Point by point response to the referees' comments:

Response to referee 1

Referee: Engel and Galgani present data on the enrichment of organic matter in the microlayer collected from an upwelling system. In brief, the idea of enrichment of organic matter in the microlayer is not new (has been published before with way more discussion), the data added to the pool collected by others is incremental only (i.e. it does not illuminate us beyond what is known). Additionally the section on air-sea gas exchange and aerosol is odd. No data of the former sections is discussed here, and it stands like a little review. Some of the approaches are questionable (TOC/DOC measurement, microlayer sampling). See below for detail

Response: The referee claims that our study does not provide novel insight to the topic of organic matter enrichment in the microlayer and that the data added are incremental. The referee's comment is unjustified. Our study is not about an idea but provides new data and additional evidence of organic matter (OM) enrichment in the SML. Our study is specific as it provides novel observations of OM enrichment in eastern boundary upwelling systems in general and in the Peruvian upwelling regime in particular. We moreover show the very first extensive field data set for the accumulation of proteinaceous gels, i.e. CSP, in the microlayer, potentially leading to different exported organic aerosol components from the ocean. There is no previous study that includes size distributions of marine gel particles in the SML and no previous study has shown the effect of wind speed on gel particle accumulation in the microlayer in this detail, i.e. including CSP and size distributions.

Response to detailed comments:

Referee: Page 10580 Line 23: Sieburth (1983) suggested for the first time that the SML has a gel-like nature. It has been then experimentally confirmed by Wurl and Holmes (2008) and later summarized by Cunliffe and Murrell (2009). In this context here, Sieburth (1983) should be cited.

Response: Reference to Sieburth (1983) was added.

Referee: Line 15: Authors need to be more careful in the selection of citation. The term "dynamics" means a process over time, and Bigg et al. (2004) didn't report data on phytoplankton dynamics. Authors need to check other citations.

Response: We agree with the referee and changed 'dynamics' to 'abundance'; the reference to Bigg et al. 2004 was removed.

Referee: Page 10581, Line 29: Authors use the term "sea-surface microlayer" and its acronym SML randomly

Response: We revised the text according to the suggestion. Sea surface microlayer is used the first time of mention and abbreviated afterwards; same for other abbreviations.

Referee: Line 25: Isn't it the first data set? In this case calling it the "most extensive" is a bit unusual.
Response: We agree with the referee and specified that it is the first data set on the organic SML for the upwelling region off Peru and the first data set for gel particles in EBUS so far.

Referee: Page 10583**,** Line 16: The withdrawal rate of 20 cm/s by Harvey and Burzell (1972) has been revised by Carlson (1982) to 5-6 cm/s. As clearly shown by Carlson (1982) fast withdrawal rates collects thicker layers, and his revised rate of 5-6 cm/s correspond to a thickness of about 50-60µm. Zhang et al. (2003) showed experimentally that the SML has a typical thickness, although varying with sea state, of 60µm. The methodological flaw of Engel's and Galgani's study causes underestimations of enrichments as bulk water probably diluted collected SML.
Carlson, D. (1982). A field evaluation of plate and screen microlayer sampling techniques. Mar. Chem. 11, 189-208.
Zhang, Z., Cai, W., Liu, L., Liu, C., and Chen, F. (2003). Direct determination of thickness of sea surface microlayer using a pH microelectrode at original location, S China Ser. B, 46, 339–351.
Line 1: The formula represents the thickness of the collected water layer, not necessarily thickness from SML. There is no formula to calculate the thickness of the dynamic SML, even though it is assumed to be in a range of 40-100µm depending on sea state.
Zhang et al's study (2003) supports it by lab experiments.
Response: Sampling the SML has been and still is conducted with different techniques, at different withdrawel rates, and in different environments (in the lab, from shore, at open sea), leading to a range of estimated sampling SML thickness in the literature. For the glass plate approach many factors have been shown to influence the thickness of the SML besides the withdrawel rate, such as the time of dripping after withdrawel of the plate and glass plate dimensions. Galgani and Engel (2013) showed that also organic matter accumulation leads to a thickening of the SML. Hence, even at lower withdrawel speed the SML thickness can vary. Hatcher and Parker (1974) estimated a SML thickness of ~22 µm for a withdrawal rate of 6-7 cm s-1, as compared to the 60-100 µm sampled at 20 cm s-1 by Harvey and Burzell (1972). This is in accordance with observations by Zhang et al. (1998) showing a SML thickness of 50-60 µm for 20 cm s-1, while a withdrawel rate of 5-6 cm s-1 in their study yielded an SML thickness of 10-20 µm. We added a paragraph to the discussion section: 3.2. SML properties and organic matter accumulation, where we deal with the influence of withdrawel rate on SML thickness in more detail.
There is currently no unique standard method or standard withdrawel rate to sample the SML. There is also no method to determine the 'real' SML thickness in situ. Hence, the thickness of the sampled SML has to be determined for each study individually. This was done in our study and the calculated SML thickness of 49±8.9 µm (n = 39) makes our results well comparable to earlier findings obtained for SML of similar thickness and is well within the range of SML thickness reported for glass plate sampling (20-100µm). The determined SML thickness is in good accordance with previous studies sampling with the glass plate at the same rate of ~20 cm

s-1 (e.g. Zhang et al. 1998, Galgani and Engel 2013). We will refer to it as the apparent sampling thickness in the revised version.

For field research, it is nearly impossible to sample the SML manually from a shaking zodiac at open sea with an exact rate. On the other hand, it has also been shown that long sampling times bear the risk of organic matter alterations (Kuznetsova et al., 2004). The aim of this study was to compare SML properties from 39 stations in the Peruvian upwelling region. Therefore, it is important that the sampling procedure is the same at each station and the sampled thickness is comparable. This was well achieved. The referee comment that our SML sampling is flawed is therefore unjustified.

Referee: Line 14: Authors analyzed TOC/DOC according to Sugimura and Suzuki (1988), but Suzuki (1993) retracted the paper as their method produced erroneous data (shown by Benner and Strom, 1993). I am surprised seeing a citation to Sugimura's and Suzuki's paper. Despite some QA measures, no results are presented and calibration every 8-10 days seems with my experience inappropriate. I have to assume that TOC/DOC data in this study lack on accuracy.
Suzuki, Y. (1993). On the measurement of DOC and DON in seawater. Mar. Chem.
41, 287–288.
Benner, R., Strom, M. (1993). A critical evaluation of the analytical blank associated
with DOC measurements by high-temperature catalytic oxidation. Mar. Chem. 41,
Line 1: Again, calibration every 8-10 days seems inappropriate for the encountered
concentrations on TN and TDN.
Response: The high temperature combustion (HTC) method is a state of the art method for analyzing TOC/DOC in seawater. It was originally described by Sugimura and Suzuki (1988), and it is for this reason why it is listed as a correct reference, which is the case in many publications that apply this method. Doing so is in accordance with the rules of good scientific practice. Since the 1990's, the HTC method has been shown to give accurate results, provided that care is taken for determining instrumental blanks and conditioning of HTC columns; this was also emphasized by Benner and Strom (1993). As written in our method section, we determine MilliQ blanks on a daily basis as well as the instrument blank with the instrument blank checking program. Sample analysis was only started when the instrument blank was <1 µM C. On every measurement day, we also use Deep Sea seawater reference material (Hansell lab, RSMAS, University of Miami). Likewise, we apply two check standards with known DOC quantity in the range of the sample concentration. This way the validity of the system calibration (slope) is checked every time before sample analysis.
A new calibration of the system becomes necessary when the results for the daily standards fall out of a given range. If a system needs to be recalibrated often, it may indicate a potential instability of the instrument. By no means can the quality of our data be questioned by the interval time during two system calibrations. The same applies for TDN.

Referee: Line 8: The reported thickness of collected layer (50m) can't be right, not with the

fast withdrawal rate of 20 cm/s the authors applied here. The reported thickness corresponds to a withdrawal rate of 5-6 m/s. The authors should note that the cited paper of Cunliffe et al. (2013) refers to SML sampling guidelines clearly suggesting 5 cm/s as a rate.
Response: See comment above.

Referee: Page 10589 to 10592 A more through data analysis (e.g. multivariate analysis) would be beneficial to describe new insights into enrichment patterns. The presented coefficients represent a moderate correlation, but most of the findings in the current paper have been reported in the past, and it is not clear what the new results are.
Response: We correlate our data to wind speed and temperature as the main physical drivers for organic matter accumulation in the SML at the study site. It is a straightforward approach to understand how SML formation may be related to the upwelling of colder water or to wind speed as factor that disrupts the SML. We see no benefit in applying a multivariate statistical approach in this particular case.

Referee: Page 10596, Line 11: Lower TEP enrichment could be an artifact of fast withdrawal rates applied to the glass plate sampler. Line 15: How about losses of TEP, POC via increased sea spray? Line 17: Data on size distributions are not discussed.
And:
Page 10597, Line 8: Any reference to TEP enrichments in slicks?
Response: The withdrawel rate that we applied was not too fast; it yielded a sampling thickness comparable to earlier studies. Moreover, EF for TEP were not low everywhere but dependent on the wind field and station. We added a section to discuss the size distribution of gels in more detail.

Referee: Page 10597-10600, Both sections on effects of the SML on air-sea gas exchange and aerosol composition are well known, and extensively reviewed in the past (Liss and Duce, 1997; Cunliffe et al. 2013; Carpenter and Nightingle, 2015). These sections seem like afterthoughts without much discussion on own observation, and if so data are over-interpreted. For example, the statement “SML may play a particularly important role for exchange of relevant climate gases” is just a repetition of other recent studies and reviews (Salter et al., 2011; Cunliffe et al., 2013). So what is new here?
Response: We do not agree with the referee’s evaluation. The discussion of our observations includes many details and is well balanced. We specifically discuss how the observed enrichment of specified organic components in the SML may impact fluxes of climate relevant gases like N2O that are emitted from the sampled OMZ region off Peru. Sentences like the one noted by the referee are to facilitate an introduction of the topic to those readers who are not familiar with the potential role of the SML in air sea interactions. To the best of our knowledge this is the first discussion on the role of SML for gas exchange and aerosol production in EBUs.

Referee: Table 3: The column heads are wrong as no temperature or wind speed are presented,

but correlation coefficients.
Response: WE specified the column heads to indicate that the correlation coefficients for temperature and wind speed are shown.

Referee: Figures 2,4 and 5: Are over interpreted by the knitting algorithm. What settings in ODV have been applied?
Response: We added the detail to explain what OVD settings have been used for spatial interpolation of our data.

