The organic sea surface microlayer in the upwelling region off Peru and potential implications for air-sea exchange processes

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Abstract: The sea surface microlayer (SML) is at the very surface of the ocean, linking the hydrosphere with the atmosphere. The presence and enrichment of organic compounds in the SML have been suggested to influence air-sea gas exchange processes as well as the emission of primary organic aerosols. Here, we report on organic matter components collected from an approximately 50µm thick SML and from the underlying water (ULW), ~20 cm below the SML, in December 2012 during the SOPRAN METEOR 91 cruise to the highly productive, coastal upwelling regime off Peru. Samples were collected at 37 stations including coastal upwelling sites and off-shore stations with less organic matter and were analyzed for total and dissolved high molecular weight (>1kDa) combined carbohydrates (TCCHO, DCCHO), free amino acids (FAA), total and dissolved hydrolysable amino acids (THAA, DHAA), transparent exopolymer particles (TEP), Coomassie stainable particles (CSP), total and dissolved organic carbon (TOC, DOC), total and dissolved nitrogen (TN, TDN), as well as bacterial and phytoplankton abundance. Our results showed a close coupling between organic matter concentrations in the water column and in the SML for almost all components except for FAA and DHAA that showed highest enrichment in the SML on average. Accumulation of gel particles, i.e. TEP and CSP, in the SML differed spatially. While CSP abundance in the SML was not related to wind speed, TEP abundance decreased with wind speed, leading to a depletion of TEP in the SML at about 5 m s^{-1}. Our study provides insight to the physical and biological control of organic matter enrichment in the SML, and discusses the potential role of organic matter in the SML for air-sea exchange processes.

1. Introduction

The sea-surface microlayer (SML) is the uppermost layer of the water-column and the interface between the ocean and the atmosphere. The accumulation of organic matter, distinct physical and chemical properties and a specific organismal community (neuston) distinguish the SML as a unique biogeochemical and ecological system. It has been suggested that the SML has a gel-like nature (Cunliffe and Murrell, 2009; Sieburth, 1983) of varying thickness (20-150 µm, Cunliffe et al., 2013) with dissolved polymeric carbohydrates and amino acids present as well as gel particles, such as transparent exopolymer particles (TEP) of polysaccharidic composition, and Coomassie stainable particles (CSP) of proteinaceous composition. These gelatinous compounds originate from high molecular weight polymers that are released form phytoplankton and bacterial cells by exudation and cell break up (Chin et al., 1998; Engel et al., 2004; Verdugo et al., 2004). Polysaccharide-rich gels, like TEP, were attributed mainly to phytoplankton exudation (Passow, 2002), while the production of protein-containing gels, such as CSP, has been related to cell lysis and decomposition, as well as to the absorption of proteins onto non-proteinaceous particles (Long and Azam, 1996). Gels are transported to the SML by rising bubbles (Azetsu-Scott and Passow, 2004; Zhou et al., 1998) or are produced from dissolved precursors directly at the air-sea interface during surface wave action (Wurl et al., 2011). Gel particles can promote microbial biofilm formation (Bar-Zeev et al., 2012) and mediate vertical organic matter transport, either to the atmosphere (Leck and Bigg, 2005; Orellana et al., 2011) or to the deep ocean (Passow, 2002).

Accumulation of organic matter in the SML may be tightly coupled to phytoplankton abundance in the water-column (Bigg et al., 2004; Galgani et al., 2014; Gao et al., 2012; Matrai et al., 2008).

Thus, organic matter accumulation and composition in the SML may also reflect the sensitivity of marine microorganisms in the surface ocean to environmental changes, which was shown during previous mesocosms studies (Engel et al., 2013; Riebesell et al., 2009; Schulz et al., 2013). Distinct from the SML and on top of it lies the nanolayer, a monomolecular film, which, like the SML, shows seasonality features with carbohydrate-rich polymeric material being most abundant during the summer months and possibly related to a combination of primary production (phytoplankton abundance) and photochemical and/or microbial reworking of organic matter (Laß et al., 2013).

In our study we focused on the upper micrometers of the water-air interface that we operationally defined as SML, whose compositional changes and accumulation of organic matter may influence two air-sea interface processes necessary to understand oceanic feedbacks on the atmosphere: sea-spray aerosol (SSA) emission and air-sea gas exchange (Cunliffe et al., 2013). During biologically productive periods, a high amount of SSA with a predominant organic composition is emitted from the ocean's surface (O'Dowd et al., 2004). These compounds primarily reveal a polysaccharidic, gel-like composition, suggesting that the abundance and size of dissolved polysaccharides and marine gels in the sea surface may influence the organic fraction of SSA (Orellana et al., 2011; Russell et al., 2010). It has also been shown that the presence of biogenic surface active substances (surfactants) in the SML leads to capillary wave damping and alter the molecular diffusion of gases (Frew et al., 1990; Liss and Duce, 2005) and therewith affects gas exchange rates particularly at lower wind speed (Jähne and Haußecker, 1998). In this respect, the understanding of sources, composition and fate of biological components in the surface layer becomes of particular relevance for environments, where biological productivity is high like in coastal upwelling regimes.

Off Peru, the coastal upwelling region extends between approximately 4°S and 40°S. In this area, upwelling processes are sustained by winds throughout the year but feature high inter-annual variability induced by the El Niño-Southern Oscillation (ENSO) cycle (Tarazona and Arntz, 2001). Eastern Boundary Upwelling Systems (EBUS's) like the system off Peru are characterized by high biological productivity supported by deep upwelling of nutrients and often associated with subsurface Oxygen Minimum Zones (OMZ's). The supply of oxygen to the OMZ is largely controlled by physical, i.e. diffusive and advective, mechanisms, whereas biological processes, i.e. respiration of organic matter, provide sinks (Lachkar and Gruber, 2011).

OMZ's are significant source regions for major climate relevant gases such as carbon dioxide, methane, hydrogen sulfide and nitrous oxide (Paulmier et al., 2008; Paulmier et al., 2011). Processes affecting gas exchange in these regions need to be understood in order to accurately estimate trace gas fluxes from the ocean to the atmosphere and consequences on climate. In 2008, the VAMOS Ocean-Cloud-Atmosphere-Land Study Regional Experiment (VOCALS-REx) and the Chilean Upwelling Experiment (VOCALS-CUpEx) conducted between Southern Peru and Northern Chile focused on the link between aerosols, clouds and precipitation as well as on physical and chemical couplings between the upper ocean and the lower atmosphere (Garreaud et al., 2011; Wood et al., 2011). During the SOPRAN cruise METEOR91 (M91), we studied organic matter components at the very sea surface since properties of the SML may represent a major uncertainty for gas, heat and aerosol fluxes in this specific region and in other oceanic environments. During our cruise, organic matter concentration and composition of the SML and the underlying seawater were studied on 37 different stations, providing the first SML data-set for the upwelling system off Peru, including the first data-set on gel particles in EBU's so far.

2. Material and Methods

2.1. Field information and sampling

The *R*/V METEOR cruise M91 studied the upwelling region off Peru (Bange, 2013). Samples were collected between 4.59° S and 82.0°W, and 15.4°S and 77.5°W from December 03 to 23 in 2012. The overall goal of M91 was to conduct an integrated biogeochemical study on the upwelling region off Peru in order to assess the importance of OMZ's for the sea-air exchange of various climate-relevant trace gases and for tropospheric chemistry. Salinity and temperature were measured with a CTD at each station. Global and UV radiation and wind speed data were retrieved from the DShip database for the time of sampling based on the sensors installed on board.

On 37 different stations between 5°S and 16°S off the Peruvian coast (Figure 1), a total of 39 SML samples was collected from a rubber boat using a glass plate sampler according to the original approach described by Harvey and Burzell (1972). Different methods have been developed to sample and investigate the SML. These methods do not only differ in terms of application but also with respect to the thickness of the SML sampled as well as to selective removal of certain components. Several studies evaluated these methods against each other. A recent summary can be found in the 'Guide to best practices to study the ocean's surface' (Cunliffe and Wurl, 2014). During this study, we applied the glass plate technique because it allows for sampling of a relatively large volume needed to analyze different organic components while keeping the simultaneous sampling of ULW minimal. Two stations were sampled twice in a time frame of 24 hours (stations 12_1 and 12_3, 16_2 and 16_3). Our glass plate with the dimensions of 500 mm (length) x 250 mm (width) x 5 mm (thickness) was made of borosilicate glass and had an effective sampling surface area of 2000 cm^2 (considering both sides). For each sample, the glass plate was inserted into the water perpendicular to the surface and withdrawn

143 slowly at a rate of approximately 20 cm sec^{-1}. The sample, retained on the glass because of
144 surface tension, was removed with the help of a Teflon wiper. Samples were collected as far
145 upwind of the ship as possible and away from the path taken by the ship to avoid contamination.
146 For each sample the glass plate was dipped and wiped about twenty times. The exact number of
147 dips and the total volume collected were recorded. Samples were collected into acid cleaned
148 (HCl, 10%) and Milli-Q washed glass bottles, and the first milliliters were used to rinse the
149 bottles and then discarded. Prior to each sampling, both glass plate and wiper were washed with
150 HCl (10%) and intensively rinsed with Milli-Q water. At the sampling site, both instruments were
151 copiously rinsed with seawater in order to minimize any possible contamination with alien
152 material while handling or transporting the devices.
153 The apparent thickness (d) of the layer sampled with the glass plate was determined as follows:

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

155 Where V is the SML volume collected, i.e. 60-140 mL, A is the sampling area of the glass plate
156 (A = 2000 cm^2) and n is the number of dips (Cunliffe and Wurl, 2014). We will use d (µm) as an
157 operational estimate for the thickness of the SML.
158 At the same stations, after sampling the SML, about 500 mL samples were collected from the
159 underlying seawater (ULW) at ~ 20 cm depth by holding an acid cleaned (HCl 10%) and Milli-Q
160 rinsed borosilicate glass bottle. The bottle was open and closed underwater to avoid simultaneous
161 sampling of SML water. For safety reasons sampling for the SML from a rubber boat could be
162 made only during daylight hours.
163

164 **2.2 Chemical and biological analyses**

165 **2.2.1. Total organic carbon (TOC) and dissolved organic carbon (DOC)**

Samples for TOC and DOC (20 ml) were collected in combusted glass ampoules, DOC after filtration through combusted GF/F filters (8 hours, 500º C). Samples were acidified with 80 µL of 85% phosphoric acid, heat sealed immediately, and stored at 4°C in the dark until analysis. DOC and TOC samples were analyzed by applying the high-temperature catalytic oxidation method (TOC -VCSH, Shimadzu) modified from Sugimura and Suzuki (1988). The instrument was calibrated every 8-10 days by measuring standard solutions of 0, 500, 1000, 1500, 2500 and 5000 µg C L^{-1}, prepared from a potassium hydrogen phthalate standard (Merck 109017). Every measurement day, ultrapure (MilliQ) water was used to determine the instrument blank, which was accepted for values <1 µmol C L^{-1}. TOC analysis was validated on every measurement day with deep seawater reference (DSR) material provided by the Consensus Reference Materials Project of RSMAS (University of Miami) yielding values within the certified range of 42-45 µmol C L^{-1}. Additionally, two internal standards with DOC within the range of those in samples were prepared each measurement day using a potassium hydrogen phthalate (Merck 109017). DOC and TOC concentration was determined in each sample from 5 to 8 injections. The precision was <4% estimated as the standard deviation of replicate measurements divided by the mean. Particulate organic carbon (POC) was determined as the difference between TOC and DOC.

