein-like CDOM fluorophores. CDOM enrichment in the SML has been observed in different marine regions associated with enrichment in phenolic compounds, MAAs and humic acids (Carlson, 1982; Carlson and Mayer, 1980; Tilstone et al., 2010; Zhang and Yang, 2013). Here, the accumulation of protein-like CDOM may have derived from high primary production in the euphotic zone, but likely had a major microbial source directly in the microlayer. Accumulation of amino acids in the SML has been related to a reduced bacterial activity, being the SML an extreme environment where the consumption of amino acids may be lower (Santos et al., 2012). A reduced bacterial activity may thus also explain the observed amino acids enrichment in the SML of the Peruvian upwelling region (Engel and Galgani, 2015). Our study suggests that microbial DOM release through lysis and exudation as a response to the extreme environmental conditions represents another source of proteinaceous compounds in the SML, thus modifying the organic properties of the surface biofilm. HMW DOM of more humic and refractory composition (F3, F5) instead, may have originated from the ULW and the deeper water column where microbial production and degradation processes would have been stimulated by the nutrient rich waters of the upwelling.

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We may assume that in the SML, exposure to light may have determined three main processes: (1) microbial release of protein-like, HMW DOM as a sunscreen function, (2) increased availability of biological substrate by DOM photolysis and (3) further photochemical degradation of microbially-altered DOM.

Photochemical DOM breakdown is able to produce LMW species, and to alter the HMW fraction making it more available for microbial attack (Kieber et al., 1989). However, in surface waters of the open ocean DOM photolysis may not necessarily imply higher bacterial productivity, as photochemistry may lead to a net loss of bioavailable substrates (Kieber, 2000).

Therefore, the interplay of photochemical and microbial degradation controls the accumulation and loss of organic compounds in the top layer of the ocean, thus implying DOM alteration processes with direct consequences on the gas fluxes across the water–air interface. High microbial DOM respiration can lead to higher production of CO₂ in the SML (Garabétian, 1990). A recent study reports that high concentrations of isoprene are released from photosensitized DOM reactions in the SML, proving an abiotic source of this gas uncoupled from biological production (Ciuraru et al., 2015).

It remains unclear whether in the Peruvian EBUS an increase in bioavailable carbon may have implied a higher heterotrophic respiration and CO₂ production in the SML, and this is an attractive hypothesis for future studies in this direction. It may be suggested however, that a net DOM production in the SML may take place independently of the biological productivity of the underlying waters as a sole microbial response to light exposure. Nevertheless, the dynamics of a surface-active biofilm enriched in organic matter depend both on microbial and photochemical DOM alteration processes that need deeper investigations in climate-relevant marine regions such as the OMZ off Peru. We assessed the enrichment of light-absorbing organic material in the SML of a highly productive oceanic system, which may interfere with correct estimates of primary production from remote measurements. To conclude, we suggest that further primary production estimates may take into account the CDOM enrichment in the first centimeters of the ocean.

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References

- Amon, R. M. W. and Fitznar, H. P.: Linkages among the bioreactivity, chemical composition, and diagenetic state of marine dissolved organic matter, *Limnol. Oceanogr.*, 42, 287–297, 2001.
- Aoki, S., Ohara, S., Kimura, K., Mizuguchi, H., Fuse, Y., and Yamada, E.: Characterization of dissolved organic matter released from microcystis aeruginosa, *Anal. Sci.*, 24, 389–394, doi:10.2116/analsci.24.389, 2008.
- Arístegui, J., Barton, E. D., Tett, P., Montero, M. F., García-Muñoz, M., Basterretxea, G., Cus-satlegras, A.-S., Ojeda, A., and de Armas, D.: Variability in plankton community structure, metabolism, and vertical carbon fluxes along an upwelling filament (Cape Juby, NW Africa), *Prog. Oceanogr.*, 62, 95–113, doi:10.1016/j.pcean.2004.07.004, 2004.
- Bange, H. W., Rapsomanikis, S., and Andreae, M. O.: Nitrous oxide cycling in the Arabian Sea, *J. Geophys. Res.-Oceans*, 106, 1053–1065, doi:10.1029/1999jc000284, 2001.
- Benner, R.: Chemical composition and reactivity, in: *Biogeochemistry of Marine Dissolved Organic Matter*, edited by: Hansell, D. A. and Carlson, D. J., Academic Press – Elsevier, 59–90, 2002.
- Bhatia, S., Garg, A., Sharma, K., Kumar, S., Sharma, A., and Purohit, A. P.: Mycosporine and mycosporine-like amino acids: a paramount tool against ultra violet irradiation, *Pharmacog-nosy Reviews*, 5, 138–146, doi:10.4103/0973-7847.91107, 2011.

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- Bigg, K. E., Leck, C., and Tranvik, L.: Particulates of the surface microlayer of open water in the central Arctic Ocean in summer, *Mar. Chem.*, 91, 131–141, doi:10.1016/j.marchem.2004.06.005, 2004.
- Bopp, L., Le Quéré, C., Heimann, M., Manning, A. C., and Monfray, P.: Climate-induced oceanic oxygen fluxes: implications for the contemporary carbon budget, *Global Biogeochem. Cy.*, 16, 6-1–6-13, doi:10.1029/2001GB001445, 2002.
- Bracchini, L., Dattilo, A. M., Falcucci, M., Hull, V., Tognazzi, A., Rossi, C., and Loiselle, S. A.: Competition for spectral irradiance between epilimnetic optically active dissolved and suspended matter and phytoplankton in the metalimnion. Consequences for limnology and chemistry, *Photochem. Photobio. S.*, 10, 1000–1013, doi:10.1039/c0pp00291g, 2011.
- Bricaud, A., Morel, A., and Prieur, L.: Absorption by dissolved organic matter of the sea (yellow substance) in the UV and visible domains, *Limnol. Oceanogr.*, 26, 43–53, 1981.
- Cao, Q., Gor, G. Y., Krogh-Jespersen, K., and Khriachtchev, L.: Non-covalent interactions of nitrous oxide with aromatic compounds: spectroscopic and computational evidence for the formation of 1:1 complexes, *J. Chem. Phys.*, 140, 144304, doi:10.1063/1.4870516, 2014.
- Capone, D. G. and Hutchins, D. A.: Microbial biogeochemistry of coastal upwelling regimes in a changing ocean, *Nat. Geosci.*, 6, 711–717, doi:10.1038/ngeo1916, available at: <http://www.nature.com/ngeo/journal/v6/n9/abs/ngeo1916.html> (last access: 25 September 2015), 2013.
- Carlson, C. A.: Production and Removal Processes, in: *Biogeochemistry of Marine Dissolved Organic Matter*, edited by: Hansell, D. A. and Carlson, C. A., Academic Press – Elsevier, 91–150, 2002.
- Carlson, D. J.: Surface microlayer phenolic enrichments indicate sea surface slicks, *Nature*, 296, 426–429, 1982.
- Carlson, D. J. and Mayer, L. M.: Enrichment of dissolved phenolic material in the surface microlayer of coastal waters, *Nature*, 286, 482–483, 1980.
- Chavez, F. P. and Messié, M.: A comparison of Eastern Boundary Upwelling Ecosystems, *Prog. Oceanogr.*, 83, 80–96, doi:10.1016/j.pocean.2009.07.032, 2009.
- Ciuraru, R., Fine, L., Pinxteren, M. V., D'Anna, B., Herrmann, H., and George, C.: Unravelling new processes at interfaces: photochemical isoprene production at the sea surface, *Environ. Sci. Technol.*, 49, 13199–13205, doi:10.1021/acs.est.5b02388, 2015.
- Coble, P.: Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy, *Mar. Chem.*, 51, 325–356, 1996.