Referee: Figure 6: The y-axis needs to be revised to make it more readable. Why the authors do not presented POC enrichments. POC is known to be well enriched.
Response: The figure has been revised (larger font size, grid lines) to make it more readable. POC enrichment factors were added.

Referee: Figure 7: Why does Figure 7b contain much fewer data points than Figure 7a? I understand that the authors measured each parameter at every station
Response: As explained in the legend of this figure, figure 7b only shows Enrichment Factors for TEP for samples collected at similar water temperature. Thus 7b is a subset of 7a and therefore has less data points.

Response to referee 2 (Michael Cunliffe)

Referee: Engel and Galgani present a detailed data set collected from the SML and underlying waters in the upwelling region off Peru. The data provided add to our understanding of the structure and potential function of the SML. The key finding is the obvious link between increased upwelling-induced biological activity and enrichment in the SML.

I have a few very minor edits that should be addressed before final publication.

Abstract – the abstract is well written but it must also include a summary of the major findings and conclusions.

Response: We have fully revised the abstract to include a summary of major findings.

Referee Page 10581 L 19 "Processes determining organic:::." this statement needs a reference.
Response: Reference was added

Referee Page 10582 L 11 change sentence "all long the year.." this does not make sense.
Response: Revised in the new version.

Referee Page 10582 L 21 change sentence "drove our attention.." again, this does not make sense.
Response: Revised in the new version.

Referee Page 10591 your conclusion about the inverse relationship between temperature and organic compounds – is this a direct temperature effect or the effect of the upwelling system? I suspect the latter but please clarify.
Response: Revised in the new version.

Response to anonymous referee #3

Referee: ‘This manuscript presents data for a range of biogeochemical parameters collected from the surface microlayer (SML) and the water immediately below (UWL) from the Eastern Tropical South Pacific. The authors attempt to use the data they collected to argue that their presence or absence will impact air/sea gas exchange in this region. However no firm conclusions are reached and a number of the findings are lacking convincing evidence. Indeed the main focus of this paper is on particles (TEP and CSP) which would appear to have no direct influence on air/sea gas exchange based on the data presented. The manuscript contains a lot of unsupported speculation and this in part arises from missing data on some key parameters (surfactants, nutrients, chlorophyll etc) and the lack of information on the analytical precision and accuracy of the data that was measured (no information on standards, CRMs etc). There is also no appraisal of the biases that using a glass plate for sampling the SML might lead to, this is not to say this type of sampling should not be performed but to explain to the reader the potential chemical and physical reasons why a bias might occur.’

Response: The referee’s evaluation focuses only on one aspect of our study, i.e. the role of the microlayer on gas-exchange. It is a misunderstanding that the main focus of our publication is on the role of TEP and CSP on gas exchange. In fact, the main aspect of our publication is the accumulation of different dissolved and particulate organic matter components in the highly productive upwelling region off Peru and their relationship to environmental parameters such as wind speed and temperature. We further discuss implications of our findings on air- sea exchange processes including gas exchange (both direct and indirect), where we mainly discuss known surfactant substances such as carbohydrates and amino acids as well as consequences for primary aerosol formation; here we mainly discuss the potential role of TEP and CSP. Since there have been no previous studies on the role of organic matter in the SML for air-sea gas and particles exchange in such oceanic region, we discussed potential implications of our findings based on data and previous literature. We would not define our results as “unsupported speculations”. This interpretation is unjustified.

Referee: Air-Sea Gas exchange (1) – Influence of particles on exchange rates
The focus of this paper at present is on TEP and CSP both of which are particles, thus it is hard to see how particles at such low concentrations can influence the air/sea gas exchange which is the theme of this paper. While the concentrations of TEP and CSP may be influenced by processes that also impact air/sea gas exchange neither of them has ever been identified as a controlling mechanism on flux rates as it is the surface film on the microlayer that is key there.

Response: As mentioned above, the topic of our study was an investigation of the accumulation of organic components in the SML and potential implications for air-sea exchange; not the role of gel particles in gas exchange. Having mentioned this, the fact that there are currently no studies on the effect of gels on gas exchange does not mean that there is none. Future studies may test such a hypothesis.

Referee: Air-Sea Gas exchange (2) – Other parameters of relevance
'The manuscript present no data on either primary productivity or total chlorophyll concentrations along the transects, additionally there are also no measurements of nutrients (either for the SML or ULW). Thus there is no data to support any claims about the productivity of one site versus another.' While it is noted that there are data for picoplankton, it should be remembered that diatoms make up the bulk of the phytoplankton in the productive regions and they are not included in the flow cytometry data.
Response: We use temperature as an indicator for upwelling of cold water along the Peruvian coast. Differences in organic matter production were derived from several measurements of organic matter including organic carbon, picoplankton abundance and semi-labile (fresh) organic matter such as carbohydrates and amino acids. Strong horizontal differences in organic matter concentration were revealed with highest values consistently observed at the upwelling site, leading us to conclude that there is high biological production at this site. Observations on organic matter concentrations are well suited to infer the productivity of a system. Nevertheless, our observation agree well with nitrate distributions and Chl a concentrations as published elsewhere for this cruise (Arévalo-Martínez et al. 2015; Nature Geoscience, 8, 530–533; Hu et al., BGD, 2, 7257–7299, 2). We refer to these publications in the revised version.

The referee moreover states that the lack of data on a variety of parameters such as Chl a, nutrients, diatoms, surfactants and bacteria on gels weakens this publication. We agree that it would have been nice to do more, but due to Zodiac time constrains and manpower we were limited to those parameters that we found most relevant to link water column organic biogeochemistry to SML characteristics.

Referee– 'Relevance to the Peru region Importance in Peru region for atmosphere VOCALS and VAMOS experiments in the same region (Chand et al., 2010; Garreaud et al., 2011; Hawkins et al., 2010; Wood et al., 2011; Yang et al., 2011).'
Response: 'We will address suggested previous findings for the study region where appropriate. However, we do not intend to give a review of previous studies on air-sea exchange as this lies beyond the scope of this publication.'

Referee: 'The authors should be aware of the limitations of using a glass plate for sampling the microlayer and that by using such a device they are operationally defining the SML. Additionally the physical and chemical properties of the glass plate will have a strong impact on the results – it isn't straightforward comparing sampling from a bottle below the SML with what is recovered from a glass plate.

The actual physical thickness of the SML depends on how you define it chemically. While recent measurements based on pH microelectrode measurements (Zhang et al., 2003) have place it at around 50μm and this has been taken up as a standard definition (Wurl and Obbard, 2004), other techniques have indicated that there may be present an organic layer only a few nm thick (Laß and Friedrichs, 2011; Laß et al., 2010). The implication is here that while the glass plate may recover a volume equivalent to a 50μm SML this may

overestimate the organic SML and lead to it being diluted with UWL. Thus it should always be remembered that these measurements are operationally defined.'
Response: The referee is correct that the definition and interpretation of field data are ultimately linked to and limited by the sampling strategy. This is especially true for the microlayer as different devices sample different SML thickness. We will address this concern in the revised version and explain that we define the SML operationally. It has to be emphasized though that the nano-layer (monomolecular layer) is different from the microlayer, the latter being in the focus of this study. Organics matter concentration in the SML may be underestimated by dilution with underlying water. This is taken into account by the calculation of enrichment factors. We used the glass plate to sample the upper 50µm, because for this defined SML we can compare our data to previous publications.

Referee: The authors are also referred to the recent work on the storage of such samples (Schneider-Zapp et al., 2013).
Response: Schneider-Zapp et al- 2013 investigated different storage procedures specific for CDOM and SAS samples. We do not present such data in this study.

Referee: Other users of glass plates have used much slower withdrawal speeds (e.g. 5-6 cm s-1 (Wurl et al., 2011) as the withdrawal rate is apparently related to the sampling thickness (Zhang et al., 1998). Comparisons between samplers also indicate that the glass plate is not ideal for bacterial sampling, with either metal screen (GarcÄsÌ Ąa-Flor et al., 2005) or polycarbonate filters proving more effective (Cunliffe et al., 2009). It is well known in this field that there is a sample bias depending on the type of sampler employed (Agogue et al., 2004) and this information needs to be better relayed to the reader in the manuscript.
Response: We will address the potential bias of different sampling strategies in the revised version. However, we want to emphasize that there is no current consensus on which sampling strategy is best suited, e.g. for bacteria. Stolle et al. (2009, 2011) used the glass plate approach for a large survey on bacterial abundance, activities and community composition and observed that the glass plate approach is not inferior to other sampling devices. Many reviews on pros and cons of different sampling devices have been published and are summarized in the 'Guide to best practices to study the ocean's surface'. We will refer to this work rather than reviewing the literature in this study.

Stolle, C. et al. (2009). Bacterial activity in the sea-surface microlayer: in situ investigations in the Baltic Sea and the influence of sampling devices. AQUATIC MICROBIAL ECOLOGY, 58, 1: 67-78

Stolle, C. et al. (2011). Bacterioneuston Community Structure in the Southern Baltic Sea and Its Dependence on Meteorological Conditions. APPLIED AND ENVIRONMENTAL MICROBIOLOGY, 77, 11: 3726-3733.

Referee: In the case of TEP there is still no study to my knowledge that has shown that the act of sampling by glass plate does not induce the formation of TEP. While it has always been assumed that there are no loss to the walls of sample bottles, one study (Zhou et al., 1998) did indicate that bacteria were lost to the walls and that TEP may also be lost to the

walls. Thus under the conditions of glass plate sampling with such a high surface area to volume ratio it is conceivable that this may induce particle aggregation, particularly with regard to the shearing motion of removing the plate vertically. These processes would be significantly reduced when a bottle is filled with water under the water.
Response: The referee speculates on a potential bias of the sampling method.

The referee referred to the study by Wurl et al. (2011). This study also showed that sampling the SML with a glass plate does not produce artefacts in TEP concentration and that the amount of TEP sticking to glass plate and glass bottle walls is negligible. (O. Wurl, L. Miller and S. Vagle, "Production and Fate of Transparent Exopolymer Particles in the Ocean," Journal of Geophysical Research, Vol. 116, 2011, Article ID: C00H13.) Given the low absolute concentration of polysaccharides in natural samples a generation of TEP by the act of sampling is unlikely. If the glass plate sampling would induce TEP formation, we would expect a clear enrichment of TEP in SML samples, particularly in those of high polysaccharide concentration. This was not observed. We will refer to the work of Wurl et al. 2011 in the revised version. In the revised version we also compared the slopes of size distributions between the SML and ULW. If sampling introduces a bias due to aggregation, we would expect higher slope values as more particles are shifted into larger size classes. This was not observed; the slopes were either the same or the SML slopes were steeper showing relatively more of the smaller particles. Moreover, we identified spatial differences in the slope ratio, which would be impossible assuming a random or one-directional bias by the method.