2.2.2. Total nitrogen (TN) and total dissolved nitrogen (TDN)

TN and TDN were determined simultaneously with TOC and DOC, respectively, using the TNM-1 detector on the Shimadzu analyzer. Nitrogen in the samples is combusted and converted to NOx, which chemiluminesces when mixed with ozone and can be detected using a photomultiplier (Dickson et al., 2007). Calibration of the instrument was done every 8-10 days by measuring standard solutions of 0, 100, 250, 500 and 800 µg N L^{-1}, prepared with potassium nitrate Suprapur® (Merck 105065). Particulate nitrogen (PN) was determined as the difference

between TN and TDN. Deep seawater reference (DSR) material provided by the Consensus Reference Materials Project of RSMAS (University of Miami) was used on every measurement day and yielded values within the certified range of 31-33 µmol N L^{-1}. The precision was <2% estimated as the standard deviation of 5-8 measurements divided by the mean.

2.2.3. Total, dissolved and free amino acids

For total hydrolysable amino acids (THAA), 5 mL of sample were filled into pre-combusted glass vials (8 hours, 500°C) and stored at –20 °C until analysis. Samples for dissolved hydrolysable (DHAA) and free amino acids (FAA) were additionally filtered through 0.45 µm Millipore Acrodisc® syringe filters and then stored in the same way as samples for THAA. Analysis was performed according to Lindroth & Mopper (1979) and Dittmar et al. (2009) with some modifications. Duplicate samples were hydrolyzed for 20h at 100°C with hydrochloric acid (suprapur, Merck) and neutralized by acid evaporation under vacuum in a microwave at 60°C. Samples were washed with water to remove remaining acid. Analysis was performed on a 1260 HPLC system (Agilent). Thirteen different amino acids were separated with a C18 column (Phenomenex Kinetex, 2.6 µm, 150 x 4.6 mm) after in-line derivatization with o-phtaldialdehyde and mercaptoethanol. The following standard amino acids were used: aspartic acid (AsX), glutamic acid (GlX), serine (Ser), arginine (Arg), glycine (Gly), threonine (Thr), alanine (Ala), tyrosine (Tyr), valine (Val), phenylalanine (Phe), isoleucine (Ileu), leucine (Leu), γ- amino butyric acid (GABA). α- amino butyric acid was used as an internal standard to account for losses during handling. Solvent A was 5% acetonitrile (LiChrosolv, Merck, HPLC gradient grade) in sodium-di-hydrogen-phosphate (Merck, suprapur) Buffer (PH 7.0). Solvent B was acetonitrile. A gradient was run from 100% solvent A to 78% solvent A in 50 minutes. FAA were determined from DHAA samples without prior hydrolysis in separate analyses. Particulate

hydrolysable amino acids (PHAA) were determined by subtracting DHAA from THAA. The detection limit for individual amino acids was 2 nmol monomer L^{-1}. The precision was <5%, estimated as the standard deviation of replicate measurements divided by the mean.

2.2.4. Total and dissolved combined carbohydrates

For total and dissolved combined carbohydrates > 1 kDa (TCCHO and DCCHO), 20 mL were filled into pre-combusted glass vials (8 hours, 500 °C) and kept frozen at -20 °C until analysis. Samples for DCCHO were additionally filtered through 0.45 µm Pall Acrodisc® syringe filters. The analysis was conducted according to Engel and Händel (2011) applying high performance anion exchange chromatography coupled with pulsed amperometric detection (HPAEC-PAD) on a Dionex ICS 3000. Samples were desalinated by membrane dialysis (1 kDa MWCO, Spectra Por) for 5 h at 1 °C, hydrolyzed for 20 h at 100°C with 0.4 M HCl final concentration, and neutralized through acid evaporation under vacuum and nitrogen atmosphere (1h, 60 °C) Two replicate samples were analyzed. The retention of carbohydrates on exchange columns, and thus the reproducibility of results are highly sensitive to changes in temperature (Panagiotopoulos et al., 2001; Yu and Mou, 2006). For our system, best resolution of sugars was obtained at 25 °C and therefore applied constantly during all analyses. In order to minimize degradation of samples before analysis, the temperature in the auto-sampler was kept at 4 °C. The system was calibrated with a mixed sugar standard solution including a) the neutral sugars: fucose (4.6 µM, Fuc), rhamnose (3.1 µM, Rha), arabinose (2.0 µM, Ara), galactose (2.4 µM, Gal), xylose/ mannose (3.1 µM, Xyl/ Man), glucose (2.4 µM, Glc), b) the amino sugars: galactosamine (2.0 µM, GalN), glucosamine (2.8 µM, GlcN), and c) the acidic sugars: galacturonic acid (2.8 µM, Gal-URA), gluconic acid (5.1 µM, Glu-Ac), glucuronic acid (3.0 µM, Glc-URA) and muramic acid (1.9 µM, Mur-Ac). Regular calibration was performed by injecting 12.5 µl, 15.0 µl, 17.5 µl and 20 µl of

mixed standard solution. Linearity of the calibration curves of individual sugar standards was verified in the concentration range 10 nM-10 µM. Therefore, the standard mixture was diluted 10, 20, 50, and 100 fold with Milli-Q water. Injection volume for samples and for the blank was 17.5 µl. To check the performance of carbohydrate analysis and stability of the HPLC-PAD system, a 17.5 µl standard solution was analyzed after every second sample. The detection limit was 10 nM for each sugar with a standard deviation between replicate runs of <2%. Milli-Q water was used as blank to account for potential contamination during sample handling. Blanks were treated and analyzed in the same way as the samples. Blank concentration was subtracted from sample concentration if above the detection limit. Particulate combined carbohydrates (PCCHO) were determined as the difference between TCCHO and DCCHO.

2.2.5. Gel particles

Total area, particle numbers and equivalent spherical diameter (d_p) 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 Alcian Blue solution for polysaccharidic gels, i.e. transparent exopolymer particles (TEP), and 1 mL 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. The size-frequency distribution of gel particles was described by:

$$\frac{dN}{d(d_p)} = k d_p^{\delta} \quad (2)$$

where dN is the number of particles per unit water volume in the size range d_p to (d_p + $d(d_p)$) (Mari and Kiørboe, 1996). The factor k is a constant that depends on the total number of particles

per volume, and δ (δ < 0) describes the spectral slope of the size distribution. The value δ is related to the slope of the cumulative size distribution $N = a d_p^{\beta}$ by $\delta = \beta + 1$, where N is the total number of particles per unit water volume. The less negative is δ, the greater is the fraction of larger gels. Both δ and k were derived from regressions of $\log(dN/d(d_p))$ versus $\log(d_p)$ over the size range 1.05-14.14 µm ESD.

Formation of exopolymeric gel particles, e.g. TEP, can be described in terms of coagulation kinetics (Engel et al., 2004; Mari and Burd, 1998). Aggregates can be described using a fractal scaling relationship, e.g. $M \sim L^D$, where M is the mass of the aggregate, L the size and D is the fractal dimension, which is controlled by the size of particles that form the aggregate as well as by the processes of particle collision, e.g Bownian Motion, shear, or differential settlement (Meakin, 1991). Assuming that TEP are formed by shear induced coagulation D can be estimated from δ (Mari and Burd, 1998):

(3) $$D = \frac{(64 - \partial)}{26.2}$$

2.2.6. 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 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) versus green fluorescence (FL1). Heterotrophic bacteria were distinguished from photosynthetic prokaryotes (e.g. *Prochlorococcus*) by their signature in a plot of red fluorescence (FL2) versus green fluorescence (FL 1). Yellow-green latex beads

(Polysciences, 0.5 µm) were used as internal standard. Sampling bacterioneuston with a glass plate does not bias cell abundance measurements (Stolle et al., 2009).

2.2.7. Phytoplankton

For photoautotrophic cell numbers <20 µm, 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 at high flow rate (~39-41 µL min^{-1}) with the addition of 1µm-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 (characteristic for cyanobacterial, mainly *Synechococcus* populations) fluorescence. Cell counts were analyzed using BD CellQuest Pro-Software. Two groups were distinguished: Non-cyanobacterial-type phytoplankton (NCPL) and cyanobacterial-type phytoplankton (CPL).

2.3. Data analysis

The relative concentration of a substance A in the SML was compared to the underlying water (ULW) by the enrichment factor (EF), defined by:

$$EF = (A)_{SML} / (A)_{ULW} \quad (4)$$

Where (A) is the concentration of a given parameter in the SML or ULW, respectively (GESAMP, 1995). Because the concentration of a component is normalized to its values in the underlying water, EF for different components can be readily compared. Enrichment of a component is indicated by EF > 1, depletion by EF < 1.

Differences in data as revealed by statistical tests (*t*-test) were accepted as significant for $p < 0.05$. Average values for total concentrations are given by their arithmetic mean, averages for ratios by their geometric mean. Average values are reported with ±1 standard deviation (SD). Calculations, statistical tests and illustration of the data were performed with the software packages Microsoft Office Excel 2010, Sigma Plot 12.0 (Systat) and Ocean Data View (Schlitzer, 2013). Weighted-average gridding was used in ODV to display data in the SML according to data coverage with automatic scale lengths (53 permille x-scale length, 40 permille y-scale length).