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- Coble, P. G.: Marine optical biogeochemistry: the chemistry of ocean color, *Chem. Rev.*, 107, 402–418, 2007.
- Cunliffe, M., Upstill-Goddard, R. C., and Murrell, J. C.: Microbiology of aquatic surface microlayers, *FEMS Microbiol. Rev.*, 35, 233–246, doi:10.1111/j.1574-6976.2010.00246.x, 2011.
- 5 Cunliffe, M., Engel, A., Frka, S., Gašparović, B., Guitart, C., Murrell, J. C., Salter, M., Stolle, C., Upstill-Goddard, R., and Wurl, O.: Sea surface microlayers: a unified physicochemical and biological perspective of the air–ocean interface, *Prog. Oceanogr.*, 109, 104–116, doi:10.1016/j.pocean.2012.08.004, 2013.
- Davis, J. and Benner, R.: Quantitative estimates of labile and semi-labile dissolved organic carbon in the western Arctic Ocean: a molecular approach, *Limnol. Oceanogr.*, 52, 2434–2444, 2007.
- 10 del Giorgio, P. A. and Duarte, C. M.: Respiration in the open ocean, *Nature*, 420, 379–384, 2002.
- Engel, A.: Determination of marine gel particles, in: *Practical Guidelines for the Analysis of Seawater*, CRC Press, 2009.
- 15 Engel, A. and Galgani, L.: The organic sea surface microlayer in the upwelling region off Peru and implications for air–sea exchange processes, *Biogeosciences Discuss.*, 12, 10579–10619, doi:10.5194/bgd-12-10579-2015, 2015.
- Galgani, L., Stolle, C., Endres, S., Schulz, K. G., and Engel, A.: Effects of ocean acidification on the biogenic composition of the sea-surface microlayer: results from a mesocosm study, *J. Geophys. Res-Oceans*, 119, 7911–7924, doi:10.1002/2014jc010188, 2014.
- 20 Gao, Q., Leck, C., Rauschenberg, C., and Matrai, P. A.: On the chemical dynamics of extracellular polysaccharides in the high Arctic surface microlayer, *Ocean Sci.*, 8, 401–418, doi:10.5194/os-8-401-2012, 2012.
- Garabétian, F.: Production de CO₂ à l'interface air-mer. Une approche par l'étude des phénomènes respiratoires dans la microcouche de surface. CO₂ production at the sea–air interface. An approach by the study of respiratory processes in surface microlayer, *Int. Rev. Hydrobiol.*, 75, 219–229, doi:10.1002/iroh.19900750208, 1990.
- 25 Garcia-Pichel, F., Wingard, C. E., and Castenholz, R. W.: Evidence regarding the UV sunscreen role of a mycosporine-like compound in the cyanobacterium *gloeocapsa* sp, *Appl. Environ. Microb.*, 59, 170–176, 1993.
- 30 Hardy, J. T.: The sea surface microlayer: biology, chemistry and anthropogenic enrichment, *Progr. Oceanogr.*, 11, 307–328, doi:10.1016/0079-6611(82)90001-5, 1982.

- Harvey, G. W. and Burzell, L. A.: A simple microlayer method for small samples, *Limnol. Oceanogr.*, 11, 608–614, 1972.
- Helms, J. R., Stubbins, A., Ritchie, J. D., Minor, E. C., Kieber, D. J., and Mopper, K.: Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter, *Limnol. Oceanogr.*, 53, 955–969, 2008.
- Huguet, A., Vacher, L., Relexans, S., Saubusse, S., Froidefond, J. M., and Parlanti, E.: Properties of fluorescent dissolved organic matter in the Gironde Estuary, *Org. Geochem.*, 40, 706–719, doi:10.1016/j.orggeochem.2009.03.002, 2009.
- Ishii, S. K. L. and Boyer, T. H.: Behavior of reoccurring PARAFAC components in fluorescent dissolved organic matter in natural and engineered systems: a critical review, *Environ. Sci. Technol.*, 46, 2006–2017, doi:10.1021/es2043504, 2012.
- Jørgensen, L., Stedmon, C. A., Kragh, T., Markager, S., Middelboe, M., and Søndergaard, M.: Global trends in the fluorescence characteristics and distribution of marine dissolved organic matter, *Mar. Chem.*, 126, 139–148, doi:10.1016/j.marchem.2011.05.002, 2011.
- Kaiser, K. and Benner, R.: Biochemical composition and size distribution of organic matter at the Pacific and Atlantic time-series stations, *Mar. Chem.*, 113, 63–77, doi:10.1016/j.marchem.2008.12.004, 2009.
- Keeling, R. F., Körtzinger, A., and Gruber, N.: Ocean deoxygenation in a warming world, *Annu. Rev. Mar. Sci.*, 2, 199–229, doi:10.1146/annurev.marine.010908.163855, 2010.
- Kieber, D. J.: Photochemical production of biological substrates. The effects of UV radiation in the marine environment, Cambridge University Press, 2000.
- Kieber, D. J., McDaniel, J., and Mopper, K.: Photochemical source of biological substrates in sea water: implications for carbon cycling, *Nature*, 341, 637–639, 1989.
- Kuznetsova, M., Lee, C., and Aller, J.: Enrichment of amino acids in the sea surface microlayer at coastal and open ocean sites in the North Atlantic Ocean, *Limnol. Oceanogr.*, 49, 1605–1619, 2004.
- Lachkar, Z. and Gruber, N.: What controls biological production in coastal upwelling systems? Insights from a comparative modeling study, *Biogeosciences*, 8, 2961–2976, doi:10.5194/bg-8-2961-2011, 2011.
- Lawaetz, A. J. and Stedmon, C. A.: Fluorescence intensity calibration using the raman scatter peak of water, *Appl. Spectrosc.*, 63, 936–940, doi:10.1366/000370209788964548, 2009.