Referee: The manuscript currently lacks any information regarding the precision or accuracy of the analytical measurements, particularly pertaining to the amino acid and carbohydrate analyses. Thus at present it is not possible to gauge the analytical quality of this work and thus the validity of statements regarding enrichment or depletion in the SML.
Response: The analyses for amino acids and carbohydrates were performed with high accuracy according to published methods (Lindroth and Mopper (1979), Dittmar et al. (2009), Engel and Händel (2011)) that we referred to. We will include information on the used standards as well as on accuracy and precision in the revised version (amino acids, precision: 2 nmol monomer L^{-1}, accuracy standard deviation between replicate analysis of<5%; carbohydrates, precision 10 nmol monomer L^{-1} with accuracy: standard deviation between replicate analysis of<2%).

Referee: The Marine Nanolayer: Somewhat surprisingly, given the authors affiliations, they make no mention of the new technique (vibrational-sum frequency spectroscopy) for probing the nanolayer at the surface of the SML (Laß et al., 2013; Laß and Friedrichs, 2011; Laß et al., 2010). Including this in the overall introduction and discussion would help to explain further what is known about the SML and how it's composition differs vertically. Additionally the technique used in probing the nanolayer composition is also routinely used to look at the impact of different components on the air/water boundary (Meister et al., 2014; Schach et al., 2014). Similarly a different technique, cavity ring down spectroscopy, has suggested that the air/sea flux of halogens may be impacted by organic components in the microlayer (Hayase et al., 2012; Hayase et al., 2011).

Response: We will make reference to the nanolayer as part of the microlayer and new findings on organic components revealed in the nanolayer in the introduction of the revised version. However, we want to emphasize that the nanolayer was not scope of this study.

Referee: Earlier work (Liu and Dickhut, 1998) has shown that the effective SML measured by a glass plate decreases with wind speed. Other users of glass plates have used much slower withdrawal speeds (e.g. 5-6 cm s-1 (Wurl et al., 2011) as the withdrawal rate is apparently related to the sampling thickness (Zhang et al., 1998).

Response: There is currently no unique standard method or standard withdrawal rate to sample the SML. There is also no method to determine the 'real' SML thickness in situ. Hence, the thickness of the sampled SML has to be determined for each study individually. This was done in our study and the calculated SML thickness of 49±8.9 μm standard deviation (n = 39) makes our results well comparable to earlier findings obtained for SML of similar thickness and is well within the range of SML thickness reported for glass plate sampling (20-100μm). The determined SML thickness is in good accordance with previous studies sampling with the glass plate at the same rate of ~20 cm s-1 (e.g. Zhang et al. 1998, Galgani and Engel 2013). We will refer to it as the apparent sampling thickness in the revised version.

Referee: Bias of glass plate sampling at higher wind speed: 'Additionally the glass plate has been found to only be effective up to conditions below Beaufort 3 (Guitart et al., 2004) as the (Falkowska, 1999) ' and 'Glass plate sampling is only valid up to 3-5 m s-1 (Beaufort 3) (Falkowska, 1999; Guitart et al., 2004) so are the offshore stations subjected to a bias here? and 'Earlier work (Liu and Dickhut, 1998) has shown that the effective SML measured by a glass plate decreases with wind speed.' and 'Wind speeds of 7-9.2 ms-1 are above the usual threshold for using a glass plate (see above) are these measurements then an artefact of the sampling?' and other related comments.

Response: The statement that glass plate sampling is only valid up to 3-5 m s-1 is NOT supported by the references given by the referee. Guitart et al. 2004 did not investigate the effect of wind speed on glass plate sampling but referred in their methods to Falkowska 1999. Falkowska 1999 described for the Bay of Gdansk that the microlayer thickness sampled with the glass plate was larger when the wind speed was higher. This was a scientific result and was interpreted as a thickening of the SML due to higher upward transport of organics (by e.g. bubble adsorption) to the microlayer at higher wind speed (up to 8m s-1 above which the turbulence regime shifted, leading to a decrease in SML thickness).

Liu and Dickhut, 1998, did not use a glass plate, but worked with a teflon coated stainless steel rotating drum. They showed a decrease the SML thickness with decreasing wind speed for the Chesapeak Bay. This again was a scientific result.

There is no bias in the glass plate method itself at higher wind speed. All references given by the referee in this respect are are miscited.

Referee P10584, L6: Was the bottle opened and closed below the surface? Otherwise you will also be sampling the SML in part –this is why GO-FLO bottles don't open until they are at a safe depth below the SML, to avoid contamination from the surface
Response: Yes, the bottle for collecting ULW was opened and closed below the surface. We will provide a more detailed description of sampling in the revised version.

Referee: P105998, L24: The study by Cao et al. (2014) was performed in the absence of water and is investigating gas/solid phase interactions! – given the zwitterion nature of amino acids it is very unlikely that such 1:1 complexes would be formed in seawater. Thus the speculations in the rest of the paragraph are not supported by any evidence and should be removed.
Response:P105998, L24: Cao et al. (2014) report an elemental study involving infrared spectroscopic experiments and quantum chemical calculations on interactions of N2O with phenols, suggesting a possible important role of N2O in biological processes by binding to the phenolic groups of tyrosine and phenylalanine. Although experiment cannot be directly translated to our setting, it provides interesting ideas to be tested in the field for the interactions of N2O with biological macromolecules. Cao and colleagues found π non-covalent interactions between N2O and phenols. Non-covalent interactions are very important in biological processes, as they determine the structure of macromolecules such as proteins and DNA. These interactions do not depend on positive or negative charges on the zwitterionic amino acids but on interactions of π-electrons of the aromatic group (phenol) with N2O. We therefore do not understand the referee's comment. However, we will rephrase this paragraph to better explain the potential interactions between N2O and phenolic groups of amino acids and to indicate that this would need further investigations.

Referee: Fractal dimension: The parameter D1 is not used in any specific context nor adequately explained it is therefore difficult to see the reason why it is calculated here and how it helps to explain or understand any of the processes being discussed here. Either use it or lose it.
Response: the revised version, better explain why the fractal dimension has been calculated in this study.

Referee: P10582, L18: There is no mention here of the importance of these fluxes to the atmospheric chemistry of the region – see the general comment on this above. P10583, L14:
Response: We gave reference to the VAMOS and VOCALS experiment to the introduction.

Referee: What type of silicate glass? Most glasses are silicate but there are important chemical and physical differences between quartz and borosilicate for example. Please provide more detailed information on this.
Response: We added that we used borosilicate glass in this study.

Referee: P10583, L16: How was the rate controlled? What was the variability in the withdrawal rate? As noted above the withdrawal rate is an important aspect of the operational definition of the SML here (Zhang et al., 1998).
Response: The rate was estimated by measuring the time of withdrawal. Variability was asses for the SML thickness, which was <10% standard deviation of the mean.

Referee: P10583, L18: You mean upwind of the vessel?
Response: Yes; changed in the revised version.

Referee: P10583, L25: From where and how was this seawater obtained? This is important for cross-contamination of the samples.
Response: Given in the revised version.

Referee: P10584, L2: It needs to be stated that this is an operational definition of the SML it is not a physical description (Zhang et al., 1998).
Response: Yes; changed in the revised version.

Referee: P10584, L6: Was the bottle opened and closed below the surface? Otherwise you will also be sampling the SML in part – this is why GO-FLO bottles don't open until they are at a safe depth below the SML, to avoid contamination from the surface.
Response: Yes; changed in the revised version.

Referee: P10584, L15: The current citation (Sugimura
and Suzuki, 1988) does not reflect the state of the art and in particular the work that went in to solving the problem of the blank with this method (Peltzer et al., 1996; Sharp et al., 1993a; Sharp et al., 1995; Sharp et al., 2002; Sharp et al., 1993b; Suzuki et al., 1992). So to be consistent with the best practice it would be better to update this citation to one of those that utilized the corrected method.
Response: There were many improvements of the original method described by Sugimura and Suzuki, 1988. We added all details that are necessary to solve the 'blank' problem and to achieve reliable data, including CRM.

Referee: P10585, L25: Were any standards or CRMs run for the amino acids? How was the concentration in seawater determined?
Response: Yes; described in the revised version.

Referee: P10586, L10: As above, were any standards or CRMs run for the carbohydrates? How was the concentration in seawater determined?
Response: Yes; described in the revised version.

Referee: P10586, L21:
How were the errors determined in these measurements? How can the reader assess if there are significant differences between the values.
Response: Yes; described in the revised version.

Referee: P10586, L23: How can it be constant if the value depends on N? As dN is a variable here, please clarify this description. (i.e. did you mean proportional to N or dN). I am aware that the definition in the original paper is similarly badly worded (Mari and Kiørboe,

1996). The point is that if it is dependent on N then it is dependent on the volume being analyzed.
Response: We are not sure if we understand the referee's point. N is the cumulative number of particles per water volume. dN is the number of particles per unit water volume in the size range dp to (dp + d(dp)). 'k' is the constant in the power law function dN/d(dp)=kd-d. We clarified that N is the total number per unit water volume; hence N is standardized to volume.

Referee: P10587, L4: What is the purpose of this parameter? It is a little unsatisfactory that it is from unpublished data that is referred to in another work. There are other studies that have determined the fractal dimensions of particles (Li et al., 1998).
Response: see response above.

Referee: P10587, L7: Please provide information on how errors were estimated for these parameters.
Response: Data fits to the function were very well described for each sample with $r^2>0.90$, yielding a standard error of <20%.

Referee: P10587, L22:
How were Prochlorococcus cells distinguished from bacteria in this work? Presumably Prochlorococcus was abundant but only had very low amounts of chlorophyll.
Response: We specified that heterotrophic bacteria were clearly distinguished from photosynthetic prokaryotes (e.g. Prochlorococcus) by their signature in a plot of red fluorescence (FL2) versus green fluorescence (FL 1).

Referee: L23: Glass plate sampling is only valid up to 3-5 m s-1 (Beaufort 3) (Falkowska, 1999; Guitart et al., 2004) so are the offshore stations subjected to a bias here?
Response: This statement is unsupported, see response above.