3. Results

3.1. The physical environment

Coastal upwelling off Peru can occur throughout the year (Carr and Kearns, 2003). During the M91 cruise upwelling and upwelling velocities were determined from $^{3}He/^{4}He$ disequilibrium (Steinfeldt et al., 2015). High upwelling velocities of $>3x10^{-5}$ m s^{-1} were observed south of Lima (stations 10, 14, 15) (Figure 1). The coastal upwelling of deep water resulted in strong gradients of surface seawater temperature and salinity along the Peruvian shelf as well as with increasing distance to the shelf during M91. Salinity measured at about 1 m depth corresponding to the ship's keel varied between 32 and 35 with the lowest values occurring close to the coast at stations 10_1 to 10_4, 14_1 and 14_2 and 15_1 to 15_3 Here, temperatures were below the average of all surface stations (19.25±1.7°C), indicating the colder, upwelling deep water (Table 1, Figure 2). Wind speed encountered during the cruise ranged between 0.6 and 9.0 m s^{-1} with the lower wind speeds also observed closer to the coast, i.e. between 12° and 14°S and at the northern stations (Figure 2). Thus, higher wind speed was observed at the more off-shore stations having higher surface water temperatures, leading to significant co-variation between surface water temperature and wind speed (Figure 3). Global radiation and UV radiation varied between

10 and 1103 W m^{-2}, and between 0.8 and 71 W m^{-2}, respectively, with no significant impact of SML organic matter accumulation.

3.2. SML properties and organic matter accumulation

Estimates for SML thickness are depending on the method applied to sample the SML (Carlson, 1982; Zhang et al., 1998). For the glass plate technique, Zhang et al. (1998) showed that SML thickness decreases with increasing withdrawal rates; i.e. from 50-60 µm for a withdrawal rate of 20 cm s^{-1}, to 10-20 µm at rate of 5-6 cm s^{-1}. Their results confirmed earlier studies that generally revealed thinner SML layers at slower withdrawal rates (Carlson, 1982; Harvey and Burzell, 1972; Hatcher and Parker, 1974). During this study, the SML was sampled with the glass plate at ~20 cm s^{-1}, yielding a thickness between 45 and 60 µm, with an overall mean value of 49± 8.89 µm (n=39). This value is in good accordance with the proposed apparent sampling thickness of 50±10 µm (Zhang et al., 1998) and fits well to previous observations for the SML sampled with a glass plate at the same withdrawal rate (Cunliffe et al., 2011; Galgani and Engel, 2013; Galgani et al., 2014; Zhang et al., 1998; Zhang, 2003). Using direct pH microelectrode measurements, Zhang (2003) later confirmed an *in situ* thickness of ~60 µm for the SML, which they defined as the layer of sudden change of physico-chemical properties.

We therefore assume that samples obtained from the SML during this study well represented the SML, as defined by Zhang (2003). Thickness of the SML as determined during this study increased significantly with amount of organic substances in the SML, determined as TOC concentration (p<0.005; n=39). This corroborates earlier findings from experimental studies showing that organic matter produced by phytoplankton increases the thickness of SML sampled with a glass plate (Galgani and Engel, 2013). No correlation instead was observed between SML

359 thickness and wind speed (r=-0.11, n=39) or between SML thickness and temperature (r=-0.06;
360 n=39).
361
362 Unless stated otherwise, all observations described in this paragraph relate to the SML. In
363 general, concentration of organic components in the SML showed spatial distribution patterns
364 resembling those of temperature and wind speed (Figures 3, 4, 5). Highest concentration values
365 for nearly all organic components were observed at the upwelling stations 10_1 to 10_4, 14_1
366 and 14_2 and 15_1 to 15_3 (Figure 1) in accordance with high estimated primary production
367 rates (Steinfeldt et al., 2015) and high Chl *a* concentrations (Hu et al., 2015) determined in
368 surface waters at these sites during M91.
369 Phytoneuston abundances (<20 µm) varied between $3.7x10^3$ and $1.9x10^5$ mL^{-1} for
370 cyanobacterial-type phytoplankton (CPL) (mainly *Synechococcus spp.*) and between $5.4x10^3$ and
371 $3.0x10^5$ mL^{-1} for other non-cyanobacterial-type phytoplankton (NCPL). Generally, highest
372 abundance was determined on and close to the upwelling stations (Figure 4). On all other
373 stations, cell abundance of CPL and NCPL differed spatially, with higher abundance of NCPL at
374 the southern stations and higher numbers of CPL at the northern stations (Figure 4). NCPL and
375 CPL were closely related to cell abundance in the ULW (Table 3).
376 Heterotrophic bacteria were determined in abundances between $3.0x10^4$ and $8.5x10^6$ mL^{-1}
377 with highest numbers observed at the upwelling stations and southeast of the upwelling (Figure
378 4). Heterotrophic bacteria in the SML were highly positively correlated to abundances in the
379 ULW (r=0.94; n=*36* p<0.001) and negatively influenced by wind speed, although less clearly
380 (r=-0.37; n=*36* p=0.01). No significant influence on heterotrophic bacteria abundance was
381 detected with respect to global radiation or UV radiation.

TOC concentration ranged between 82 and 199 µmol L^{-1}, and was clearly higher than DOC concentration on all stations. Particulate Organic Carbon (POC) concentration was calculated as the difference between TOC and DOC and ranged from 2.3 to 96 µmol L^{-1}. Highest POC concentration was observed at the upwelling stations (Figure 5). In general, POC concentration was highly correlated to temperature (r=-0.67, n=39 p<0.001) and to wind speed (r= -0.48, n=39 p<0.001) (Table 3). DOC concentration ranged between 71 and 122 µmol L^{-1} (Table 2) and, in contrast to POC, was not significantly related to temperature or wind speed (Table 3). Relatively high DOC concentrations of about 100 µmol L^{-1} were observed at stations 9 and 9_2 (Figure 5), but excluding these stations from analysis did not reveal a correlation to temperature or wind speed either. DOC is a bulk measure and is quantitatively dominated by refractory compounds that are independent from recent biological productivity. More closely linked to productivity and likely stimulated by the upwelling of nutrients along the Peruvian coast are labile and semi-labile compounds such as dissolved combined carbohydrates and amino acids. Indeed, both DCCHO and DHAA reached highest concentrations at the upwelling stations (Figure 5). Thereby, maximum concentration of DCCHO of 2670 nmol L^{-1} (mean: 1110±550 nmol L^{-1}) was observed at station 15_2, slightly south of the station 14_1 exhibiting highest DHAA concentrations of 2020 nmol L^{-1} (mean: 770 ± 360 nmol L^{-1}) (Table 2). In general high DCCHO concentration was more focused to the upwelling, and exhibited strong horizontal gradients to the northern and southern stations.

DHAA concentration was on average lower than DCCHO concentration (Table 2) and horizontal differences were less pronounced than for DCCHO. Both components of semi-labile DOC were inversely correlated to temperature (DCCHO r=-0.44, n=39, p<0.001; DHAA: r=-0.47, n=30, p<0.001), linking their accumulation in the SML to productivity in the cold upwelling waters.

406 Concentrations of carbohydrates and amino acid in particles, and in gels (i.e. TEP, CSP) in
407 particular, were highest at the coastal upwelling stations also. Particulate carbohydrates and
408 amino acids (PCCHO, PHAA) were highly correlated to POC concentrations (PCCHO: r=0.70,
409 n=39, p<0.001; PHAA: r=0.81, n=30, p<0.001).

410 In general, numerical abundance as well as total area were about 10-fold higher for CSP
411 than for TEP (Table 2). Spatial variability of gel particles abundance was high, and yielded
412 lowest values of total TEP area of 6.9 mm^2 L^{-1} at station 13_1 and highest values of 408 mm^2 L^{-1}
413 at station 15_1, about 100 nautical miles apart. The highest abundance of both TEP and CSP was
414 observed close to the coastal upwelling, but apart from these stations, the distribution of TEP in
415 the SML clearly differed from that of CSP (Figure 5). While higher TEP abundance was
416 observed at the northern stations, CSP abundance was more pronounced at the southern stations.
417 Moreover, stations of highest and lowest concentration of CSP were different from those of TEP.
418 Lowest value of CSP total area of 137 mm^2 L^{-1} was observed at station 11_1 and highest values
419 of 3051 mm^2 L^{-1} at station 14_1.

420

421 **3.3. Accumulation patterns in the SML**

422 For almost all components investigated during this study, concentration in the SML was
423 significantly related to the respective concentration in the ULW (Table 3). Thereby, correlations
424 between SML and ULW were strongest for combined carbohydrates, particularly for DCCHO.
425 Close correlations were also observed for bulk organic carbon measurements, i.e. TOC, DOC,
426 and derived therefrom POC. For dissolved nitrogenous compounds, i.e. TDN, FAA and DHAA
427 no relationship between SML and ULW concentrations was observed, suggesting that loss or
428 gain of these compounds in the SML were faster than exchange processes with the ULW.
429 Temperature had an effect on most organic compounds in the SML, with generally higher

concentrations at lower temperature (Table 3). This can largely be attributed to the higher production of organic matter at the colder upwelling sites. Concentrations of particulate components POC, TEP, PHCHO, PHAA and particulate nitrogen (PN) were also inversely related to wind speed, whereas DCCHO and DHAA were inversely related to temperature but not to wind speed. Clear differences were observed for the two different gel particle types determined in this study. In contrast to TEP, neither abundance nor total area of CSP were related to wind speed, nor to seawater temperature. Instead abundance of CSP in the SML was mostly related to their abundance in ULW. However, with the exception of CSP, particulate components in the SML were affected by changes in wind speed more than concentration of dissolved compounds (Table 3).