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- Lindroth, P. and Mopper, K.: High performance liquid chromatographic determination of subpicomole amounts of amino acids by precolumn fluorescence derivatization with o-phthaldialdehyde, *Anal. Chem.*, 51, 1667–1674, doi:10.1021/ac50047a019, 1979.
- Liss, P. S. and Duce, R. A.: *The Sea Surface and Global Change*, Cambridge University Press, 2005.
- Liu, H. and Fang, H. H. P.: Characterization of electrostatic binding sites of extracellular polymers by linear programming analysis of titration data, *Biotechnol. Bioeng.*, 80, 806–811, doi:10.1002/bit.10432, 2002.
- Loiselle, S., Vione, D., Minero, C., Maurino, V., Tognazzi, A., Dattilo, A. M., Rossi, C., and Bracchini, L.: Chemical and optical phototransformation of dissolved organic matter, *Water Res.*, 46, 3197–3207, doi:10.1016/j.watres.2012.02.047, 2012.
- Matrai, P. A., Tranvik, L., Leck, C., and Knulst, J. C.: Are high Arctic surface microlayers a potential source of aerosol organic precursors?, *Mar. Chem.*, 108, 109–122, doi:10.1016/j.marchem.2007.11.001, 2008.
- Miller, W. L. and Zepp, R. G.: Photochemical production of dissolved inorganic carbon from terrestrial organic matter: significance to the oceanic organic carbon cycle, *Geophys. Res. Lett.*, 22, 417–420, doi:10.1029/94gl03344, 1995.
- Mopper, K. and Schultz, C. A.: Fluorescence as a possible tool for studying the nature and water column distribution of DOC components, *Mar. Chem.*, 41, 229–238, doi:10.1016/0304-4203(93)90124-7, 1993.
- Mostofa, K. G., Liu, C.-Q., Yoshioka, T., Vione, D., Zhang, Y., and Sakugawa, H.: Fluorescent dissolved organic matter in natural waters, in: *Photobiogeochemistry of Organic Matter*, edited by: Mostofa, K. M. G., Yoshioka, T., Mottaleb, A., and Vione, D., Environmental Science and Engineering, Springer, Berlin, Heidelberg, 429–559, 2013.
- Muller-Karger, F. E., Varela, R., Thunell, R., Luerssen, R., Hu, C., and Walsh, J. J.: The importance of continental margins in the global carbon cycle, *Geophys. Res. Lett.*, 32, L01602, doi:10.1029/2004GL021346, 2005.
- Murphy, K. R., Stedmon, C. A., Waite, T. D., and Ruiz, G. M.: Distinguishing between terrestrial and autochthonous organic matter sources in marine environments using fluorescence spectroscopy, *Mar. Chem.*, 108, 40–58, doi:10.1016/j.marchem.2007.10.003, 2008.
- Murphy, K. R., Stedmon, C. A., Graeber, D., and Bro, R.: Fluorescence spectroscopy and multi-way techniques. PARAFAC, *Anal. Methods*, 5, 6557–6566, doi:10.1039/c3ay41160e, 2013.

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Nelson, N. B. and Siegel, D. A.: The global distribution and dynamics of chromophoric dissolved organic matter, *Ann. Rev. Mar. Sci.*, 5, 447–476, doi:10.1146/annurev-marine-120710-100751, 2013.

Nieto-Cid, M., Álvarez-Salgado, X. A., Gago, J., and Pérez, F. F.: DOM fluorescence, a tracer for biogeochemical processes in a coastal upwelling system (NW Iberian Peninsula), *Mar. Ecol.-Prog. Ser.*, 297, 33–50, doi:10.3354/meps297033, 2005.

Ortega-Retuerta, E., Passow, U., Duarte, C. M., and Reche, I.: Effects of ultraviolet B radiation on (not so) transparent exopolymer particles, *Biogeosciences*, 6, 3071–3080, doi:10.5194/bg-6-3071-2009, 2009.

Paulmier, A. and Ruiz-Pino, D.: Oxygen minimum zones (OMZs) in the modern ocean, *Prog. Oceanogr.*, 80, 113–128, doi:10.1016/j.pocean.2008.08.001, 2009.

Paulmier, A., Ruiz-Pino, D., and Garçon, V.: The oxygen minimum zone (OMZ) off Chile as intense source of CO₂ and N₂O, *Cont. Shelf Res.*, 28, 2746–2756, doi:10.1016/j.csr.2008.09.012, 2008.

Paulmier, A., Ruiz-Pino, D., and Garçon, V.: CO₂ maximum in the oxygen minimum zone (OMZ), *Biogeosciences*, 8, 239–252, doi:10.5194/bg-8-239-2011, 2011.

Riebesell, U., Kortzinger, A., and Oschlies, A.: Sensitivities of marine carbon fluxes to ocean change, *P. Natl. Acad. Sci. USA*, 106, 20602–20609, doi:10.1073/pnas.0813291106, 2009.

Rosenberg, R., Arntz, W. E., de Flores, E. C., Flores, L. A., Carbajal, G., Finger, I., and Tarazona, J.: Benthos biomass and oxygen deficiency in the upwelling system off Peru, *J. Mar. Res.*, 41, 263–279, doi:10.1357/002224083788520153, 1983.

Santín, C., Yamashita, Y., Otero, X. L., Álvarez, M. Á., and Jaffé, R.: Characterizing humic substances from estuarine soils and sediments by excitation-emission matrix spectroscopy and parallel factor analysis, *Biogeochemistry*, 96, 131–147, doi:10.1007/s10533-009-9349-1, 2009.

Santos, A. L., Oliveira, V., Baptista, I., Henriques, I., Gomes, N. C., Almeida, A., Correia, A., and Cunha, A.: Effects of UV-B radiation on the structural and physiological diversity of bacterioneuston and bacterioplankton, *Appl. Environ. Microb.*, 78, 2066–2069, doi:10.1128/aem.06344-11, 2012.

Schneider-Zapp, K., Salter, M. E., Mann, P. J., and Upstill-Goddard, R. C.: Technical Note: Comparison of storage strategies of sea surface microlayer samples, *Biogeosciences*, 10, 4927–4936, doi:10.5194/bg-10-4927-2013, 2013.

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Senesi, N.: Molecular and quantitative aspects of the chemistry of fulvic acid and its interactions with metal ions and organic chemicals, *Anal. Chim. Acta*, 232, 77–106, doi:10.1016/S0003-2670(00)81226-X, 1990.

Senesi, N., Miano, T. M., Provenzano, M. R., and Brunetti, G.: Characterization, differentiation and classification of humic substances by fluorescence spectroscopy, *Soil Sci.*, 152, 259–271, 1991.

Shick, J. M. and Dunlap, W. C.: Mycosporine-like amino acids and related gadusols: biosynthesis, accumulation, and UV-protective functions in aquatic organisms, *Annu. Rev. Physiol.*, 64, 223–262, doi:10.1146/annurev.physiol.64.081501.155802, 2002.

Singh, S., D'Sa, E. J., and Swenson, E. M.: Chromophoric dissolved organic matter (CDOM) variability in Barataria Basin using excitation–emission matrix (EEM) fluorescence and parallel factor analysis (PARAFAC), *Sci. Total Environ.*, 408, 3211–3222, doi:10.1016/j.scitotenv.2010.03.044, 2010.

Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L.: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University Press, Cambridge, UK and New York, NY, USA, 2007.

Stedmon, C. A. and Bro, R.: Characterizing dissolved organic matter fluorescence with parallel factor analysis: a tutorial, *Limnol. Oceanogr.-Meth.*, 6, 572–579, 2008.

Stedmon, C. A. and Markager, S.: Resolving the variability in dissolved organic matter fluorescence in a temperate estuary and its catchment using PARAFAC analysis, *Limnol. Oceanogr.*, 50, 686–697, doi:10.4319/lo.2005.50.2.0686, 2005a.