Referee: P10589, L10: This is a purely operational definition and is dependent on the withdrawing speed (Zhang et al., 1998) and sampling device (Falkowska, 1999), thus it would be helpful to the reader here if the authors explained this further.
Response: We added information on the relationship between SML thickness and withdrawal speed.

Referee: P10589, L20: Does this include Prochlorococcus?
Response: See response above
Referee: P10589, L25: Does this number include misidentified Prochlorococcus?
Response: See response above

Referee: P10590, L15: Was the DHCHO really determined to this level of precision (implies 1 in 2668)?
Response: We adjusted the numbers according to the precision level.

Referee: P10592, L2: This statement is not supported by any evidence

as there is no information about the loss rate from particles and the comparison being made is amino acids to carbohydrates.
Response: Sentence was removed.

Referee: P10591, L4-6: Please clarify here what is being compared; in one sentence it is the sum of the particle surface areas, in the other it is apparently numerical abundance? Which is the better measure of TEP or CSP?
Response: We revised this paragraph to clarify when area and when abundance is used for comparison.

Referee: P10591, L21: Though temperature itself is a proxy for upwelling/productivity so the correlation could just have easily been with dissolved nutrients (see general comment above).
Response: Nutrients can be utilized fast and may not be a reliable indicator for upwelling. In addition to temperature we therefore also compared data on 3He/4He disequilibrium (Steinfeldt et al., 2015), allowing for a very accurate measurement for upwelling.

Referee: P10592, L14-17: Wind speeds of 7-9.2 ms-1 are above the usual threshold for using a glass plate (see above) are these measurements then an artefact of the sampling?
Response: This statement is unsupported, see response above.

Referee: P10592, L20: The lack of enrichment could also indicate that the operational system employed was not sampling just the SML but also the ULW – see the general comment on this above.
Response: This is speculative. We compare data that were obtained with the same method within this study and in previously published studies. The 'lack of enrichment' is a scientific result.

Referee: P10592, L26: This could also indicate a lower recovery of bacteria using a glass plate as has been observed previously (Cunliffe et al., 2009).
Response: This is speculative. We do not find a lower recovery in other particulate measurements (e.g. gels). Stolle et al tested different sampling techniques and did not find a bias when using the glass plate.

Referee: P10592, L28: Or as above it could just mean the glass plate does not collect particles as well as a bottle.
Response: See response above

Referee: P10593, L5: How was the error calculated here? What was the number of samples used to calculate this value? Regards the error term if the value of d ranges from -2.63 to -1.38 what was the mean value? This is a somewhat odd parameter as it doesn't vary very much due to the parameterization, so what is the value of using it?
Response: The slope of size distributions is a valuable value and of widespread use in particle dynamics. We give more detail in the revised version, as well as the number of samples.

Referee: P10593, L13: Given the equation used to estimate D1 this could have been predicted from the onset, so what is the relevance of this?

Response: See response above

Referee: P10593, L19: Again this could be a sampling issue due to issues with glass plate sampling under higher wind speeds.
Response: See response above

Referee: P10594, L15: So why do we need to sample the SML if the UWL is easier to sample and shows the same horizontal trends. Also the reason why they may be the same is that the glass plate samples contain both SML and UWL.
Response: We show that not all components in the SML are related to the ULW. Moreover, the relationship to the ULW does not tell the EF. Therefore, SML needs to be measured independently.

Referee: P10595, L5: If the turnover times are so short then how does sampling only during the day impact the results? Presumably there could be a strong diel cycle for these amino acids?
Response: Could be, but it is not possible to sample in open sea from a Zodiak at night.

Referee: P10595,
L10: As noted earlier this result could be simply due to the glass plate undersampling bacteria.
Response: See response above

Referee: P10595, L13-20: This explanation seems a bit of a stretch given the authors provide no information on the instantaneous UV-B conditions encountered during this expedition and thus this section should be removed. If the authors do have such data then they should use it, the data provided in Table 3 should also state if the data is for the whole cruise or just for the sampling periods. If the latter is the case, then it should include the time frames and times of sampling.
Response: Data on light and instantaneous UV-B radiation were given in table 1. It was stated that the data were obtained during the M91 cruise. We will add the information that the data are given as average for the date of sampling at the respective stations.

Referee: P10595, L27: (sp) sea P10595, L10:
Again the sampling method may also explain these results (Falkowska, 1999).
Response: See response above

Referee: P10596, L6: By this mechanism the insertion of a glass plate would also facilitate the production of TEP.
Response: This is a speculation of the referee and not supported by our findings.

Referee: P10597, L7: This is highly speculative and unlikely as there is unlikely to be enough amino acid present to form a monolayer at the surface. Please rephrase or remove the latter part of this sentence.

Response: We assume that the referee was referring to P10599, L7? We removed this sentence.

Referee: P10597, L23: Please rephrase this sentence as dissolved organic matter also includes carbohydrates and amino acids so it is not an independent variable here. Additionally the way the sentence is written it implies that dissolved carbohydrates and amino acids have been shown to impact kw – there is no evidence for this to date. It is only for CDOM in general.
Response: Sentence was changed to : '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).'

Referee: P10598,L8: What is meant by a discontinuous concentration? Do you mean a strong gradient across the SML? Please rephrase this.
Response: Passage has been revised.

Referee: P105998, L24-28: An amino acid is described as phenilanine – there is no such amino acid – I can only assume the authors are referring to phenylalanine. This should be corrected throughout the manuscript.
Response: Yes, changed accordingly.

Referee: P10599, L19: Please see also the recent work published in Nature this year on aerosol production (Wilson et al., 2015).
Response: We added a reference to Wilson et al. 2015.

Referee: P105600, L2-16: These two paragraphs don't actually address anything specific with regard to organic aerosol production and therefore could simply be removed.
Response: Paragraphs have been revised.

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~~, and central to a range of global biogeochemical and climate-related processes.~~. 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. ~~Among these organic compounds, primarily of plankton origin, are dissolved exopolymers, specifically polysaccharides and proteins, and gel particles, such as Transparent Exopolymer Particles (TEP) and Coomassie Stainable Particles (CSP). These organic substances often accumulate in the surface ocean when plankton productivity is high. Here, we report results obtained~~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 ~~from the SML and from ~20 cm below, and were analyzed for polysaccharidic and proteinaceous compounds, gel particles, total and dissolved organic carbon, bacterial and phytoplankton abundance.~~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

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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)~~(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~~transparent exopolymer particles (TEP) of polysaccharidic composition, and Coomassie ~~Stainable~~

~~Particles~~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, known as transparent exopolymer particles (TEP), were attributed mainly to phytoplankton exudation (Passow, 2002), while the production of protein-containing gels, such as coomassie stainable particles (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)~~(Chin et al., 1998; Engel et al., 2004; Verdugo et al., 2004) ~~or to the deep ocean (Passow, 2002).~~

. 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 ~~dynamics~~abundance in the water-column ~~(Bigg et al., 2004; Gao et al., 2012 ; Matrai et al., 2008~~(Bigg et al., 2004; Galgani et al., 2014; Gao et al., 2012; Matrai et al., 2008)~~; Galgani et al., 2014).~~. 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). Processes determining~~(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 ~~accumulation and~~ (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 ~~in the SML~~ and accumulation of organic matter may ~~be relevant for~~influence two ~~main processes that occur at the~~ air-sea interface ~~and are important~~processes necessary to understand oceanic ~~feedback~~feedbacks on ~~atmospheric dynamics~~the atmosphere: sea-spray aerosol (SSA) emission and ~~composition and~~ air-sea gas exchange ~~processes.~~(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~~(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 surface active substances (surfactants) in the sea surface microlayer,~~

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~~like biogenic material as polysaccharides and amino acids, 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).~~(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 ~~of the ocean~~ becomes of particular relevance for environments, where biological productivity is high like in coastal upwelling regimes.

~~The~~ Off Peru, the coastal upwelling ~~coastal~~ region ~~off Peru~~ extends between approximately 4°S and ~~about~~ 40°S. In this area, upwelling processes are sustained by winds ~~all along~~throughout the year but feature high inter-annual ~~ecosystem~~ variability induced by the El Niño-Southern Oscillation (ENSO) cycle ~~(Tarazona and Arntz, 2001).~~(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 (~~OMZs~~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).~~ (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)~~(Paulmier et al., 2008; Paulmier et al., 2011). Processes affecting gas exchange in these

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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.

~~During the SOPRAN cruise METEOR91 (M91), we drove our attention to organic matter components at the surface since properties of the SML may represent a major uncertainty for gas, heat and aerosol fluxes in this region. During our cruise, organic matter concentration and composition of the SML and the underlying seawater was studied on 39 different stations, providing the most extensive data set the SML 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).~~(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 ~~December~~ in 2012. The overall goal of M91 was to conduct an integrated

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biogeochemical study on the upwelling region off Peru in order to assess the importance of ~~oxygen minimum zones (OMZs)~~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.

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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).~~(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 ~~silicate~~borosilicate glass and had an effective sampling surface area of ~~2000cm^2~~2000 cm^2 (considering both sides). For each sample, the glass plate was inserted into the water perpendicular to the surface and withdrawn slowly at a ~~controlled~~ rate of ~~∼~~approximately 20 cm sec^{-1}. The sample, retained on the glass because of surface tension, was removed with the help of a Teflon wiper. Samples were collected ~~against wind direction~~as far upwind of the ship as possible and away from the path taken by the ship to avoid contamination ~~with the rubber boat~~

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~~and for~~. For each sample the glass plate was dipped and wiped about twenty times. The exact number of dips and the total volume collected were recorded. Samples were collected into acid cleaned (HCl, 10%) and Milli-Q washed glass bottles, and the first milliliters were ~~discarded and~~ used to rinse the bottles and then discarded. Prior to each sampling, both glass plate and wiper were washed with HCl (10%) and intensively rinsed with Milli-Q water. At the sampling site, both instruments were copiously rinsed with seawater in order to minimize any possible contamination with alien material while handling or transporting the devices.

The ~~SML~~apparent thickness (d~~, *m*)~~) of the layer sampled with the glass plate was ~~estimated~~determined as follows:

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

Where *V* is the SML volume collected, i.e. 60-140 mL, *A* is the sampling area of the glass plate (A = 2000 cm²) and *n* is the number of dips~~.~~ (Cunliffe and Wurl, 2014). We will use *d* (µm) as an operational estimate for the thickness of the SML.