Enrichment factors indicated a general accumulation of organic matter in the SML with respect to the ULW (Figure 6), which happened at most stations. Thereby, clear differences were observed between EF values of different components. The highest enrichment was observed for FAA that were enriched more than 10-fold at some stations. Moreover, FAA were consistently enriched in the SML, except for one station where the lowest FAA concentration was determined (49 nmol L^{-1}). The largest variability of EF was observed for abundance and total area of gel particles. For TEP total area, values of EF ranged between 0.2-12, with highest EF observed at the coastal upwelling station 14_1, where the wind speed recorded was 0.6 m s^{-1}. In proximity of this station, the lowest EF of TEP was determined (station 15_3) indicating a clear depletion at wind speed of 7 m s^{-1}. The EF of CSP total area ranged between 0.4 and 4.8. Thus highest EF of CSP was clearly lower than for TEP, and in contrast to TEP it was observed at the more offshore station 18_2 at a higher wind speed rate of 9.2 m s^{-1}. Total and dissolved hydrolysable amino acids (THAA, DHAA) were enriched in the SML at almost all stations (Figure 6), with EF in the range

453 0.8 - 4.6 (DHAA) and 0.4 - 3.4 (THAA). Median EFs were 1.7 and 1.4 for DHAA and THAA,
454 respectively.
455 Concentration of TCCHO, DCCHO in the SML were often similar to the ULW, with EF values
456 ranging between 0.6 and 1.4 (DCCHO) and between 0.3 and 1.7 (TCCHO), respectively.
457 In general, variability of EF was smaller for dissolved than for particulate organic compounds,
458 suggesting differences in the accumulation dynamics.
459 In contrast to all organic, chemical compounds, bacteria were found to be depleted in the SML at
460 almost all stations (Figure 6), having a median EF of 0.8
461

462 **3.4. Size distribution of gel particles within the SML**

463 Abundance of gel particles in the SML and ULW decreased with increasing particle size
464 according to the power law function given in eq. 2 (Figure 8). The parameter δ describes the
465 slope of the particles size spectrum. Lower values of δ indicate relatively higher abundance of
466 smaller particles. Data fits to the function were very well described for each sample with r^2>0.90,
467 yielding a standard error for δ of <20%. For TEP, δ varied between -2.63 and -1.38 (mean
468 value: -1.86, SD: 0.27, n=39) for particles in the SML and between -2.25 and -1.25 (mean value:
469 -1.70, SD: 0.30, n=39) for particles in the ULW. To compare the size distribution of TEP in the
470 SML and the ULW, we calculated the slope ratio ($\delta^* = \delta_{SML} / \delta_{ULW}$) (Figure 9). Size distributions of
471 TEP in the SML and ULW were generally quite similar yielding δ^*_{TEP} in the range of 0.78-1.42,
472 with a median value of 1.1. Nevertheless, spatial differences were observed, with δ^*_{TEP} <0.95 at
473 the more coastal northern stations and δ^*_{TEP} >1.1 more offshore at the southern stations (Figure
474 9). At the upwelling stations with high TEP abundance slopes of SML and ULW were very
475 similar, yielding δ^*_{TEP} in the range 0.95 - 1.1. This showed a relatively higher abundance of
476 smaller TEP in the SML at the offshore stations, whereas relatively more, larger sized TEP were

present close to the coast in the northern part of the study region. This comparison also showed that sampling of TEP from the SML with a glass plate does not bias TEP size distribution, e.g. by inducing particle aggregation during sampling. Such a bias would be expected especially at stations where TEP was highly abundant, like at the upwelling stations. However, particularly at those stations no difference in size distributions of TEP in the SML and ULW was observed. Fractal scaling exponents of TEP were estimated from eq. 3 and yielded D=2.51 for both SML and ULW samples (D_{SML}=2.51±0.015 n=39; D_{ULW}=2.51±0.011). The very similar fractal dimension for TEP in the SML and ULW suggests that TEP in the SML and in the bulk water are formed by similar aggregation processes. The value of D=2.51 estimated in this study is close to 2.55 proposed by Mari and Burd (1998) for seawater TEP.

In the SML, the number of TEP in the smallest size class (1.25-1.77 µm) ranged from 96 to 1.38×10^4 mL^{-1}, and included on average 61±5.2% of all TEP. For CSP, variability of abundance in the 1.25-1.77 µm size class was much smaller and ranged between 1.46×10^4 and 2.33×10^5 mL^{-1}. Although CSP thus represented the largest fraction of small gel particles, the relative abundance of CSP in the smallest size fraction was lower, yielding an average contribution of 52±6.0% of all CSP. Similar to TEP, size distribution of CSP followed the power law relationship of eq. 2, yielding δ values between -1.12 and -2.01 (mean value: -1.44, SD: 0.20) for particles in the SML and between -1.11 and -1.88 (mean value: -1.39, SD: 0.17) for particles in the ULW. With D=2.50±0.008, the fractal dimension of CSP was almost identical to that of TEP, suggesting that similar processes, i.e. shear induced aggregation, are responsible for CSP formation. The slope ratio, δ^*, for CSP varied between 0.77 and 1.32, with a median value of 1.0. No spatial pattern was observed for the distribution of δ^*_{CSP}. Slopes of the size distribution of CSP in the SML and ULW were not significantly different (p=0.176, n=32, paired t-test),

indicating that CSP size distribution, similarly to TEP, is not biased by the sampling approach of the glass plate.

No overall relationship was established between the slope of the size distribution of TEP and wind velocity (δ_{TEP} vs. wind speed: r=-0.19, n= 39, p=0.20). However, TEP size distribution was much steeper at the station with highest wind speed compared to the one with lowest wind velocity (δ_{TEP} at 0.6 m s^{-1}= -1.51, r^2=0.95, n=7; δ_{TEP} at 9.0 m s^{-1}= -2.31, r^2=0.95, n=7) (Figure 8a). In particular, at the high wind speed a loss of larger TEP, i.e. >7 µm was observed in the SML compared to the ULW and relative to the low wind speed station.

For CSP a significant inverse relationship was observed between the slope δ and wind speed (δ_{CSP} vs. wind speed: r=-0.61, n=37, p<0.001). A loss of larger CSP was also observed by direct comparison between low and high wind speed stations (δ_{CSP} at 0.6 m s^{-1}= -1.12, r^2=0.92, n=7; δ_{TEP} at 9.0 m s^{-1}= -1.45, r^2=0.97, n=7) (Figure 8b).

4. Discussion

It has been suggested that the presence of organic matter in the SML influences a series of processes relevant to air-sea exchange of gases, dissolved and particulate components. EBU'S are characterized by high biological productivity and strong across shelf gradients of organic matter concentration (Capone and Hutchins, 2013). Therefore EBU'S are ideal model systems to study the linkages of biological productivity and SML properties, with respect to characteristics of organic matter composition and factors controlling organic matter enrichment in the SML.

4.1. Organic matter characteristics of the SML in the upwelling region off Peru

Strong horizontal gradients in organic matter concentration of the SML were observed for the coastal and shelf-break region off Peru with generally higher organic matter concentrations in the

524 SML towards the area of upwelling of colder, nutrient-rich deep water. Hence, increasing
525 ecosystem productivity is one likely factor responsible for higher concentrations of organic
526 components in the SML. Significant correlations between organic matter concentration in the
527 SML and in the ULW were determined and showed that the SML basically reflects the
528 underlying seawater system. The close connectivity between SML organic properties and
529 biological development was also shown during a recent mesocosm study, indicating that
530 ecosystem changes impact SML organic matter composition and concentration (Galgani et al.,
531 2014). Despite this finding that relates to a more general characteristic of the SML, clear
532 differences in the accumulation behavior of different organic matter components were determined
533 during this study and are in good accordance with previous observations. A generally higher
534 SML accumulation was observed for amino acids compared to carbohydrates. Significant
535 enrichment of amino acids in the SML has been determined previously for coastal as well as open
536 ocean sites, and higher accumulation of FAA compared to DHAA and THAA, as also observed
537 during this study, appears to be a consistent SML feature (Carlucci et al., 1992; Henrichs and
538 Williams, 1985; Kuznetsova and Lee, 2002, 2001; Kuznetsova et al., 2004; Reinthaler et al.,
539 2008). As for this study, wind velocity and temperature have not been identified as physical
540 factors responsible for amino acid enrichment in the past (Kuznetsova et al., 2004). FAA and
541 DHAA are labile to semi-labile substrates and taken-up by heterotrophic microorganisms (Keil
542 and Kirchman, 1992). Turnover times of these components in the water column are usually in the
543 range of minutes to days (Benner, 2002; Fuhrman and Ferguson, 1986). The observed
544 accumulation of FAA and DHAA in the SML may therefore be related to a reduced activity of
545 bacteria. For different coastal Baltic Sea sites, Stolle et al. (2009) determined a lowered bacterial
546 biomass production in the SML, despite bacterial cell numbers being similar to those in the
547 ULW. During M91 bacteria were mostly depleted in the SML compared to the ULW supporting

548 the idea of the SML being an ‘extreme environment’ for bacteria. Earlier studies showed that
549 some bacteria may be adapted to UV radiation in the SML as well as in the ULW (Agogué et al.,
550 2005; Carlucci et al., 1985). Amino acid consumption by bacterioneuston under UV-B stress may
551 be reduced (Santos et al., 2012), which may give an explanation for the higher concentrations of
552 FAA and DHAA in the SML during M91. However, no significant correlation between bacterial
553 abundance and UV radiation or between UV radiation and amino acid concentrations in the
554 different pools was observed during this study, suggesting that at most stations history rather than
555 instantaneous UV radiation is if at all responsible for controlling bacteria and organic matter
556 components in the SML.
557 SML thickness during this study was significantly related to TOC concentration, but not to wind
558 speed. A thickening of the SML with increasing wind speed up to 8 m s^{-1} has been observed by
559 Falkowska (1999) from samples collected in the Baltic Sea and explained by increased advective
560 transport of organic matter to the SML, e.g. through bubble adsorption, at higher turbulence.
561 During M91, accumulation of organic matter in the SML was higher at the upwelling stations
562 where wind speed often was quite low. Hence, a higher source of organic matter in the ULW may
563 have counterbalanced the wind speed effect.
564
565 Wind speed, however, was determined as a factor controlling accumulation of particulate
566 material, in particular TEP, in the SML in addition to the dynamics occurring in the ULW. TEP
567 are marine gel particles hypothesized to be neutrally or positively buoyant thanks to their high
568 water content (Azetsu-Scott and Passow, 2004; Engel and Schartau, 1999). TEP were moreover
569 suggested to form within the SML, either by wind-shear induced aggregation of precursors or due
570 to coalescence of pre-cursor molecules, primarily polysaccharides, when entrained air bubbles
571 burst at the sear surface (Wurl et al., 2011). Adsorption of DOM onto bubble surfaces and TEP

formation by bubble bursting have been determined during experimental flotation and bubbling studies using surface seawater from different locations (Wallace and Duce, 1978; Zhou et al., 1998). Bubble scavenging of DOM in the upper water column may thus be responsible for high concentrations of TEP at the SML, because more TEP precursors are lifted up the water-column (Gao et al., 2012; Wurl et al., 2011). In addition, compression and dilatation of the SML due to capillary waves may increase the rate of polymer collision, subsequently facilitating gel aggregation (Carlson, 1993). During M91, TEP enrichment in the SML was inversely related to wind speed, supporting earlier observations of Wurl and colleagues (Wurl et al., 2009; Wurl et al., 2011). However, in contrast to earlier observations showing EF values >1 for TEP in the SML also at higher wind speed, we found the SML to be depleted of TEP at wind speed of ~ 5 m s^{-1} and above. It has been suggested that TEP aggregation rates in the SML are higher than in the ULW, due to enhance collision rates by shear or bubble bursting. TEP have been shown to control coagulation efficiencies of solid particles, such as diatoms and coccolithophores (Chow et al., 2015; Engel, 2000; Logan et al., 1995). At higher wind speed, increased aggregation rates of TEP with solid particles, eventually containing mineral ballast, may thus favor the formation of aggregates that become negatively buoyant and sink out of the SML. This, may explain the observed loss of larger TEP (>7 µm) from the SML relative to the ULW and to the SML at low wind speed. Enhanced aggregation rates could then also explain the inverse relationship between POC and wind speed, observed during this study.