Stedmon, C. A. and Markager, S.: Tracing the production and degradation of autochthonous fractions of dissolved organic matter by fluorescence analysis, *Limnol. Oceanogr.*, 50, 1415–1426, doi:10.4319/lo.2005.50.5.1415, 2005b.

Stedmon, C. A., Markager, S., Tranvik, L., Kronberg, L., Slätis, T., and Martinsen, W.: Photochemical production of ammonium and transformation of dissolved organic matter in the Baltic Sea, *Mar. Chem.*, 104, 227–240, doi:10.1016/j.marchem.2006.11.005, 2007.

Stramma, L., Johnson, G. C., Sprintall, J., and Mohrholz, V.: Expanding oxygen-minimum zones in the tropical oceans, *Science*, 320, 655–658, doi:10.1126/science.1153847, 2008.

Swan, C. M., Siegel, D. A., Nelson, N. B., Carlson, C. A., and Nasir, E.: Biogeochemical and hydrographic controls on chromophoric dissolved organic matter distribution in the Pacific Ocean, *Deep-Sea Res. Pt I*, 56, 2175–2192, doi:10.1016/j.dsr.2009.09.002, 2009.

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Tilstone, G. H., Airs, R. L., Vicente, V. M., Widdicombe, C., and Llewellyn, C.: High concentrations of mycosporine-like amino acids and colored dissolved organic matter in the sea surface microlayer off the Iberian Peninsula, *Limnol. Oceanogr.*, 55, 1835–1850, doi:10.4319/lo.2010.55.5.1835, 2010.

5 Van Blough, N.: Photochemistry in the Sea-Surface Microlayer. The Sea Surface and Global Change, Cambridge University Press, 2005.

Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R., and Mopper, K.: Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon, *Environ. Sci. Technol.*, 37, 4702–4708, doi:10.1021/es030360x, 2003.

10 Wurl, O. and Holmes, M.: The gelatinous nature of the sea-surface microlayer, *Mar. Chem.*, 110, 89–97, doi:10.1016/j.marchem.2008.02.009, 2008.

Yamashita, Y. and Jaffé, R.: Characterizing the interactions between trace metals and dissolved organic matter using excitation – emission matrix and parallel factor analysis, *Environ. Sci. Technol.*, 42, 7374–7379, doi:10.1021/es801357h, 2008.

15 Yamashita, Y. and Tanoue, E.: Chemical characterization of protein-like fluorophores in DOM in relation to aromatic amino acids, *Mar. Chem.*, 82, 255–271, doi:10.1016/s0304-4203(03)00073-2, 2003.

Yamashita, Y., Jaffé, R., Maie, N., and Tanoue, E.: Assessing the dynamics of dissolved organic matter (DOM) in coastal environments by excitation emission matrix fluorescence and parallel factor analysis (EEM-PARAFAC), *Limnol. Oceanogr.*, 53, 1900–1908, 2008.

20 Yamashita, Y., Cory, R. M., Nishioka, J., Kuma, K., Tanoue, E., and Jaffé, R.: Fluorescence characteristics of dissolved organic matter in the deep waters of the Okhotsk Sea and the northwestern North Pacific Ocean, *Deep-Sea Res. Pt II*, 57, 1478–1485, doi:10.1016/j.dsr2.2010.02.016, 2010.

25 Zhang, J. and Yang, G.: Chemical properties of colored dissolved organic matter in the sea-surface microlayer and subsurface water of Jiaozhou Bay, China in autumn and winter, *Acta Oceanol. Sin.*, 32, 26–39, doi:10.1007/s13131-013-0306-4, 2013.

30 Zhang, Z., Liu, L., Wu, Z., Li, J., and Ding, H.: Physicochemical studies of the sea surface microlayer: I. Thickness of the sea surface microlayer and its experimental determination, *J. Colloid Interf. Sci.*, 204, 294–299, doi:10.1006/jcis.1998.5538, 1998.

Zsolnay, A., Baigar, E., Jimenez, M., Steinweg, B., and Saccomandi, F.: Differentiating with fluorescence spectroscopy the sources of dissolved organic matter in soils subjected to drying, Chemosphere, 38, 45–50, doi:10.1016/S0045-6535(98)00166-0, 1999.

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Table 1. “Revisited Stations” metadata with date, local and UTC time of sampling, coordinates, and average global radiation retrieved from Dship data server of R/V *Meteor*.

Station ID	Ship Nr.	Station nr.	Samples	Date	Time [UTC]	Time [Local]	Lat, S [°]	Long, W [°]	Average Global Radiation [Wm ⁻²]
1733–5	1	S7	sml/ulw	08 Dec 2012	11:30	6:30	9°31.258'	79°17.886'	10
1733–9		S7_2	sml/ulw	08 Dec 2012	19:45	14:45	9°32.75'	79°18.43'	837
1752–2	2	S12_1	sml/ulw	13 Dec 2012	12:00	7:00	12°55.20'	78°42.00'	380.5
1752–7		S12_2	sml/ulw	13 Dec 2012	20:30	15:30	12°59.79'	78°41.00'	704.5
1752–9		S12_3	sml/ulw	13 Dec 2012	23:10	18:10	12°55.20'	78°42.03'	47
1764–4	3	S16_1	sml/ulw	17 Dec 2012	12:40	7:40	14°7.708'	76°52.759'	381
1764–6		S16_2	sml/ulw	17 Dec 2012	17:40	12:40	14°11.11'	76°55.95'	1043
1764–9		S16_3	sml/ulw	17 Dec 2012	22:00	17:00	14°11.10'	76°55.99'	161.5
1777–2	4	S20	sml/ulw	22 Dec 2012	18:00	13:00	15°31.174'	75°36.015'	1088
1777–10		S20_2	sml/ulw	23 Dec 2012	15:00	10:00	15°36.42'	75°38.60'	1046

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Table 2. Fluorescent components identified in this study in both SML and ULW samples, according to their Ex/Em maxima ranges (nm), maximum fluorescence intensity range Fmax (R.U.), corresponding peaks individuated in previous studies (peak name, region, Ex/Em ranges) and properties.

Components of this study	Ex/Em maxima [nm]	Fmax range [R.U.]	Literature peak name (region, Ex/Em)	Reference	Properties
F1	250–290/ 320–350	0.001–0.228	(T) (275/340)	A	Protein-like fluorescence of tryptophan Autochthonous material. Source: in situ primary production.
			6(B) (280/338)	B	Protein-like fluorescence of tryptophan, autochthonous material. Source: algal growth. Sink: microbial reworking, UVB.
			T (280–285/340–350)	C	Protein-like, extracted from EPS.
F2	250–260/500–520	0.048–1.709	2(A) (250/504)	D	Fulvic acid C-like allochthonous material present in all environments. Terrestrial/autochthonous fulvic acid fluorophore group.
			1(A) (250/520)	E	Fulvic acid C-like, Bay waters, allochthonous.
			2(A) (< 260/ > 500)	F	Humic Acid C-like, river and coastal waters, allochthonous. Terrestrial humic.
			1(A) (< 230–260/400–500)	G	Small sized molecules, photoresistant and biologically not available. Source: photochemistry, terrestrially derived humic acids in marine waters, highest concentrations near the water surface.
			2(A?) (250/504)	H	UVA humic-like, fulvic acid, terrestrial, autochthonous.
			C2(–) (256/> 500)	I	Humic acid C-like, estuaries of the Iberian peninsula, allochthonous.
F3	265/520–540	0.019–1.640	2(A+C) (< 240–275/434–520)	G	Larger molecules, hydrophobic compounds, photodegradable by UVA light. Source: terrestrial or microbial, intermediate inputs of minimal exposure to sunlight, biologically degraded and produced.
			C1 (~ 275/400–550)	L	Humic-like CDOM microbially produced.
			1(A/C) (< 260/466)	O	Humic-like CDOM oxidized in situ by microbial processes.