At the same stations, after sampling the SML, about 500 mL samples were collected from the underlying seawater (ULW) ~~were collected~~ at ~ 20 cm depth by holding an acid cleaned (HCl 10%) and Milli-Q rinsed borosilicate glass bottle. The bottle was open and closed underwater to avoid simultaneous sampling of SML water. For safety reasons sampling for the SML from a rubber boat could be made only during daylight hours.

2.2 Chemical and biological analyses

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) ~~after Sugimura and Suzuki (1988).~~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 ~~for setting~~to determine the instrument ~~baseline, followed by the~~ blank, which was accepted for values <1 µmol C L^{-1}. TOC analysis was validated on every measurement ~~of deep-sea water~~day with ~~known DOC/TOC concentration (Dennis Hansell,~~ deep seawater reference (DSR) material provided by the Consensus Reference Materials Project of RSMAS~~, ~~ (University of Miami) ~~to verify results~~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).~~ (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

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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~~.~~

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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~~(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~~acetonitrile

(LiChrosolv, Merck, HPLC gradient grade) in ~~Sodiumdihydrogenphospate~~sodium-di-hydrogen-phosphate (Merck, suprapur) Buffer (PH 7.0~~),~~). Solvent B was ~~Acetonitrile~~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 ~~hydrolysable~~combined carbohydrates > 1 kDa (~~THCHO~~TCCHO and ~~DHCHO~~DCCHO), 20 mL were filled into pre-combusted glass vials (8 hours, 500 °C) and kept frozen at -20 °C until analysis. Samples for ~~DHCHO~~DCCHO were additionally filtered through 0.45 µm ~~Millipore~~Pall Acrodisc® syringe filters. The analysis was conducted according to Engel and Händel ~~(2011)~~(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.~~8~~4 M HCl final concentration, and neutralized through acid evaporation ~~(N$_2$, 5h, 50~~under vacuum and nitrogen atmosphere (1h, 60 °C) Two replicate samples were analyzed. ~~Particulate hydrolysable~~The retention of carbohydrates ~~(PHCHO~~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

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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 ~~THCHO~~TCCHO and ~~DHCHO~~DCCHO.

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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).~~(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~~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: ~~The size-frequency distribution of polysaccharidic and proteinaceous gels was described by:~~

(2) $$dN/d(d_p) = kd_p^{\delta}$$

$$\frac{dN}{d(d_p)} = kd_p^{\delta}$$

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).~~(Mari and Kiørboe, 1996). The factor k is a constant that depends on the total number of particles per volume, and δ ($\delta < 0$) describes the spectral slope of the size distribution. The value δ is related to the slope of the cumulative size distribution $N= ad_p^{\beta}$ 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~~). To determine δ, data for CSP and TEP were fitted~~) over the size range 1.05-14.14 µm ESD.

~~The fractal dimension (D1) was calculated based on δ the semi-empirical relationship (Burd and Jackson, unpublished data, as referred to in Mari and Burd (1998) as applied for TEP, previously (Harlay et al. 2009):~~

~~(3) *D*1~~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 ~ 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

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Formatiert: Schriftart: Nicht Kursiv 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):

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

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). ~~Yellow-green latex beads (Polysciences, 0.5 µm) were used as internal standard.~~ 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).

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2.2.7. Phytoplankton~~:~~

For ~~autotrophic~~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 ~~1 µm~~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:

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

Where (A) is the concentration of a given parameter in the SML or ULW, respectively ~~(GESAMP, 1995).~~(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). Average values are reported with ±1 standard deviation.~~ (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).

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3. Results

3.1. The physical environment

~~Coastal~~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~~) were recorded~~), 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} ~~(data from shipboard measurements on RV Meteor were retrieved from DSHIP software),~~ respectively, with no significant impact of SML organic matter accumulation.

3.2. ~~Organic~~ SML properties and organic matter ~~in the SML~~accumulation

~~The thickness of the SML calculated from glass plate sampling during this cruise ranged between 45 and 60 µm, with an overall mean value of 49± 8.89 µm (n=39). This value is in good~~

~~accordance with previous observations for the SML when sampled with a glass plate (Cunliffe et al., 2011; Cunliffe et al., 2013).~~

~~In general, concentration of organic components in the SML showed spatial distribution patterns resembling those of temperature and wind speed (compare Figures 3, 4, 5); highest values for nearly all components were observed at the upwelling stations 10_1 to 10_4, 14_1 and 14_2 and 15_1 to 15_3 (Figure 1).~~

~~Unless stated otherwise, all observations described in this paragraph relate to the SML.~~

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 thickness and wind speed (r=-0.11, n=39) or between SML thickness and temperature (r=-0.06; n=39).

Unless stated otherwise, all observations described in this paragraph relate to the SML. In general, concentration of organic components in the SML showed spatial distribution patterns resembling those of temperature and wind speed (Figures 3, 4, 5). Highest concentration values for nearly all organic components were observed at the upwelling stations 10_1 to 10_4, 14_1 and 14_2 and 15_1 to 15_3 (Figure 1) in accordance with high estimated primary production rates (Steinfeldt et al., 2015) and high Chl *a* concentrations (Hu et al., 2015) determined in surface waters at these sites during M91.

Phytoneuston abundances ~~ranged~~(<20 µm) varied between $3.7\text{x}10^{3}$ and $1.9\text{x}10^{5}$ mL^{-1} for ~~cyanobacteria~~cyanobacterial-type phytoplankton (CPL) (mainly *Synechococcus spp.*) and between $5.4\text{x}10^{3}$ and $3.0\text{x}10^{5}$ mL^{-1} for other ~~pico- and nanoautotrophs.~~non-cyanobacterial-type phytoplankton (NCPL). Generally, highest abundance ~~of nano- and picoautotrophs in the SML was~~ was determined on and close to the upwelling stations (Figure 4). On all other stations, cell abundance of ~~cyanobacteria~~CPL and ~~phytoplankton~~NCPL differed spatially, with higher abundance of ~~phytoeukaryotes~~NCPL at the southern stations and higher numbers of ~~cyanobacteria~~CPL at the northern stations (Figure 4). NCPL and CPL were closely related to cell abundance in the ULW (Table 3).

Heterotrophic bacteria were determined in abundances between $3.0\text{x}10^{4}$ and $8.5\text{x}10^{6}$ mL^{-1} with highest numbers observed at the upwelling stations and southeast of the upwelling (Figure

4). Heterotrophic bacteria in the SML were highly positively correlated to abundances in the ULW ($r=0.94$; $n=36$ $p<0.001$) and negatively influenced by wind speed, although less clearly ($r=-0.37$; $n=36$ $p=0.01$). No significant influence on heterotrophic bacteria abundance was 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 ~~between~~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 ~~DHCHO~~DCCHO and DHAA reached highest concentrations at the upwelling stations (Figure 5). Thereby, maximum concentration of ~~DHCHO~~DCCHO of ~~2668~~2670 nmol L^{-1} (mean: ~~1111~~1110±550 nmol L^{-1}) was observed at station 15_2, slightly south of the station 14_1 exhibiting highest DHAA concentrations of ~~2017~~2020 nmol L^{-1} (mean: 770 ± ~~359~~360 nmol L^{-1}) (Table 2). In general high ~~DHCHO~~DCCHO concentration was more focused to the upwelling, and exhibited strong horizontal gradients to the northern and southern stations.

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~~DHHA~~DHAA concentration was on average lower than ~~DHCHO~~DCCHO concentration (Table 2) and horizontal differences were less pronounced than for ~~DHCHO~~DCCHO. Both components of semi-labile DOC were inversely correlated to temperature (~~DHCHO~~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.

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Concentrations of ~~combined~~ carbohydrates and amino acid in particles, and in gels (i.e. TEP, CSP) in particular, were highest at the coastal upwelling stations also. Particulate carbohydrates and amino acids (~~PHCHO~~PCCHO, PHAA) were highly correlated to POC concentrations (~~PHCHO~~PCCHO: r=0.70, n=39, p<0.001; PHAA: r=0.81, n=30, p<0.001). ~~In contrast to the dissolved components, particles contained on average higher concentrations of amino acids compared to carbohydrates (Table 2), indicating a more rapid loss of DHAA after release from particles.~~

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

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3.3. Accumulation patterns in the SML

For almost all components investigated during this study, concentration in the SML was significantly related to the respective concentration in the ULW (Table 3). Thereby, correlations between SML and ULW were strongest for combined carbohydrates, particularly for ~~DHCHO~~DCCHO. Close correlations were also observed for bulk organic carbon measurements, i.e. TOC, DOC, and derived therefrom POC. For dissolved nitrogenous compounds, i.e. TDN, FAA and DHAA no relationship between SML and ULW concentrations ~~were~~was observed, suggesting that loss or gain of these compounds in the SML were faster than exchange processes with the ULW. 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 ~~DHCHO~~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 ~~underlying seawater (~~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 ~~free amino acids (~~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}. ~~For TEP as well as for CSP median EF varied around a value of one, suggesting that marine gel accumulation is spatially highly variable, and in our cruise marine gels did not generally become enriched in the SML.~~ Total and dissolved hydrolysable amino acids (THAA, DHAA) were enriched in the SML at almost all stations (Figure 6), with EF ~~of~~in the range 0.8~~-~~ - 4.6 (DHAA) and 0.4~~-~~ - 3.4 (THAA). Median EFs were 1.7 and 1.4 for DHAA and THAA, respectively. ~~Total and dissolved hydrolysable carbohydrates (THCHO, DHCHO) concentrations~~

Concentration of TCCHO, DCCHO in the SML were often similar to the ULW, with EF values ranging between 0.6 and 1.4 (~~DHCHO~~DCCHO) and between 0.3 and 1.7 (~~THCHO~~TCCHO), respectively.

In general, variability of EF was smaller for dissolved than for particulate organic compounds, suggesting differences in the accumulation dynamics.