In contrast to TEP, no impact of wind speed was determined for CSP accumulation, or for CSP enrichment in the SML. Moreover, clear spatial differences were observed for the distribution of TEP and CSP in the SML. Although both TEP and CSP are gel particles that form from dissolved organic precursors released by microorganisms, their spatial and temporal occurrence in marine

596 systems can be quite different, e.g. TEP accumulate towards the end of phytoplankton blooms
597 while CSP rather co-occur with maximum phytoplankton abundance (Cisternas-Novoa et al.,
598 2015; Engel et al., 2015). Moreover, the depth distribution of TEP and CSP was shown to be
599 different for open ocean sites (Cisternas-Novoa et al., 2015). These spatial and temporal
600 differences in the occurrence of TEP and CSP in the water column may explain the spatial
601 separation of both types of marine gels in the SML observed during this study. However, the
602 observed differences in relation to wind speed suggest that additional factors control the
603 enrichment of TEP and CSP in the SML. It has been shown that CSP are less prone to
604 aggregation than TEP (Engel et al., 2015; Prieto et al., 2002). Similarly, CSP may be less
605 involved in aggregation formation and sinking out of the SML at higher wind speed. Yet,
606 similarly to TEP, larger CSP were observed in the SML at low wind speed suggesting that both
607 kind of gels may be involved in slick formation that becomes disrupted when wind speed
608 increases.
609
610
611 **4.2. Implications of organic matter accumulation in EBUS**
612 **4.2.1. Air-Sea gas exchange**
613 Although the SML and surface active substances (surfactants) within are widely believed
614 affecting the exchange of gases and heat at the air-sea interface (Davies, 1966; Frew, 1997; Salter
615 et al., 2011), particularly at lower wind speed (Liss, 1983), we still have little quantitative
616 knowledge on how natural organic components at the immediate sea-surface alter the gas transfer
617 velocity in water (*kw*). Our data showed a depletion of the SML with respect to TEP and POC at
618 wind speeds >5 m s^{-1}, suggesting that an effect of these 'insoluble' components on gas exchange
619 is, if any, operating only at low wind speed. Due to their fractal scaling, gel particles have a

relatively large surface to volume ratio and may act as a cover, reducing molecular diffusion rates at the interface between air and sea.

Accumulation of dissolved organic components in the SML during M91 was not related to wind speed. DCCHO and DHAA concentration representing fresh DOM were highest at the upwelling sites and therefore negatively related to seawater temperature. DOM, such as DCCHO and chromophoric dissolved organic matter (CDOM), have demonstrated surfactant properties and reduced gas transfer velocity in water (*kw*) at low wind speed in laboratory and field experiments (Frew et al., 2004; Frew et al., 1990). The reduction of *kw* is thereby believed to be related to a dampening of small, capillary waves. Salter et al. (2011) recently showed that artificial surfactants can suppress gas transfer velocity by up to 55% at sea. Suppression of k666 (i.e. *kw* normalized to a Schmidt number of 666) during their field study was depending on wind speed, but was detected up to 11 m s^{-1}, encompassing the full range of wind speed determined during M91. Thus, accumulation of natural DOM particularly in upwelling regimes with high biological production and coastal wind shelter as observed during this study may have an influence on gas exchanges rates as well.

Across the SML, the diffusivity of climate relevant gases such as methane (CH_4), has been proposed being mediated by SML bacteria, as possible sink (Upstill-Goddard et al., 2003) or source of this compound (Cunliffe et al., 2013). About ~ 30 % of the atmospheric concentration of nitrous oxide (N_2O), one of the strongest greenhouse gases and responsible for ozone depletion, is supported by oceanic sources (Solomon et al., 2007). Of total oceanic N_2O production, oxygen minimum zones (OMZs) contribute about 25-75 % (Bange et al., 2001). In EBU'S, high primary production and induced high aerobic remineralization associated with large-scale circulation maintain the presence of OMZs (Gutknecht et al., 2013; Paulmier and

644 Ruiz-Pino, 2009), which, in the last decades, have been expanding and intensifying due to
645 enhanced stratification and reduced ventilation (Keeling et al., 2010; Stramma et al., 2008).
646 During M91, N_2O concentration in surface waters was highly supersaturated at the upwelling
647 sites and in particular at station 14_1 (Arevalo-Martinez et al., 2015). Although a direct influence
648 of organic matter in the SML on gas-exchange was not investigated during M91, it can be
649 assumed that the high enrichment of organic components in the SML observed the upwelling
650 sites was one factor contributing to N_2O supersaturation.
651 Our study was intended to understand how organic matter accumulates in the SML, which might
652 mediate the transfer rate of trace- and greenhouse gases such as N_2O in oceanic regions like
653 OMZ's affected by a changing climate. A recent laboratory study reported π non-covalent
654 interactions of N_2O with phenols, suggesting a possible important role of N_2O in biological
655 processes by specifically binding to phenolic groups as those of the amino acids tyrosine and
656 phenylalanine (Cao et al., 2014). Tyrosine and phenylalanine in the SML of our study represented
657 a small molar percentage of total amino acids pool (data not shown), but were present. As we
658 found evidence of overall amino acids SML accumulation during our cruise, for those amino
659 acids in particular the median EF both in the total (THAA) and in the dissolved (DHAA) fraction
660 was > 1, suggesting a possible interaction of specific SML organics with N_2O in the coastal
661 upwelling region off Peru. Although the experiment conducted by Cao and colleagues cannot be
662 directly translated to our setting, it provides interesting ideas for the interaction of N_2O with
663 biological macromolecules worth further investigation.
664 Overall, our results showed that accumulation of organic substances occurs in EBU's and is
665 related to the increased biological production. Hence, the organic SML may play a particularly
666 important role for exchange of climate relevant gases that are associated to high organic matter
667 production and resulting anoxia in upwelling systems like the one off Peru.

668 **4.2.2. Organic aerosol production**

669 The structure of sea-spray aerosols (SSA) originating by bubble bursting at the sea surface is a
670 function of biological, chemical and physical properties of the SML, which may comprise a vast
671 array of organic surface-active compounds, microorganisms, and exopolymer gels (Leck and
672 Bigg, 2005; Quinn and Bates, 2011; Wilson et al., 2015). Despite recent evidences showing that
673 high levels of chlorophyll-*a* are not directly related to the organic carbon content of SSA (Quinn
674 et al., 2014), still organic SSA largely derive from the oceanic surface layer and therefore are also
675 subject to the effects of climate change on marine systems (Andreae and Crutzen, 1997).
676 Polysaccharides and polysaccharidic nanogels (Orellana et al., 2011; Russell et al., 2010) as well
677 as particulate amino acids and proteinaceous compounds (Kuznetsova et al., 2005) are present in
678 organic SSA particles. During M91, we found a different accumulation behavior of TEP and CSP
679 in the SML. TEP showed a close inverse relationship to wind speed, being depleted in the SML
680 above 5 m s^{-1}, while particulate proteinaceous compounds (CSP) accumulated independently of
681 wind speed. Submicron gels embedded in sea spray may represent an important source for
682 primary organic aerosols in the more offshore wind exposed regions. TEP as well as dissolved
683 polysaccharides include sugars with carboxylic groups such as uronic acids and may contribute to
684 the relatively high fraction of carboxylic acid that was observed in the organic matter component
685 of marine aerosols (Hawkins et al., 2010). In the upwelling region off Peru the wind-driven
686 export of polysaccharidic components to the atmosphere thus might represent a loss-pathway of
687 these organic compounds from the SML that would then contribute to a larger extent to the
688 organic SSA mass. Proteinaceous compounds, including CSP, are probably more stable at the sea
689 surface and may contribute to organic mass in aerosols even at higher wind speed.

690 However, future studies that investigate gel particles within the SML and in SSA are needed to
691 clarify if the observed loss of TEP from the SML at higher wind speeds is indeed related to a
692 transport of TEP to the atmosphere, or if CSP contribute to organic aerosol mass.
693 The accumulation of organic matter in the SML, and the distinct behavior of certain compounds
694 at the water-air interface is certainly an important issue for all exchange processes between the
695 ocean and the atmosphere that needs to be further exploited.
696
697
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699
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983 **Legends**

984

985 Figure 1: Maps of stations where sampling for sea surface microlayer (SML) and underlying
986 seawater (ULW) was conducted during the SOPRAN Meteor 91 cruise along the coastal
987 upwelling area off Peru in 2012.

988

989 Figure 2a, b: Surface water (1m depth) temperature (°C) and wind speed (m s^{-1}) (b) during M91.

990

991 Figure 3: Direct relationship between surface water temperature and wind speed during M91
992 SML sampling, $p<0.001$, $r= 0.58$, $n=39$. Data in dotted rectangle were selected for analysis of
993 wind speed effects at similar temperatures, see figure 7.

994

995 Figure 4: Phyto- and bacterioneuston (<20 µm) abundance (number mL^{-1}) in the SML off Peru
996 during M93: NCPL: 'Non-cyanobacterial-type' phytoplankton, CPL: 'cyanobacterial-type'
997 phytoplankton, HPL: heterotrophic bacterioplankton.

998

999 Figure 5: Surface distribution patterns of organic matter concentrations in the SML during M91
1000 showing particulate organic carbon (POC, µmol L^{-1}), dissolved organic carbon (DOC, µmol L^{-1})
1001 dissolved hydrolysable carbohydrates (DCCHO, nmol L^{-1}), dissolved hydrolysable amino acids
1002 (DHAA, nmol L^{-1}) and abundance of TEP (L^{-1}) and CSP (L^{-1}).

1003

1004 Figure 6: Box and whisker plot of enrichment factors (EF) calculated for various particulate and
1005 dissolved components during M91. Each box encloses 50% of the data with the median value of
1006 the variable displayed as a line. The bottom of the box marks the 25%, and the top the 75% limit,
1007 of data. The lines extending from the top and bottom of each box marks the 10% and 90%
1008 percentiles within the data set and the filled circles indicate the data outside of this range. For
1009 abbreviations, see text.

1010

1011 Figure 7a, b: Influence of wind speed (m s^{-1}) on the total area concentration of TEP (mm^2 L^{-1}) in
1012 the SML at all stations (a) and relationship between TEP enrichment factors (EF) and wind speed
1013 (m s^{-1}) for only those stations that showed similar sea surface temperature as indicated in figure 3.