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Table 2. Continued.

Components of this study	Ex/Em maxima [nm]	Fmax range [R.U.]	Literature peak name (region, Ex/Em)	Reference	Properties
F4	250–265/284–320	0.002–6.507	(T) (275/300)	J	Protein-like fluorescence of tyrosine. Autochthonous material. Source: in situ primary production, North Pacific and Atlantic Ocean.
			(B) (275/310)	A	Tyrosine-like, marine waters, autochthonous.
			C(T) (270–290/250–365)	K	Autochthonous protein-like hydrophobic acid fraction from phytoplankton cultures.
			C3(T)	L	Protein-like fluorescence of phenylalanine.
			Standard (255–265/284–285)	M	Protein-like fluorescence of phenylalanine. Source: standard.
F5	270–275/540–550	0.023–1.714	(B) (265–280/293–313)	M	Protein-like fluorescence of tyrosine. Source: autochthonous.
			(A,C) (< 260–270/> 508)	N	Humic acid C-like or A-like, allochthonous material in bay and marine waters.

References:

- A: Coble, 1996, Marine Chemistry 51:325–346
 B: Stedmon and Markager, 2005b, Limnology and Oceanography 50(5):1415–1426
 C: Liu and Fang 2002, Biotechnology and Bioengineering 80(7):806–811
 D: Stedmon and Markager, 2005a, Limnology and Oceanography 50(2):686–697
 E: Singh et al., 2010, Science of The Total Environment 408(16):3211–3222
 F: Yamashita and Jaffé, 2008, Environmental Science and Technology 42:7374–7379
 G: Ishii et al., 2012, Environmental Science and Technology 46:2006–2017
 H: Coble, 2007, Chemical Reviews 107(2):402:418
 I: Santin et al., 2009, Biogeochemistry (2009) 96:131–147
 J: Murphy et al., 2008, Marine Chemistry 108 (1–2):40–58
 K: Aoki et al., 2008, Analytical Sciences 24(11):1461–1467
 L: Jørgensen et al., 2011, Marine Chemistry 126:139–148
 M: Yamashita and Tanoue, 2003, Marine Chemistry 82:255–271
 N: Mostofa et al., 2013, in: Photobiogeochemistry of Organic Matter, Edited by Mostofa, K.M.G. Liu, C., Yoshioka, T., Vione, D., Zhang, Y., Sakugawa H., Springer Berlin Heidelberg, pp:429–559
 O: Yamashita et al., 2010, Deep Sea Research II 57: 1478–1485

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Table 3. Spearman Rank Order Correlation coefficients (C) between fluorescent components (F1–5) and total bacterial and phytoplankton cells, TEP and CSP particles, $SUVA_{254}$, $S(275-295)$, SR, $a(325)$, DHAA%-DOC, HIX, salinity and temperature measured in our study, both in the SML and ULW. Statistical significance was accepted for $p < 0.05$. n = number of samples. Only statistically significant correlations are shown. Bold characters indicate negative correlations.

Component [R.U.]	Statistics	Bacteria [cells mL^{-1}]	Phytoplankton [cells mL^{-1}]	TEP [L^{-1}]	CSP [L^{-1}]	$SUVA_{254}$ [mg C $L^{-1} m^{-1}$]	$S(275-295)$ [nm^{-1}]	SR	$a(325)$ [m^{-1}]	DHAA%-DOC [%]	HIX	Salinity [psu]	Temperature [$^{\circ}C$]
F1	C	–	0.33	0.30	0.24	0.64	–0.29	–0.39	0.44	0.40	–0.33	–0.24	–0.35
	p		0.012	0.01	0.04	< 0.001	0.01	<0.001	< 0.001	< 0.001	0.003	0.02	0.002
	n		57	76	76	76	76	75	76	76	76	76	76
F2	C	0.38	–	–	–	–	–	–	–	–	–	–	0.25
	p	0.001											0.03
	n	71											76
F3	C	0.35	–	–	0.41	0.29	–	–	–	–	–	–	–
	p	0.003			< 0.001	0.01							
	n	71			76	76							
F4	C	–0.43	–	–	–	–	–	–0.42	–	–	–0.55	–	–
	p	0.001						0.001			<0.001		
	n	52						56			57		
F5	C	0.27	–	–	0.41	–	–	–	–	–	–	–	–
	p	0.02			< 0.001								
	n	71			76								

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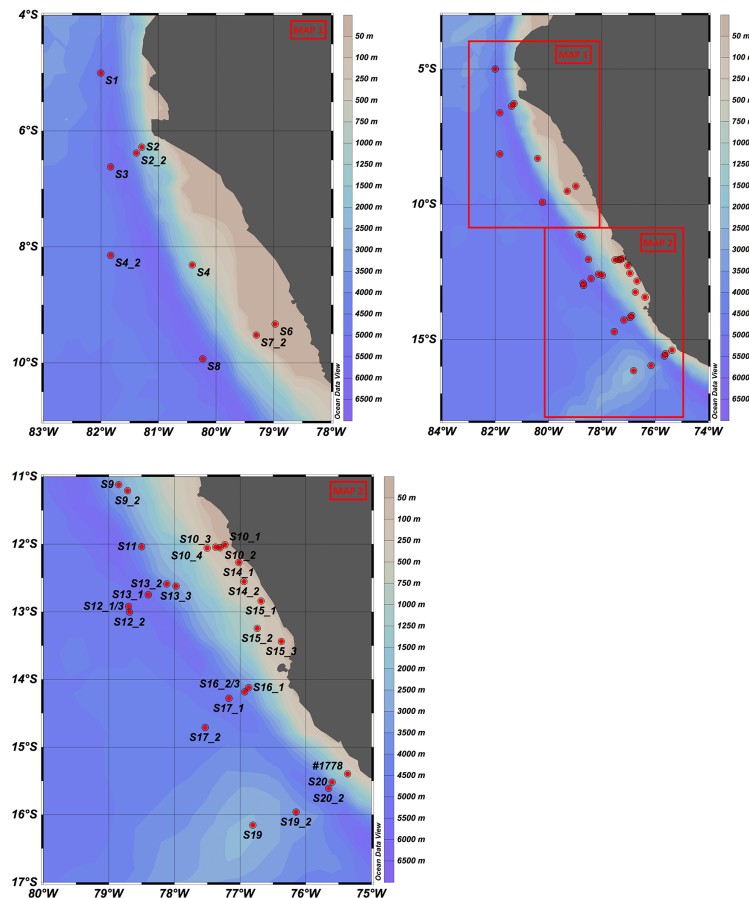


Figure 1. Maps showing all sampled stations. Revisited stations are: (1) S7 and S7_2, (2) S12_1/3 and S12_3, (3) S16_1, S16_2/3, (4) S20 and S20_2.