In contrast to all ~~other~~ organic, chemical compounds, bacteria were found to be depleted in the SML at almost all stations (Figure 6), having a median EF of 0.8.~~ Variability of EF was generally smaller for dissolved components than for particulates, suggesting again differences in the accumulation dynamics.~~

3.4. Size distribution of gel particles within the SML

~~Abundance of polysaccharidic gel particles, i.e. TEP, decreased with increasing size according to the power law function given in eq. 1 (Figure 7). The slope, δ, of the size spectrum varied between -2.63 and -1.38, revealing an average fractal scaling exponent of TEP in the SML of $D1$=2.51±0.010. This value is close to 2.55 proposed by Mari and Burd (1998) for seawater TEP.~~

~~The~~Abundance of gel particles in the SML and ULW decreased with increasing particle size according to the power law function given in eq. 2 (Figure 8). The parameter δ describes the slope of the particles size spectrum. Lower values of δ indicate relatively higher abundance of smaller particles. Data fits to the function were very well described for each sample with $r^2>0.90$, yielding a standard error for δ of <20%. For TEP, δ varied between -2.63 and -1.38 (mean value: -1.86, SD: 0.27, n=39) for particles in the SML and between -2.25 and -1.25 (mean value: -1.70, SD: 0.30, n=39) for particles in the ULW. To compare the size distribution of TEP in the SML and the ULW, we calculated the slope ratio ($\delta^*=\delta_{SML}/\delta_{ULW}$) (Figure 9). Size distributions of TEP in the SML and ULW were generally quite similar yielding δ^*_{TEP} in the range of 0.78-1.42, with a median value of 1.1. Nevertheless, spatial differences were observed, with δ^*_{TEP} <0.95 at the more coastal northern stations and δ^*_{TEP} >1.1 more offshore at the southern stations (Figure 9). At the upwelling stations with high TEP abundance slopes of SML and ULW were very similar, yielding δ^*_{TEP} in the range 0.95 - 1.1. This showed a relatively higher abundance of 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 1.38x10^4 mL^{-1}, ~~while for~~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 1.46x10^4 and 2.33x10^5 mL^{-1}~~, suggesting that proteinaceous particles represent~~. 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 ~~a D1 value of~~ 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, $\delta*$, 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 $\delta*_{CSP}$. 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

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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.

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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 ~~(Figure 8b). But here, CSP >7 µm were rather increased in the SML at low wind speed compared to the ULW and to the high wind speed station~~ (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).

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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. ~~EBUS~~EBU'S are characterized by high biological productivity and strong across shelf gradients of organic matter concentration~~. Therefore EBUS~~ (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 SML towards the area of upwelling of colder, nutrient-rich deep water. Hence, increasing ecosystem productivity is one likely factor responsible for higher concentrations of organic components in the SML. Significant correlations ~~of~~between organic matter ~~concentrations~~concentration in the SML and in the ULW were determined and showed that the SML basically reflects the underlying seawater system. The close connectivity between ~~microlayer~~SML organic properties and biological development was also shown during a recent mesocosm study, indicating that ecosystem changes impact ~~microlayer organic matter composition and concentration (Galgani et al. 2014).~~SML organic matter composition and concentration (Galgani et al., 2014). Despite this finding that relates to a more general characteristic of the SML, clear differences in the accumulation behavior of different organic matter components were determined during this study and are in good accordance with previous observations. A generally higher SML accumulation was observed for amino acids compared to carbohydrates. Significant enrichment of amino acids in the SML has been determined previously for coastal as well as open ocean sites, and higher accumulation of FAA compared to DHAA and THAA, as also observed during this study, appears to be a consistent SML feature ~~(Henrichs and Williams, 1985; Carlucci et al., 1992; Kuznetsova and Lee, 2001; Kuznetsova and Lee, 2002; Kuznetsova et al., 2004; Reinthaler et, al. 2008).~~(Carlucci et al., 1992; Henrichs and Williams, 1985; Kuznetsova and Lee, 2002, 2001; Kuznetsova et al., 2004; Reinthaler et al., 2008). As for this study, wind velocity and temperature have not been identified as physical factors responsible for amino acid enrichment in the past ~~(Kuznetsova et al., 2004). FAA and DHAA are labile to semilabile substrates and taken up by heterotrophic microorganisms (Keil and Kirchman, 1992). Turn-over times of these components in the water column are usually in the range of minutes to days (Fuhrman and Ferguson, 1986; Benner, 2002).~~(Kuznetsova et al., 2004). FAA and DHAA are labile to semi-labile substrates and taken-up by heterotrophic microorganisms (Keil and Kirchman, 1992). Turnover times of these components in the water column are usually in the range of minutes to days (Benner, 2002; Fuhrman and Ferguson, 1986). The observed accumulation of FAA and DHAA in the SML may therefore be related to a reduced activity of bacteria. For different coastal Baltic Sea sites, Stolle et al. ~~(2010)~~(2009) determined a lowered bacterial biomass production in the SML, despite bacterial cell numbers being similar to those in the ULW. During M91 bacteria were mostly depleted in the SML compared to the ULW supporting the idea of the SML being an 'extreme environment' for bacteria. Earlier studies showed that some bacteria may be adapted to UV radiation in the SML as well as in the ULW ~~(Carlucci et al., 1985; Agogue et al., 2005). Amino acid consumption by bacterioneuston under UV-B stress may be reduced (Santos et al., 2012),~~(Agogué et al., 2005; Carlucci et al., 1985). Amino acid consumption by bacterioneuston under UV-B stress may be reduced (Santos et al., 2012), which may give an explanation for the higher concentrations of FAA and DHAA in the SML during M91. However, no significant correlation between bacterial abundance and UV radiation or between UV radiation and amino acid concentrations in the different pools ~~were~~was observed during this study, suggesting that at most stations history rather than instantaneous UV radiation ~~may be~~is if at all responsible for controlling bacteria and organic matter components in the SML.

~~In addition to ULW properties, wind speed~~SML thickness during this study was significantly related to TOC concentration, but not to wind speed. A thickening of the SML with increasing wind speed up to 8 m s^{-1} has been observed by Falkowska (1999) from samples collected in the Baltic Sea and explained by increased advective transport of organic matter to the SML, e.g. through bubble adsorption, at higher turbulence. During M91, accumulation of organic matter in the SML was higher at the upwelling stations where wind speed often was quite low. Hence, a higher source of organic matter in the ULW may have counterbalanced the wind speed effect.

Wind speed, however, was determined as a factor controlling accumulation of particulate material, in particular TEP, in the SML~~.TEP are marine gel particles that have been hypothesized to be neutrally or positively buoyant thanks to a high water content (Engel and Schartau, 1999; Azetsu-Scott and Passow, 2004).~~ in addition to the dynamics occurring in the ULW. TEP are marine gel particles hypothesized to be neutrally or positively buoyant thanks to their high water content (Azetsu-Scott and Passow, 2004; Engel and Schartau, 1999). TEP were moreover suggested to form within the SML, either by wind-shear induced aggregation of precursors or due to coalescence of pre-cursor molecules, primarily polysaccharides~~ when entrained air bubbles burst at the sear surface (Wurl et al., 2011).~~, when entrained air bubbles 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).~~(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 ~~(Wurl et al., 2011; Gao et al., 2012).~~(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).~~(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).~~(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 ~~(Logan et al., 1995; Engel, 2000; Chow et al., 2015).~~(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.

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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 systems can be quite different, e.g. TEP accumulate towards the end of phytoplankton blooms while CSP rather co-occur with maximum phytoplankton abundance ~~(Cisternas- Novoa et al., 2015; Engel et al. 2015). Moreover, the depth distribution of TEP and CSP was shown to be different for open ocean sites (Cisternas-Novoa et al., 2015).~~(Cisternas-Novoa et al., 2015; Engel et al., 2015). Moreover, the depth distribution of TEP and CSP was shown to be different for open ocean sites (Cisternas-Novoa et al., 2015). These spatial and temporal differences in the occurrence of TEP and CSP in the water column may explain the spatial separation of both types of marine gels in the SML observed during this study. However, the observed differences in relation to wind speed suggest that additional factors control the enrichment of TEP and CSP in the SML. It has been shown that CSP are less prone to aggregation than TEP ~~(Prieto et al., 2002; Engel et al., 2015).~~(Engel et al., 2015; Prieto et al., 2002). Similarly, CSP may be less involved in aggregation formation and sinking out of the SML at higher wind speed. Yet, ~~an inverse~~

~~relationship between the slope of the CSP size distribution in the SML and wind speed was observed during M91, showing~~similarly to TEP, larger CSP were observed in the SML at low wind speed~~. This suggests~~ suggesting that ~~CSP as well as TEP~~both kind of gels may be involved in slick formation that becomes disrupted when wind speed increases.

4.2. Implications of organic matter accumulation in EBUS

4.2.1. Air-Sea gas exchange

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Although the SML and surface active substances (surfactants) within are widely believed affecting the exchange of gases and heat at the air-sea interface ~~(Davies, 1966; Frew, 1997; Salter et al., 2011), particularly at lower wind speeds (Liss, 1983),~~(Davies, 1966; Frew, 1997; Salter et al., 2011), particularly at lower wind speed (Liss, 1983), we still have little quantitative knowledge on how natural organic components at the immediate sea-surface alter the gas transfer velocity in water (*kw*). Our data showed a depletion of the SML with respect to TEP and POC at wind speeds >5 m s^{-1}, suggesting that an effect of these ‘insoluble’ components on gas exchange 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.

~~More independent of wind speed was the accumulation~~Accumulation of dissolved organic components in the SML during M91~~. Dissolved~~ 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~~, like dissolved carbohydrates and amino acids,~~ (CDOM), have demonstrated surfactant properties and reduced gas transfer velocity in water (*kw*) at low wind speed in laboratory ~~experiments (Goldman et al., 1988; Frew et al., 1990).~~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)~~(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 ~~organic surfactant~~DOM particularly in upwelling regimes with high biological production and coastal wind shelter as observed during this study may have ~~had~~ an influence on gas exchanges rates as well.