Filled dots indicated data from stations of similar sea surface temperature. Data in plot (a) were fitted by power law functions; the solid line represents all data, the dotted line represents data of similar sea surface temperature.

Figure 8a, b: Size frequency distribution of TEP (a) and CSP (b) observed during the M91 cruise for samples collected from the SML (open symbols) and in the ULW (filled symbols) at the stations with lowest wind speed of 0.6 m s^{-1} (triangles) and highest wind speed of 9.0 m s^{-1} (circles). Linear regression of log*(dN/d(dp))* versus log*(dp)* was fitted to the particles in the size range of 1.05 – 14.14 µm ESD.

Figure 9: Spatial distribution of the slope ratio, δ*, for TEP in the upwelling region off Peru during M91.

Tables

Table 1: Hydrographic conditions encountered during SML sampling off Peru in 2012 (M91). Data on air temperature, wind speed, global and UV radiation were obtained from the ship's DShip database for the time of sampling.

	Temperature (°C)	Salinity	Air temperature (°C)	Wind speed ($m\ s^{-1}$)	Global Radiation ($W\ m^{-2}$)	UV Radiation ($W\ m^{-2}$)
average	19.25	34.87	19.67	5.66	570	37935
SD	1.70	0.50	0.89	2.14	366	23384
Min	15.91	32.02	17.30	0.60	10	0.812
Max	21.90	35.32	21.50	9.00	1103	71.10

Table 2: Concentration of various organic components in the SML during M91, given as average (avg.) and standard deviation (SD), as well as minimum (min) and maximum (max); *n* = number of observations. For abbreviations see text.

	Unit	Avg.	SD	min	max	*n*
DOC	µmol L^{-1}	94	13	71	122	39
TOC	µmol L^{-1}	127	33	82	199	39
POC	µmol L^{-1}	33	25	2.3	96	39
TEP number	$x10^6$ L^{-1}	19	15	1.8	63	39
TEP area	mm^2 L^{-1}	100	106	6.9	408	39
DCCHO	nmol L^{-1}	1111	550	507	2668	39
PCCHO	nmol L^{-1}	1084	1300	41	5156	34
TN	µmol L^{-1}	16	4.9	8.7	28	39
TDN	µmol L^{-1}	12.5	4.0	7.7	25	39
PN	µmol L^{-1}	3.3	3.7	bd	16	39
CSP number	$x10^6$ L^{-1}	118	72	19	311	39
CSP area	mm^2 L^{-1}	1024	728	137	3051	39
FAA	nmol L^{-1}	151	104	49	531	37
DHAA	nmol L^{-1}	770	359	423	2017	30
PHAA	nmol L^{-1}	1176	774	208	3956	29
NCPL	$x10^3$ mL^{-1}	45	53	5.4	300	35
CPL	$x10^3$ mL^{-1}	27	35	3.7	193	35
Het. bacteria	$x10^4$ mL^{-1}	195	206	3	854	36

Table 3: Correlation coefficients (*r*) between concentrations of various organic components in the SML and their concentration in the underlying seawater (ULW), temperature (T, °C), and wind speed (U, m s^{-1}) at the time of sampling. Correlations yielding significance level of $p<0.01$ are marked bold. For abbreviations see text. *: only 30 samples were analyzed for NCPL and CPL from the ULW.

SML	r_{ULW}	r_T	r_U	*n*
DOC	**0.75**	-0.04	0.06	39
TOC	**0.79**	**-0.53**	-0.35	39
POC	**0.68**	**-0.67**	**-0.48**	39
TEP number	**0.51**	**-0.58**	**-0.69**	**39**
TEP area	**0.58**	**-0.65**	**-0.69**	**39**
DCCHO	**0.94**	**-0.44**	-0.29	39
PCCHO	**0.77**	**-0.59**	**-0.38**	34
TDN	0.24	-0.18	-0.05	39
PN	**0.59**	**-0.55**	**-0.43**	**39**
CSP number	**0.53**	-0.04	0.15	39
CSP area	**0.68**	-0.36	-0.31	39
FAA	0.34	-0.34	0.19	37
DHAA	0.30	**-0.47**	-0.37	30
PHAA	**0.56**	**-0.64**	**-0.53**	**29**
NCPL	**0.70***	-0,24	-0,21	35
CPL	**0.90***	-0,21	-0,31	35
Het. bacteria	**0.92**	-0.33	**-0.37**	36

Figures

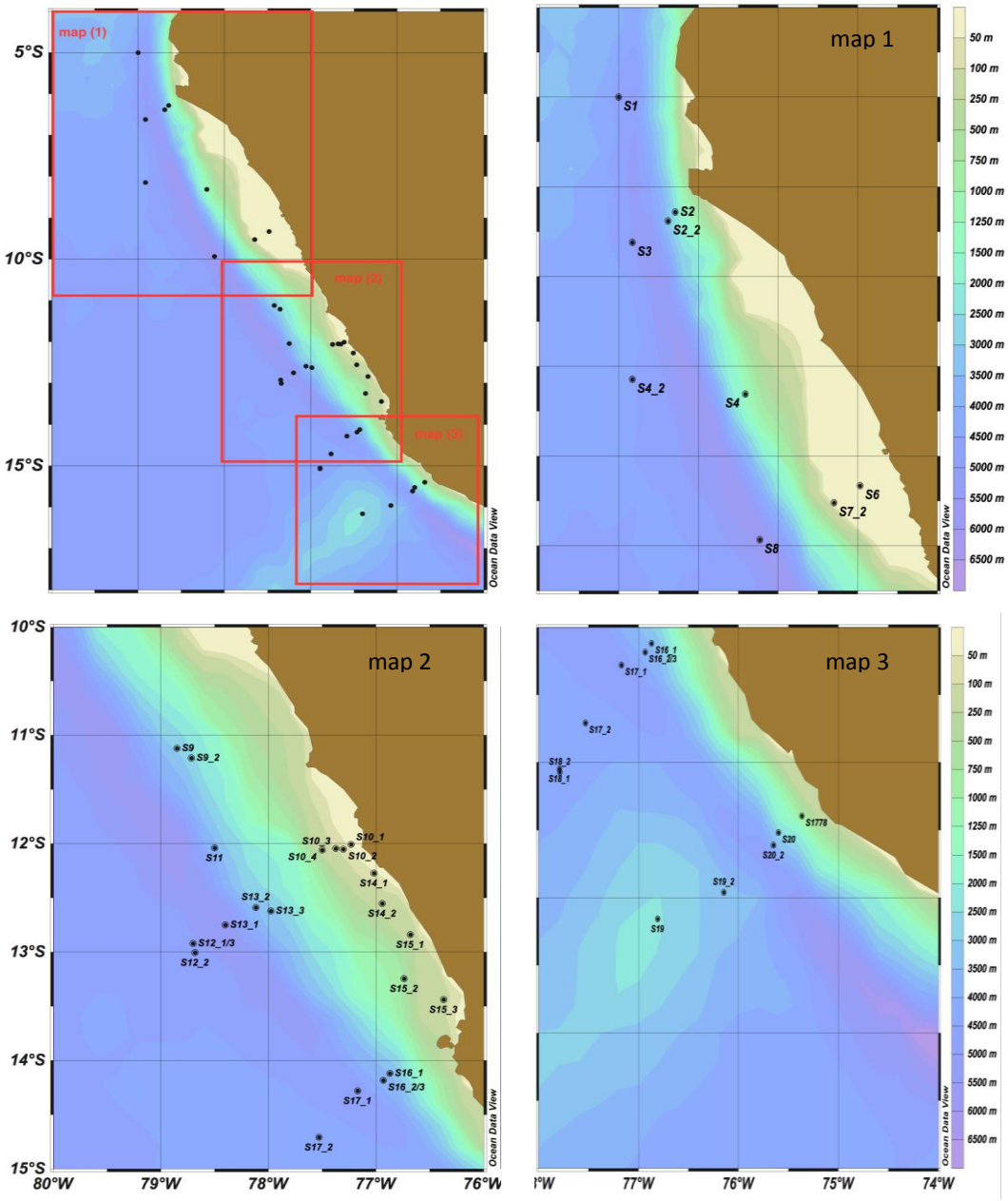


Figure 1

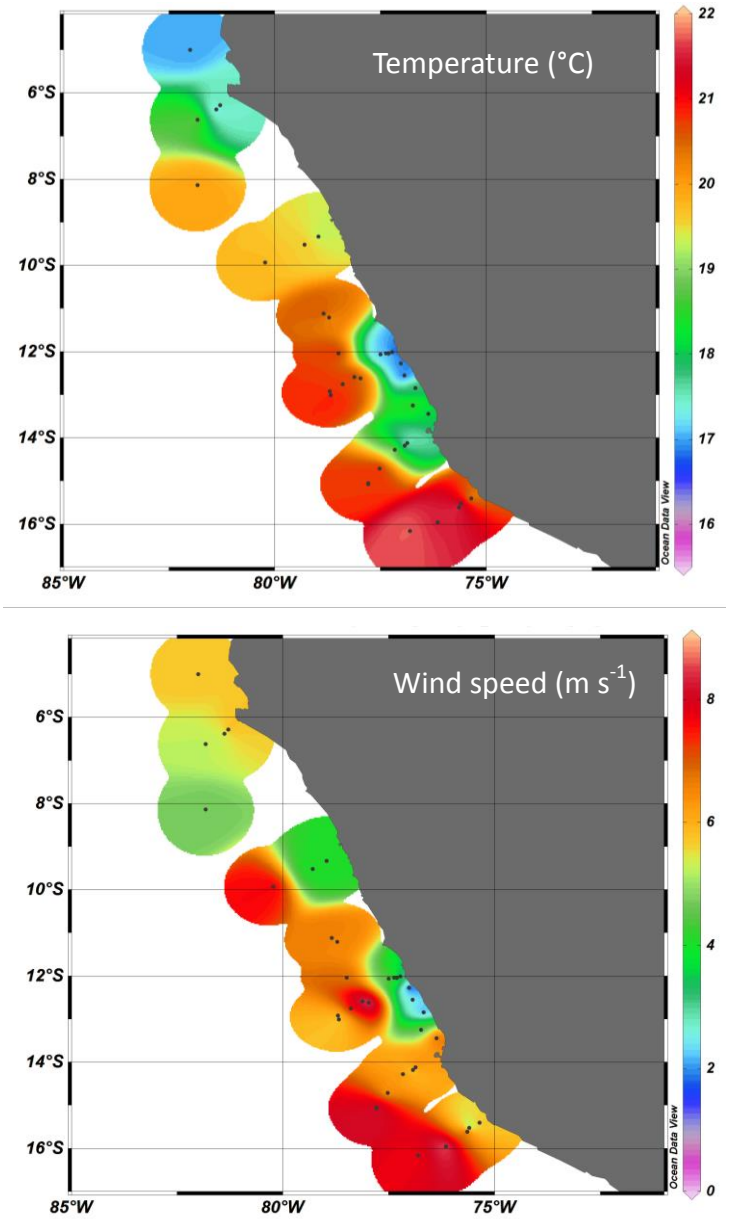

Temperature (°C)
6°S
8°S
10°S
12°S
14°S
16°S
85°W
80°W
75°W
22
21
20
19
18
17
16
Ocean Data View
Wind speed (m s-1)
6°S
8°S
10°S
12°S
14°S
16°S
85°W
80°W
75°W
8
6
4
2
0
Ocean Data View