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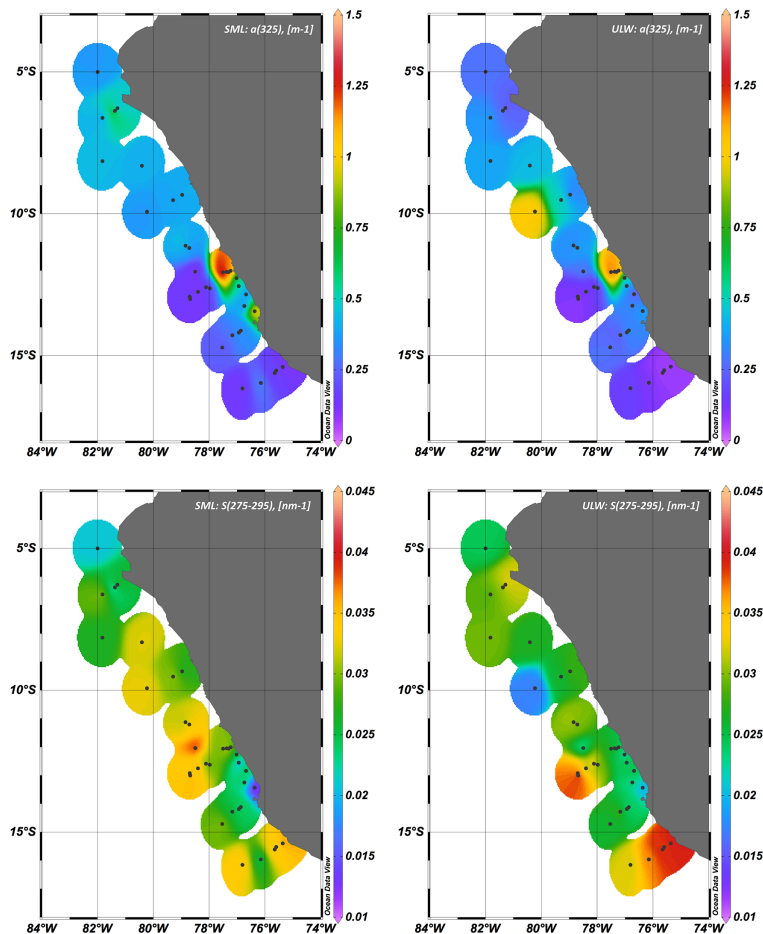


Figure 2. CDOM concentration in SML and underlying water (ULW) expressed as $a(325)$, [m^{-1}], and spectral slope parameter between 275 and 295 nm, $S(275-295)$, [nm^{-1}].

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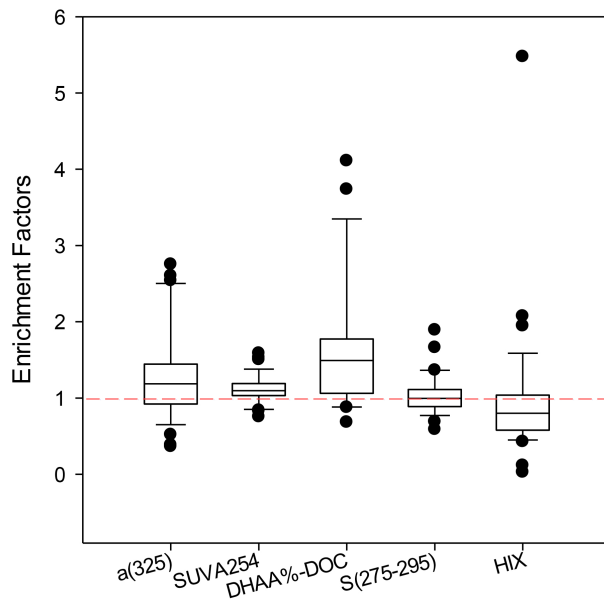


Figure 3. Enrichment factors (EF) for optical indicators for CDOM concentration ($a(325)$), aromaticity ($SUVA_{254}$, Specific Ultraviolet Absorbance of DOC measured at 254 nm), diagenetic state (DHAA%-DOC), source and molecular weight as derived from the spectral slope ($S(275-295)$), and humification index (HIX). The dashed red line at EF = 1 indicates equal values for SML and underlying water.

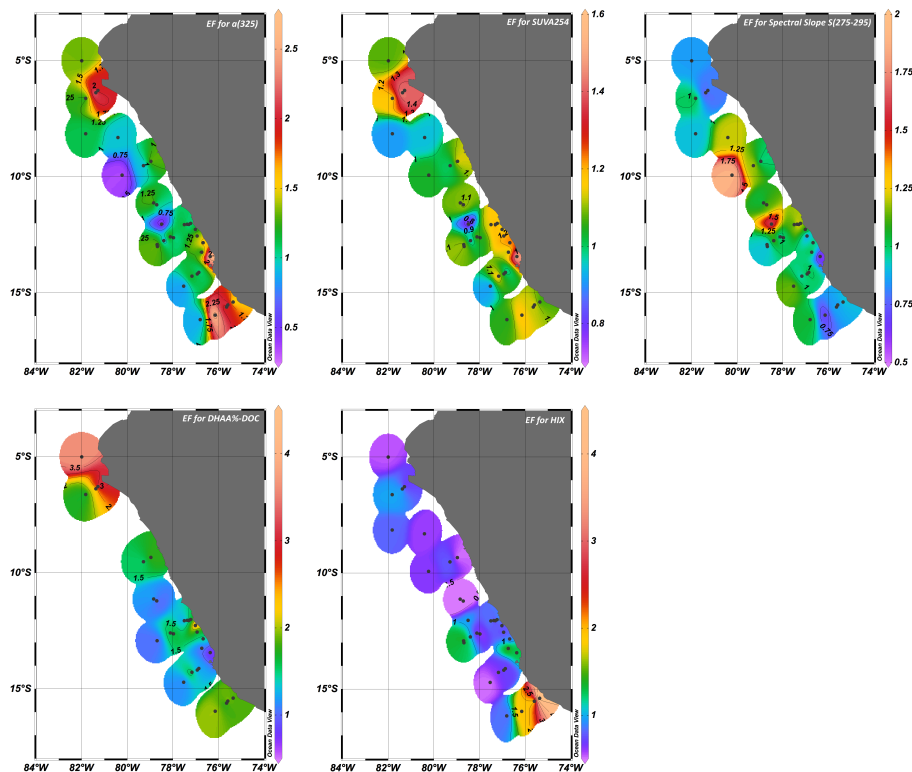


Figure 4. Enrichment factors (EF) in the Peruvian upwelling region. From the top left, EF for absorption coefficient measured at 325 nm both in SML and ULW, spectral slope parameter $S(275-295)$ as indicator for changes in DOM molecular weight, $SUVA_{254}$ as indicator for DOM aromatic content, DHAA%-DOC as indicator of DOM lability, and HIX as indicator of humic content of DOM.