~~Across the water-air interface, gases of climatic relevance exhibit different behaviors: methane (CH_4) shows a discontinuous concentration while carbon dioxide (CO_2) does not (Upstill-Goddard, 2006). CH_4 diffusivity across the SML has been proposed being mediated by SML bacteria, as possible sink (Upstill-Goddard et al., 2003) or source of this greenhouse gas (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 EBUS, high primary production and induced high aerobic remineralization associated with large scale circulation maintain the presence of OMZs (Gutknecht et al., 2013; Paulmier and Ruiz-Pino, 2009), which, in the last decades, have been expanding and intensifying due to enhanced stratification and reduced ventilation (Keeling et al., 2010; Stramma et al., 2008). Our study was intended to understand how organic matter accumulation in the SML might mediate the transfer rate of trace- and greenhouse gases like N_2O in oceanic regions like OMZs affected by a changing climate. In the case of N_2O, it has recently~~

~~been shown that it can interact with biological processes specifically by binding to aromatic groups present in certain amino acids like tyrosine and phenilanine (Cao et al., 2014). Tyrosine and phenilanine in the SML of our study represented a small molar percentage of total amino acids pool, with averages in the dissolved fraction (DHAA) of 1.5 ± 0.3 % (tyrosine) and 1.9 ± 0.3 % (phenilanine), and in the total fraction (THAA) of 2.2 ± 0.2 % (tyrosine) and 2.9 ± 0.4 % (phenilanine), but were present. As we found evidence of overall amino acids SML accumulation during our cruise, for those amino acids in particular the median EF both in the total (THAA) and in the dissolved (DHAA) fraction was > 1, suggesting a possible interaction of SML organic components with~~ ~~N_2O~~ ~~in the coastal upwelling region off Peru. In details, median EF for tyrosine was 1.5 (both THAA and DHAA) and for phenilanine we found a median EF = 1.3 (THAA) and EF = 1.7 (DHAA). Amino acids enrichment in the SML has been previously reported (Kuznetsova and Lee, 2002; Kuznetsova et al., 2004; van Pinxteren et al., 2012; Cunliffe et al., 2013; Henrichs and Williams, 1985), and might be due to high surface-active properties because of zwitterionic characteristics of the molecules, probably creating a rather stable layer even at higher wind speeds, thus representing an important barrier for air-sea gas exchange.~~

~~Overall, our results showed that accumulation of organic substances occurs in EBU's and is related to the increased productivity.~~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 Ruiz-Pino, 2009), which, in the last decades, have been expanding and intensifying due to enhanced stratification and reduced ventilation (Keeling et al., 2010; Stramma et al., 2008). During M91, N_2O concentration in surface waters was highly supersaturated at the upwelling sites and in particular at station 14_1 (Arevalo-Martinez et al., 2015). Although a direct influence of organic matter in the SML on gas-exchange was not investigated during M91, it can be assumed that the high enrichment of organic components in the SML observed the upwelling sites was one factor contributing to N_2O supersaturation.

Our study was intended to understand how organic matter accumulates in the SML, which might mediate the transfer rate of trace- and greenhouse gases such as N_2O in oceanic regions like OMZ's affected by a changing climate. A recent laboratory study reported π non-covalent interactions of N_2O with phenols, suggesting a possible important role of N_2O in biological processes by specifically binding to phenolic groups as those of the amino acids tyrosine and phenylalanine (Cao et al., 2014). Tyrosine and phenylalanine in the SML of our study represented a small molar percentage of total amino acids pool (data not shown), but were present. As we found evidence of overall amino acids SML accumulation during our cruise, for those amino acids in particular the median EF both in the total (THAA) and in the dissolved (DHAA) fraction was > 1, suggesting a possible interaction of specific SML organics with N_2O in the coastal upwelling region off Peru. Although the experiment conducted by Cao and colleagues cannot be directly translated to our setting, it provides interesting ideas for the interaction of N_2O with biological macromolecules worth further investigation.

Overall, our results showed that accumulation of organic substances occurs in EBU's and is related to the increased biological production. Hence, the organic SML may ~~be~~ play a particularly important role for exchange of climate relevant gases that are associated to high organic matter production and resulting anoxia in upwelling systems like the one off Peru.

4.2.2. Organic aerosol production

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The structure of sea-spray aerosols (SSA) originating by bubble bursting at the sea surface is a function of biological, chemical and physical properties of the SML, which may comprise a vast array of organic surface-active compounds, microorganisms, and exopolymer gels ~~(Leck and Bigg, 2005; Quinn and Bates, 2011)~~(Leck and Bigg, 2005; Quinn and Bates, 2011; Wilson et al., 2015). Despite recent evidences showing that high levels of chlorophyll-*a* are not directly related to the organic carbon content of SSA ~~(Quinn et al., 2014)~~(Quinn et al., 2014), still organic SSA largely derive from the oceanic surface layer and therefore are also subject to the effects of climate change on marine systems ~~(Andreae and Crutzen, 1997).~~(Andreae and Crutzen, 1997). Polysaccharides and polysaccharidic nanogels ~~(Russell et al., 2010; Orellana et al., 2011)~~(Orellana et al., 2011; Russell et al., 2010) as well as particulate amino acids and proteinaceous compounds ~~(Kuznetsova et al., 2005)~~(Kuznetsova et al., 2005) are present in organic SSA particles. During ~~our cruise~~M91, we found a ~~distinct behavior of dissolved and particulate compounds, the first being rather enriched in the SML (as also shown by median EF for DOC) but mainly composed of amino acids contributing to an~~ different accumulation ~~of proteinaceous material quite independently of the wind speed, as opposed to carbohydrates that had similar concentrations in the SML and ULW. Particulates compounds instead, like~~ behavior of TEP and CSP~~, did not preferentially accumulate in the SML, inferring to other processes determining their production and aggregation dynamics.~~ in the SML. TEP showed a close inverse relationship to wind speed, being depleted in the SML above 5 m s^{-1}, while ~~the SML concentration of~~ particulate proteinaceous compounds (CSP) ~~did not. As determined by the slope δ of the size distribution spectra for both TEP and CSP, the less negative is δ, the larger is the fraction of marine~~ accumulated independently of wind speed. Submicron gels ~~comprising bigger~~

~~particles, revealing that CSP were generally larger than TEP. In the light of these observations, these accumulation patterns~~embedded in sea spray may ~~suggest a compositional~~represent an important source for primary organic ~~matter partitioning~~aerosols in the ~~SML that differently affects the processes at the air-water interface relevant for climate.~~

more offshore wind exposed regions. TEP as well as dissolved polysaccharides include sugars with carboxylic groups such as uronic acids and may contribute to the relatively high fraction of carboxylic acid that was observed in the organic matter component of marine aerosols (Hawkins et al., 2010). In the upwelling region off Peru the wind-driven export of polysaccharidic components to the atmosphere thus might represent a loss-pathway of these organic compounds from the SML that would then contribute to a larger extent to the organic SSA mass. ~~Instead, amino acids and proteinaceous~~Proteinaceous compounds, including CSP, are probably more stable at the sea surface ~~exerting their influence on air-sea gas exchange by capillary wave damping.~~

~~This characteristic might be valid for many oceanic regions. EBUS~~ and ~~OMZs are special systems with high level of productivity and degradation rates, so it might be difficult to attribute specific organic sources to the processes controlling air-sea gas exchange and SSA production. However, the~~may contribute to organic mass in aerosols even at higher wind speed.

However, future studies that investigate gel particles within the SML and in SSA are needed to clarify if the observed loss of TEP from the SML at higher wind speeds is indeed related to a transport of TEP to the atmosphere, or if CSP contribute to organic aerosol mass.

The accumulation of organic matter in the SML, and the distinct behavior of certain compounds at the water-air interface is certainly an important issue for all exchange processes between the ocean and the atmosphere that ~~in the scenario of anthropogenic climate change~~ needs to be ~~deeply investigated.~~ further exploited.

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References:

Agogué, H., Casamayor, E. O., Bourrain, M., Obernosterer, I., Joux, F., Herndl, G. J., and Lebaron, P.: A survey on bacteria inhabiting the sea surface microlayer of coastal ecosystems, FEMS Microbiology Ecology, 54, 269-280, 2005.

Andreae, M. O. and Crutzen, P. J.: Atmospheric Aerosols: Biogeochemical Sources and Role in Atmospheric Chemistry, Science, 276, 1052-1058, 1997.

Arevalo-Martinez, D. L., Kock, A., Loscher, C. *R*., Schmitz, *R*. A., and Bange, H. W.: Massive nitrous oxide emissions from the tropical South Pacific Ocean, Nature Geosci, 8, 530-533, 2015.

Azetsu-Scott, K. and Passow, U.: Ascending marine particles: significance of transparent exopolymer particles (TEP) in the upper ocean. , Limnol. Oceanogr., 49, 741-748, 2004.

Bange, H. W.: Surface Ocean - Lower Atmosphere Study (SOLAS) in the upwelling region off Peru - Cruise No. M91 – December 01 – December 26, 2012 – Callao (Peru) – Callao (Peru), Bremen, 69 pp., 2013.

Bange, H. W., Rapsomanikis, S., and Andreae, M. O.: Nitrous oxide cycling in the Arabian Sea, J. Geophys. Res-Oceans, 106, 1053-1065, 2001.

Bar-Zeev, E., Berman-Frank, I., Girshevitz, O., and Berman, T.: Revised paradigm of aquatic biofilm formation facilitated by microgel transparent exopolymer particles, Proceedings of the National Academy of Sciences, 109, 9119-9124, 2012.

Benner, *R*.: Chemical composition and reactivity. In: Biogeochemistry of marine dissolved organic matter, Hansell, D. A. and Carlson, D. J. (Eds.), Academic Press - Elsevier, 2002.

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, 2004.

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, 2014.

Capone, D. G. and Hutchins, D. A.: Microbial biogeochemistry of coastal upwelling regimes in a changing ocean, Nat. Geosci., 6, 711-717, 2013.

Carlson, D.: The Early Diagenesis of Organic Matter: Reaction at the Air-Sea Interface. In: Organic Geochemistry, Engel, M. and Macko, S. (Eds.), Topics in Geobiology, Springer US, 1993.

Carlson, D. J.: A field evaluation of plate and screen microlayer sampling techniques, Mar. Chem., 11, 189-208, 1982.

Carlucci, A. F., Craven, D. B., and Henrichs, S. M.: Surface-film microheterotrophs: amino acid metabolism and solar radiation effects on their activities, Marine Biology, 85, 13-22, 1985.

Carlucci, A. F., Wolgast, D. M., and Craven, D. B.: Microbial Populations in Surface Films: Amino Acid Dynamics in Nearshore and Offshore Waters off Southern California, J. geophys. Res., 97, 5271-5280, 1992.

Carr, M.-E. and Kearns, E. J.: Production regimes in four Eastern Boundary Current systems, Deep Sea Research Part II: Topical Studies in Oceanography, 50, 3199-3221, 2003.

Chin, W.-C., Orellana, M. V., and Verdugo, P.: Spontaneous assembly of marine dissolved organic matter into polymer gels, Nature, 391, 568-572, 1998.

Chow, J. S., Lee, C., and Engel, A.: The influence of extracellular polysaccharides, growth rate, and free coccoliths on the coagulation efficiency of Emiliania huxleyi, Marine Chemistry, doi: http://dx.doi.org/10.1016/j.marchem.2015.04.010, 2015. 2015.

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Cisternas-Novoa, C., Lee, C., and Engel, A.: Transparent exopolymer particles (TEP) and Coomassie stainable particles (CSP): Differences between their origin and vertical distributions in the ocean, Marine Chemistry, doi: http://dx.doi.org/10.1016/j.marchem.2015.03.009, 2015. 2015.