Figure 2

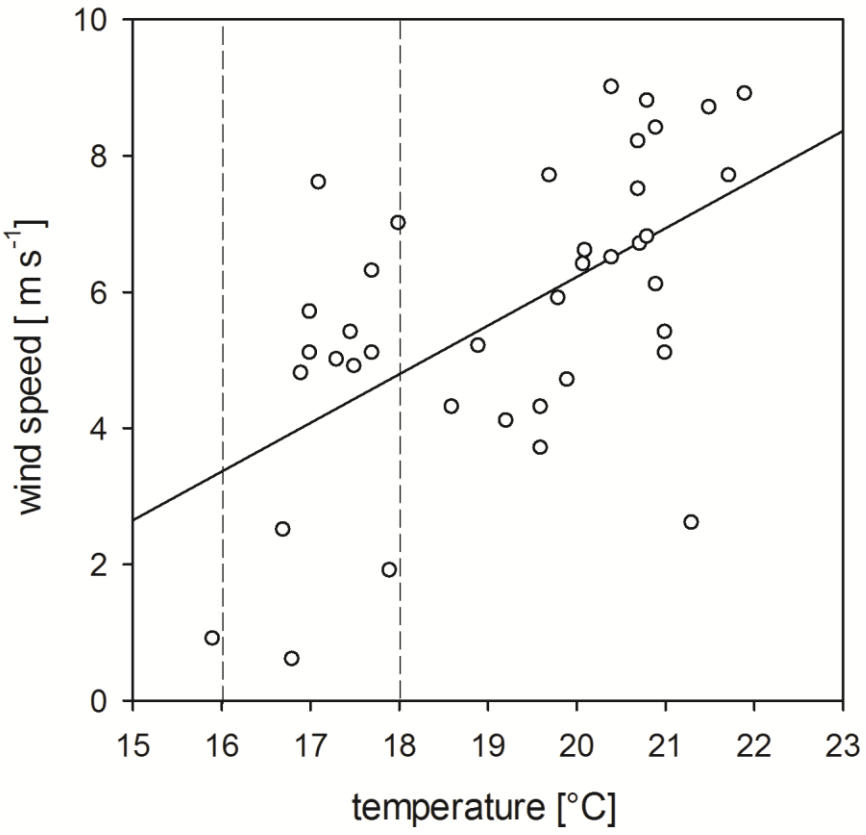


Figure 3

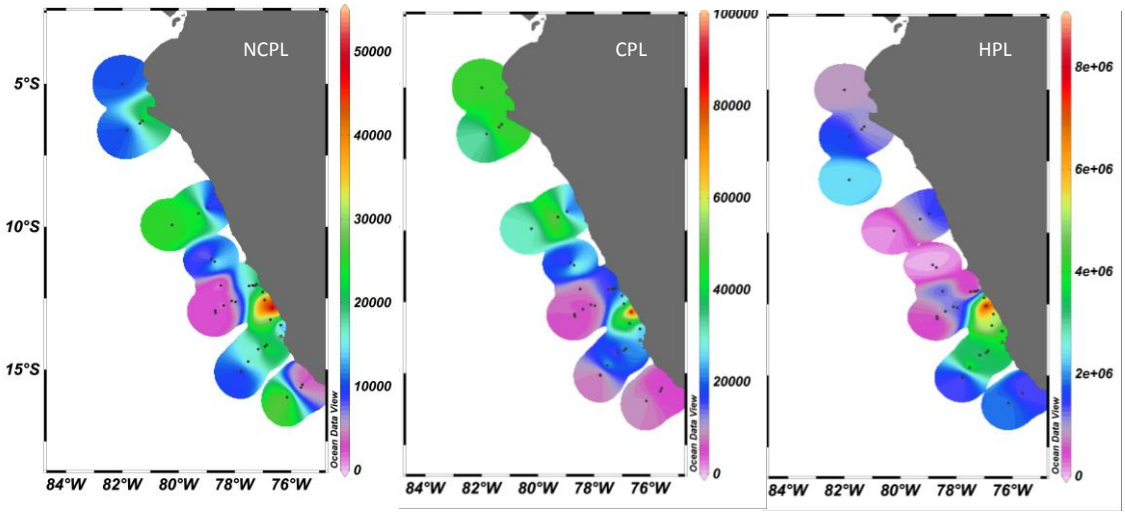


Figure 4

Figure 4

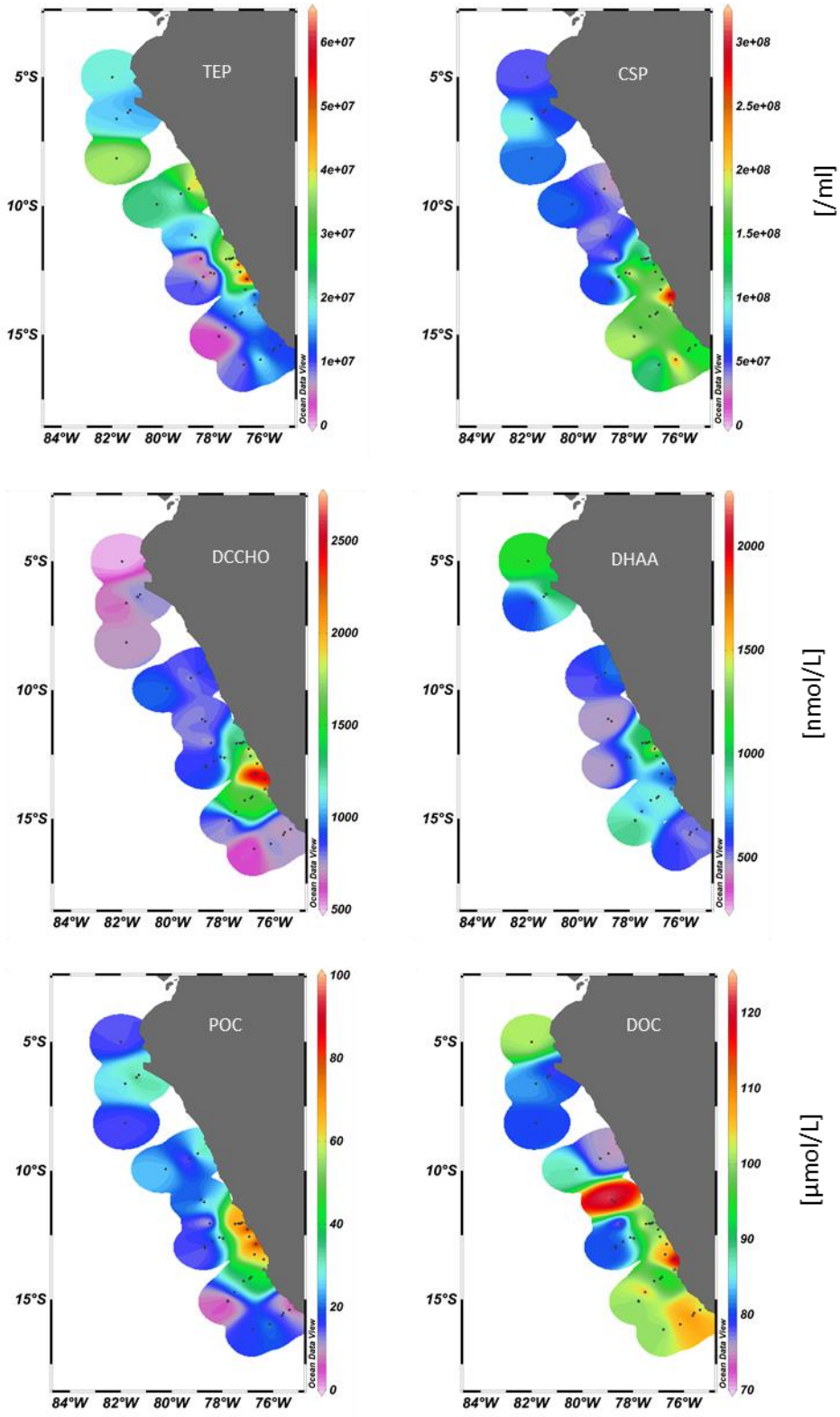

TEP
CSP
DCCHO
DHAA
POC
DOC
5°S
10°S
15°S
84°W 82°W 80°W 78°W 76°W
[/ml]
[nmol/L]
[µmol/L]