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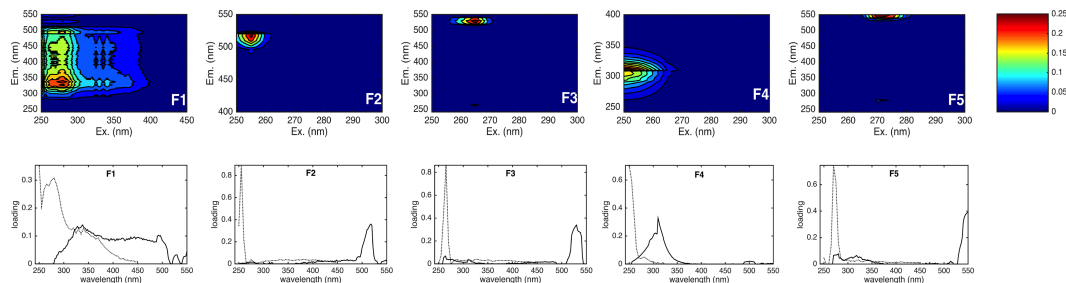


Figure 5. Contour plots of five fluorescent components as identified by PARAFAC analysis and (below) relative spectral loadings. The axes of contour plots have been scaled to better visualize the fluorescence intensities (R.U.). A figure with the complete spectrum is included in the supplementary material. The dashed black line in the spectral loadings indicates excitation maxima for each component, the solid black line indicates emission peaks.

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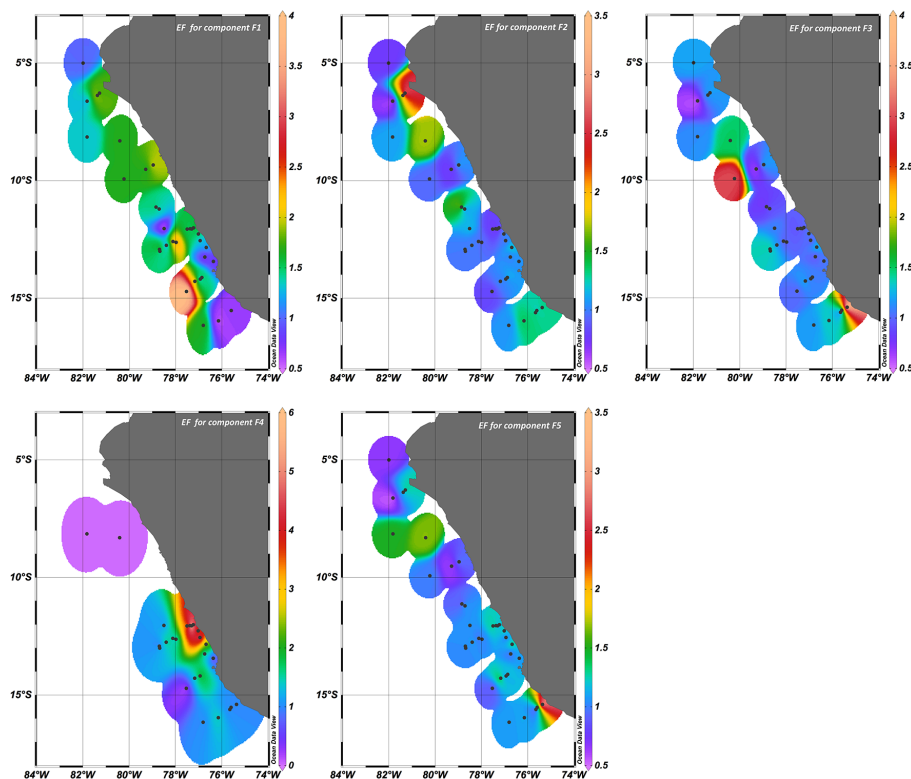


Figure 6. Distribution of enrichment factors (EF) for fluorescent components F1, F2, F3, F4, F5 identified in this study. Maximum EF for F4 has been recorded at station S10_2, with a value of 14.9. For visualization purposes, this data point is not included in the figure and fluorescence intensities have been scaled down to a maximum EF = 6.

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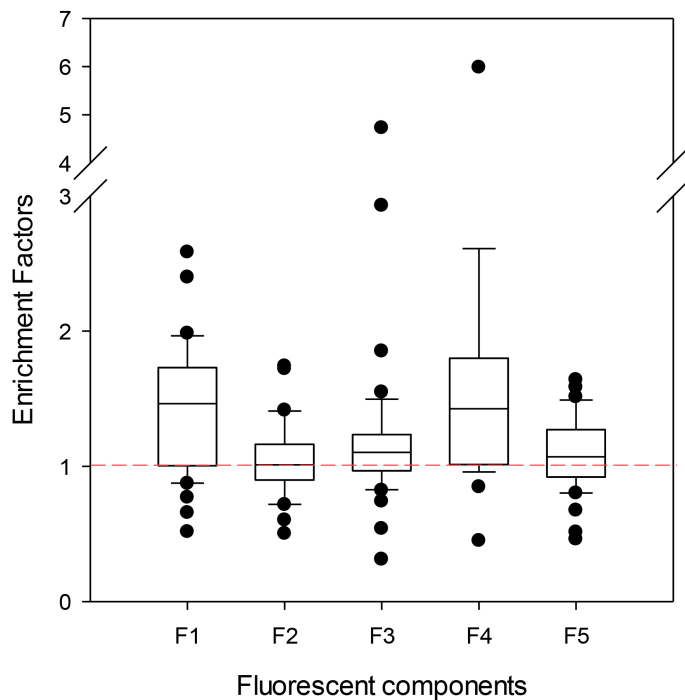


Figure 7. Enrichment factors for fluorescent components F1, F2, F3, F4, F5 identified in this study.

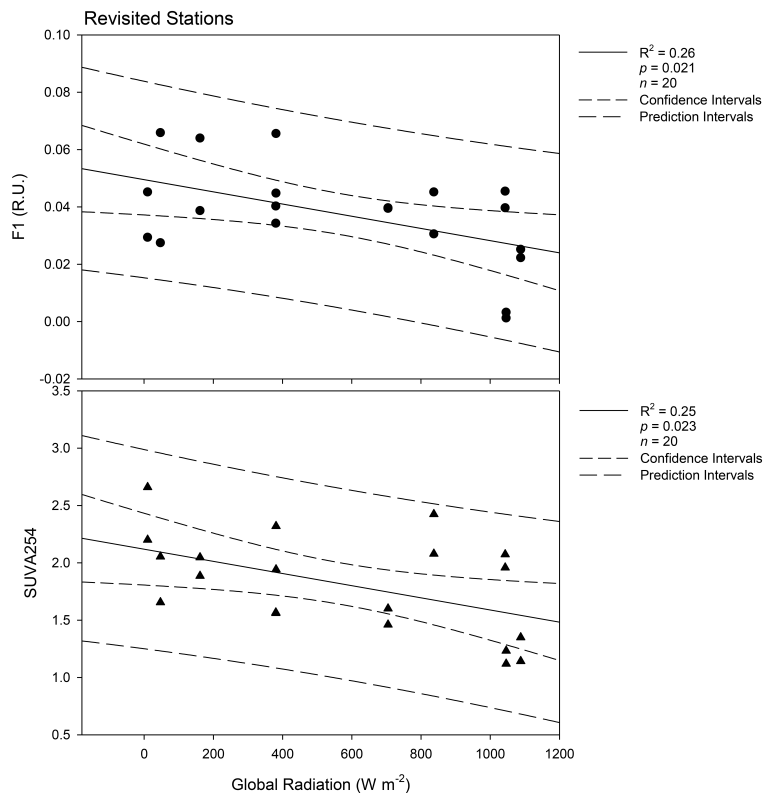


Figure 8. Linear regression of component F1 and SUVA₂₅₄ in SML and ULW samples vs. global radiation as determined on revisited stations (S7 and S7_2, S12_1/3 and S12_3, S16_1 and S16_2/3, S20 and S20_2).

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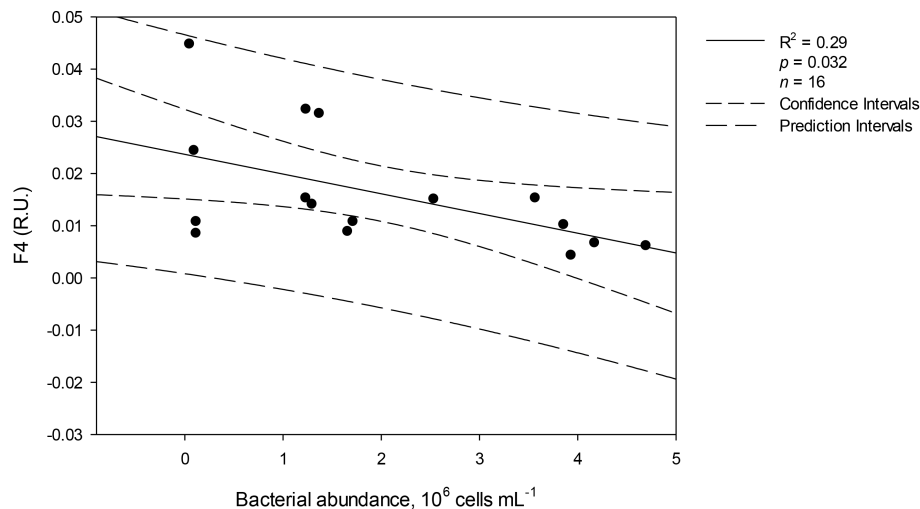


Figure 9. Linear regression of component F4 in SML and ULW samples vs. bacteria abundance as determined on revisited stations (S7 and S7_2, S12_1/3 and S12_3, S16_1 and S16_2/3, S20 and S20_2).

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Changes in optical characteristics of surface microlayers

L. Galgani and A. Engel

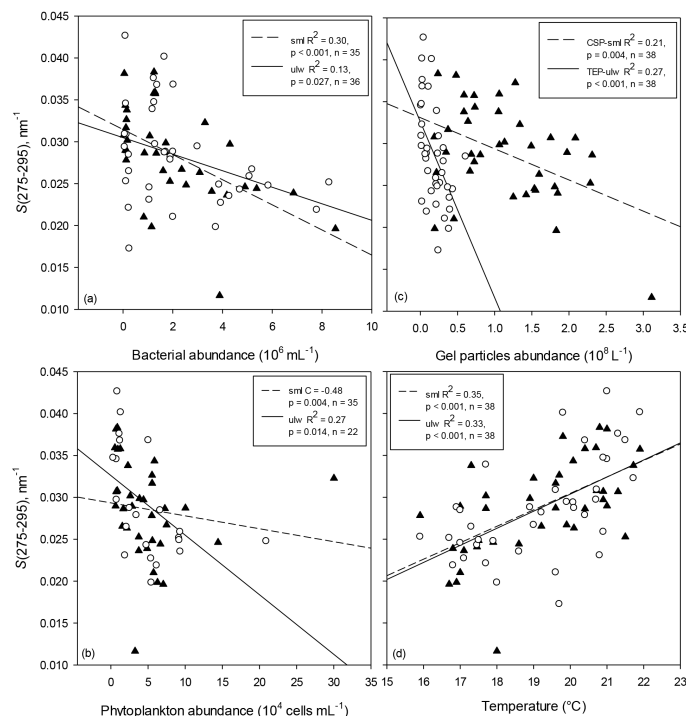


Figure 10. (a) Linear regression between bacterial abundance [$10^6 \text{ cells mL}^{-1}$] and spectral slope $S(275-295)$ [nm^{-1}] in SML and ULW. (b) Linear regression (ULW) and Spearman Rank Order Correlation (SML) between phytoplankton abundance [$10^4 \text{ cells mL}^{-1}$] and spectral slope $S(275-295)$ [nm^{-1}]. (c) Linear regression between CSP abundance [$10^8 \text{ particles L}^{-1}$] and spectral slope $S(275-295)$ [nm^{-1}] in the SML and between TEP abundance [$10^8 \text{ particles L}^{-1}$] and spectral slope $S(275-295)$ [nm^{-1}] in the ULW. (d) Linear regression between temperature [$^{\circ}\text{C}$] and $S(275-295)$ [nm^{-1}] in SML and ULW. Black triangles: SML, open dots: ULW.

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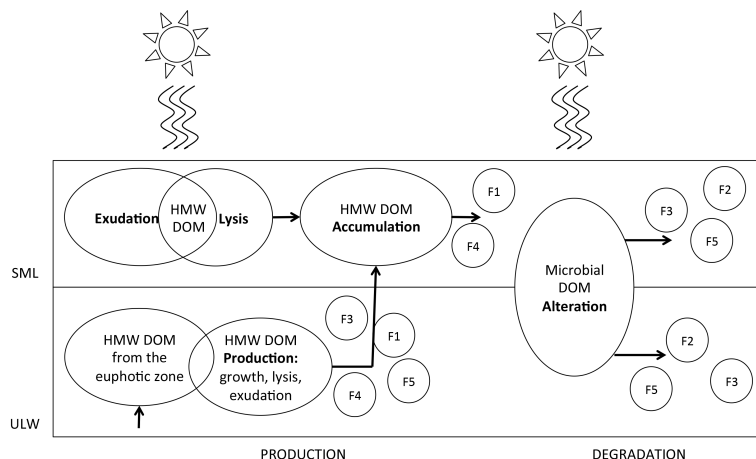


Figure 11. Conceptual model of the sources and modifications of optically active DOM in the surface microlayer (SML) and underlying seawater (ULW). The production of HMW DOM by microbial release through growth, exudation and lysis in the euphotic zone, characterized by nutrient-rich waters may lead to an accumulation of organic material in the SML as also described by the general SML enrichment in gel particles and amino acids (Engel and Galgani, 2015). The fluorophores identified (F1, F2, F3, F4, F5) contribute to the organic pool. Specific amino-acid like fluorophores (F1, F4) can accumulate in the SML with respect to the ULW. Photochemistry may enhance microbial DOM release by a) photoprotection mechanisms and b) cell-lysis processes. In SML and ULW, microbial and photochemical DOM degradation are potential sinks of the amino-acid like fluorophores (F1, F4), and potential sources of reworked DOM and more refractory humic-like components (F2, F3, F5).

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