Figure 5

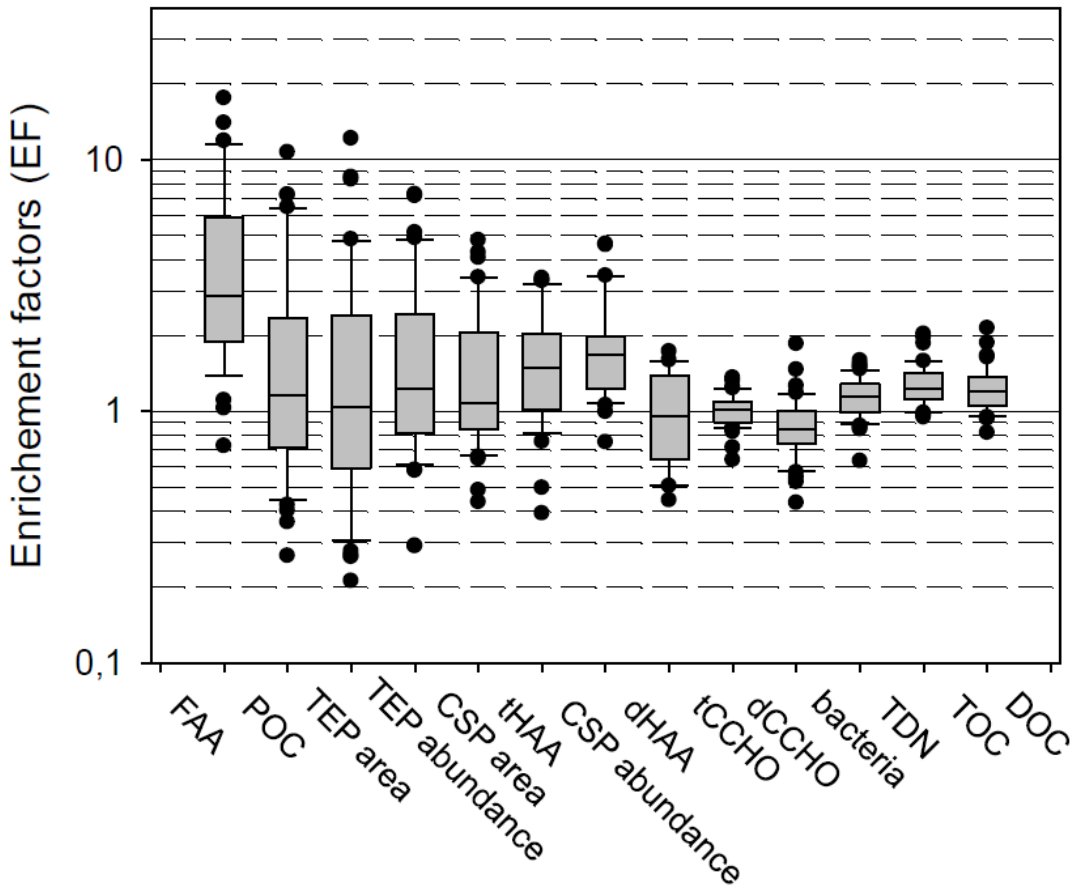
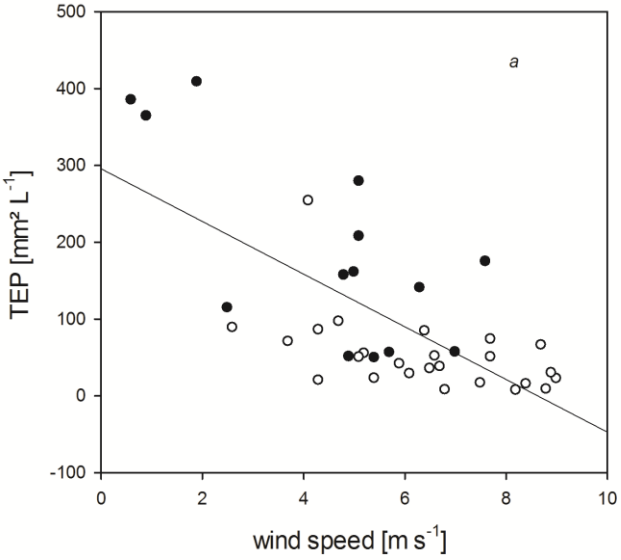
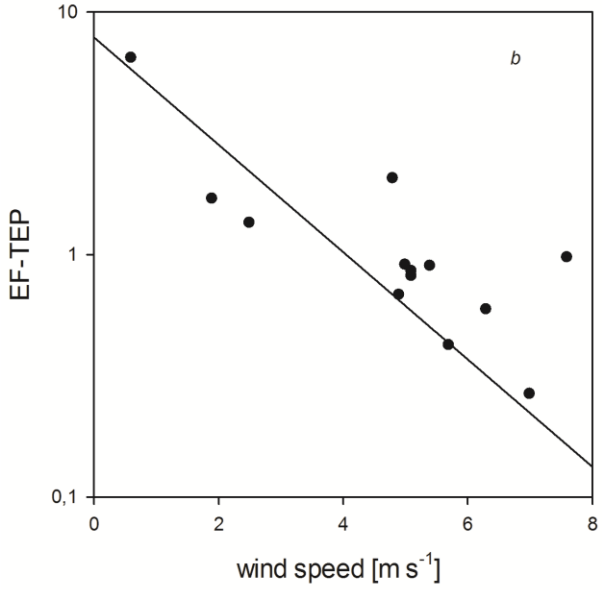

Enrichement factors (EF)
10
1
0,1
FAA
POC
TEP area
TEP abundance
CSP area
tHAA
CSP abundance
dHAA
tCCHO
dCCHO
bacteria
TDN
TOC
DOC

Figure 6

1257



1258

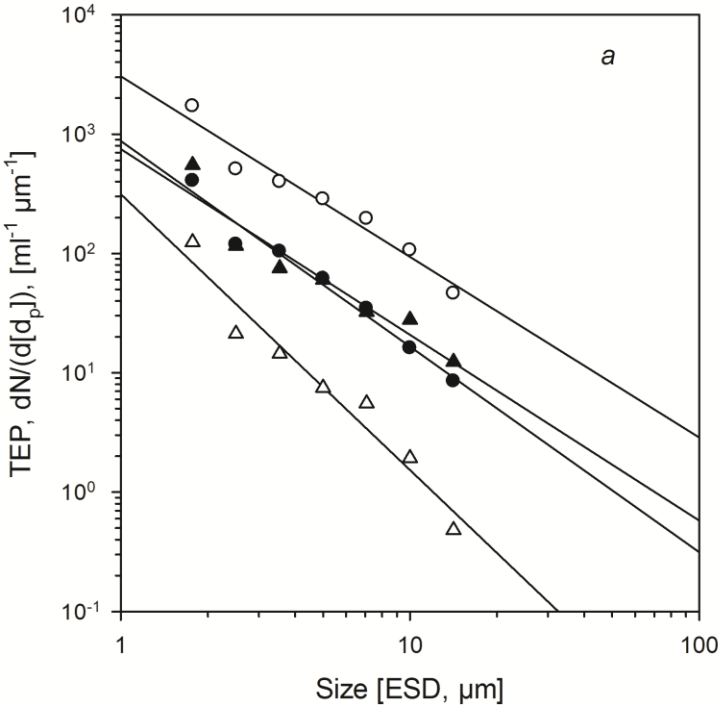


1259

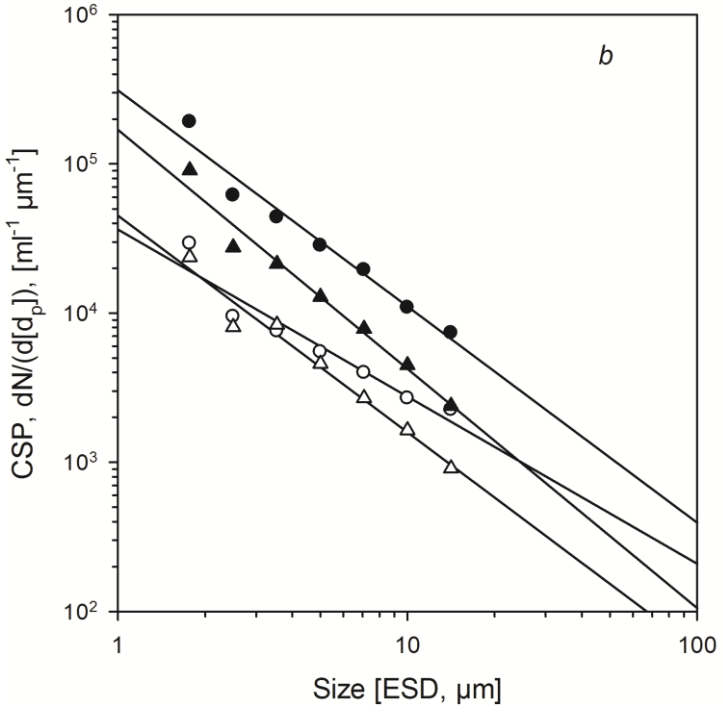
1260 Figure 7a, b

1261

1262



1263



1264

1265

1266 Figure 8a, b

1267

1268

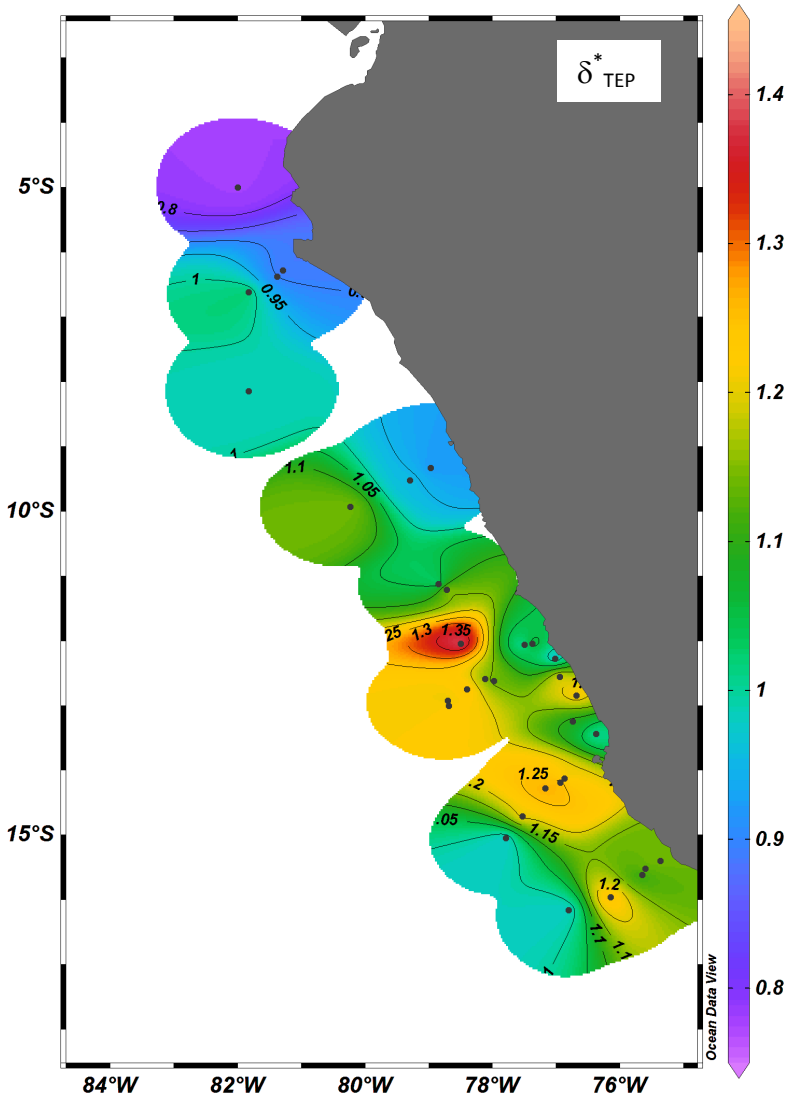

δ* TEP
1.4
1.3
1.2
1.1
1
0.9
0.8
5°S
10°S
15°S
84°W
82°W
80°W
78°W
76°W
Ocean Data View

Figure 9