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, Progr. Oceanogr., 109, 104-116, 2013.

Cunliffe, M. and Murrell, J. C.: The sea-surface microlayer is a gelatinous biofilm, The ISME journal, 3, 1001-1003, 2009.

Cunliffe, M., Upstill-Goddard, *R*. C., and Murrell, J. C.: Microbiology of aquatic surface microlayers, FEMS Microbiol. Rev., 35, 233-246, 2011.

Cunliffe, M. and Wurl, O.: Guide to best practices to study the ocean's surface., Plymouth, UK, 2014.

Davies, J. T.: The Effects of Surface Films in Damping Eddies at a Free Surface of a Turbulent Liquid, 1966.

Dickson, A. G., Sabine, C. L., and Christian, J. *R*.: Guide to best practices for ocean CO2 measurements, PICES, 2007.

Dittmar, T., Cherrier, J., and Ludwichowski, K.-U.: The Analysis of Amino Acids in Seawater. In: Practical Guidelines for the Analysis of Seawater, CRC Press, 2009.

Engel, A.: Determination of Marine Gel Particles. In: Practical Guidelines for the Analysis of Seawater, CRC Press, 2009.

Engel, A.: The role of transparent exopolymer particles (TEP) in the increase in apparent particle stickiness (α) during the decline of a diatom bloom, Journal of Plankton Research, 22, 485-497, 2000.

Engel, A., Borchard, C., Loginova, A., Meyer, J., Hauss, H., and Kiko, *R*.: Effects of varied nitrate and phosphate supply on polysaccharidic and proteinaceous gel particles production during tropical phytoplankton bloom experiments, Biogeosciences Discuss., 12, 6589-6635, 2015.

Engel, A., Borchard, C., Piontek, J., Schulz, K. G., Riebesell, U., and Bellerby, *R*.: CO2 increases 14C primary production in an Arctic plankton community, Biogeosciences, 10, 1291-1308, 2013.

Engel, A. and Händel, N.: A novel protocol for determining the concentration and composition of sugars in particulate and in high molecular weight dissolved organic matter (HMW-DOM) in seawater, Marine Chemistry, 127, 180-191, 2011.

Engel, A. and Schartau, M.: Influence of transparent exopolymer particles (TEP) on sinking velocity of Nitzschia closterium aggregates, Marine Ecology Progress Series, 182, 69-76, 1999.

Engel, A., Thoms, S., Riebesell, U., Rochelle-Newall, E., and Zondervan, I.: Polysaccharide aggregation as a potential sink of marine dissolved organic carbon, Nature, 428, 929-932, 2004.

Falkowska, L.: Sea surface microlayer: a field evaluation of teflon plate, glass plate and screen sampling techniques. Part 1. Thickness of microlayer samples and relation to wind speed, Oceanologia, 41, 211-221, 1999.

Frew, N. M.: The role of organic films in air-sea gas exchange. In: The Sea Surface and Global Change, Liss, P. S. and Duce, *R*. A. (Eds.), Cambridge University Press, UK, 1997.

Frew, N. M., Bock, E. J., Schimpf, U., Hara, T., Haußecker, H., Edson, J. B., McGillis, W. *R*., Nelson, *R*. K., McKenna, S. P., Uz, B. M., and Jähne, B.: Air-sea gas transfer: Its dependence on wind stress, small-scale roughness, and surface films, Journal of Geophysical Research: Oceans, 109, n/a-n/a, 2004.

Frew, N. M., Goldman, J. C., Dennett, M. *R*., and Johnson, A. S.: Impact of phytoplankton-generated surfactants on air-sea gas exchange, Journal of Geophysical Research: Oceans, 95, 3337-3352, 1990.

Fuhrman, J. A. and Ferguson, *R*. L.: Nanomolar concentrations and rapid turnover of dissolved free amino acids in seawater: agreement between chemical and microbiological measurements, Marine Ecology Progress Series, 33, 237-242, 1986.

Galgani, L. and Engel, A.: Accumulation of Gel Particles in the Sea-Surface Microlayer during an Experimental Study with the Diatom Thalassiosira weissflogii, International Journal of Geosciences, 4, 129-145, 2013.

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, 2014.

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, 2012.

Garreaud, *R*. D., Rutllant, J. A., Muñoz, *R*. C., Rahn, D. A., Ramos, M., and Figueroa, D.: VOCALS-CUpEx: the Chilean Upwelling Experiment, Atmos. Chem. Phys., 11, 2015-2029, 2011.

GESAMP: The Sea-Surface Microlayer and its Role in Global Change. Reports and Studies, WMO, 1995.

Gutknecht, E., Dadou, I., Marchesiello, P., Cambon, G., Le Vu, B., Sudre, J., Garçon, V., Machu, E., Rixen, T., Kock, A., Flohr, A., Paulmier, A., and Lavik, G.: Nitrogen transfers off Walvis Bay: a 3-D coupled physical/biogeochemical modeling approach in the Namibian upwelling system, Biogeosciences, 10, 4117-4135, 2013.

Harvey, G. W. and Burzell, L. A.: A simple microlayer method for small samples, Limnol. Oceanogr., 11, 608-614, 1972.

Hatcher, *R*. F. and Parker, B. C.: Laboratory comparisons of four surface microlayer samplers1, Limnology and Oceanography, 19, 162-165, 1974.

Hawkins, L. N., Russell, L. M., Covert, D. S., Quinn, P. K., and Bates, T. S.: Carboxylic acids, sulfates, and organosulfates in processed continental organic aerosol over the southeast Pacific Ocean during VOCALS-REx 2008, Journal of Geophysical Research: Atmospheres, 115, n/a-n/a, 2010.

Henrichs, S. M. and Williams, P. M.: Dissolved and particulate amino acids and carbohydrates in the sea surface microlayer, Marine Chemistry, 17, 141-163, 1985.

Hu, H., Bourbonnais, A., Larkum, J., Bange, H. W., and Altabet, M. A.: Nitrogen cycling in shallow low oxygen coastal waters off Peru from nitrite and nitrate nitrogen and oxygen isotopes, Biogeosciences Discuss., 12, 7257-7299, 2015.

Jähne, B. and Haußecker, H.: AIR-WATER GAS EXCHANGE, Annual Review of Fluid Mechanics, 30, 443-468, 1998.

Keeling, *R*. F., Körtzinger, A., and Gruber, N.: Ocean Deoxygenation in a Warming World, Annu. Rev. Mar. Sci., 2, 199-229, 2010.

Keil, *R*. G. and Kirchman, D. L.: Bacterial Hydrolysis of Protein and Methylated Protein and Its Implications for Studies of Protein Degradation in Aquatic Systems, Applied and Environmental Microbiology, 58, 1374-1375, 1992.

Kuznetsova, M. and Lee, C.: Dissolved free and combined amino acids in nearshore seawater, sea surface microlayers and foams: Influence of extracellular hydrolysis, Aquatic Sciences - Research Across Boundaries, 64, 252-268, 2002.

Kuznetsova, M. and Lee, C.: Enhanced extracellular enzymatic peptide hydrolysis in the sea-surface microlayer, Marine Chemistry, 73, 319-332, 2001.

Kuznetsova, M., Lee, C., and Aller, J.: Characterization of the proteinaceous matter in marine aerosols, Marine Chemistry, 96, 359-377, 2005.

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, 2011.

Laß, K., Bange, H. W., and Friedrichs, G.: Seasonal signatures in SFG vibrational spectra of the sea surface nanolayer at Boknis Eck Time Series Station (SW Baltic Sea), Biogeosciences, 10, 5325-5334, 2013.

Leck, C. and Bigg, E. K.: Source and evolution of the marine aerosol—A new perspective, Geophysical Research Letters, 32, L19803, 2005.

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, 1979.

Liss, P. S.: Gas Transfer: Experiments and Geochemical Implications. In: Air-Sea Exchange of Gases and Particles, Liss, P. and Slinn, W. G. (Eds.), NATO ASI Series, Springer Netherlands, 1983.

Liss, P. S. and Duce, *R.* A.: The Sea Surface and Global Change, Cambridge University Press, 2005.

Logan, B. E., Passow, U., Alldredge, A. L., Grossartt, H.-P., and Simont, M.: Rapid formation and sedimentation of large aggregates is predictable from coagulation rates (half-lives) of transparent exopolymer particles (TEP), Deep Sea Research Part II: Topical Studies in Oceanography, 42, 203-214, 1995.

Long, *R.* A. and Azam, F.: Abundant protein-containing particles in the sea, Aquatic Microbial Ecology, 10, 213-221, 1996.

Mari, X. and Burd, A.: Seasonal size spectra of transparent exopolymeric particles (TEP) in a coastal sea and comparison with those predicted using coagulation theory, Marine Ecology Progress Series, 163, 63-76, 1998.

Mari, X. and Kiørboe, T.: Abundance, size distribution and bacterial colonization of transparent exopolymeric particles (TEP) during spring in the Kattegat, Journal of Plankton Research, 18, 969-986, 1996.

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, 2008.

Meakin, P.: Fractal aggregates in geophysics, Reviews of Geophysics, 29, 317-354, 1991.

O'Dowd, C. D., Facchini, M. C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Yoon, Y. J., and Putaud, J.-P.: Biogenically driven organic contribution to marine aerosol, Nature, 431, 676-680, 2004.

Orellana, M. V., Matrai, P. A., Leck, C., Rauschenberg, C. D., Lee, A. M., and Coz, E.: Marine microgels as a source of cloud condensation nuclei in the high Arctic, Proceedings of the National Academy of Sciences, 108, 13612-13617, 2011.

Panagiotopoulos, C., Sempéré, *R.*, Lafont, *R.*, and Kerhervé, P.: Sub-ambient temperature effects on the separation of monosaccharides by high-performance anion-exchange chromatography with pulse amperometric detection: Application to marine chemistry, Journal of Chromatography A, 920, 13-22, 2001.

Passow, U.: Transparent exopolymer particles (TEP) in aquatic environments, Progress in Oceanography, 55, 287-333, 2002.

Paulmier, A. and Ruiz-Pino, D.: Oxygen minimum zones (OMZs) in the modern ocean, Progr. Oceanogr., 80, 113-128, 2009.

Paulmier, A., Ruiz-Pino, D., and Garcon, V.: The oxygen minimum zone (OMZ) off Chile as intense source of CO2 and N2O, Cont. Shelf Res. , 28, 2746-2756, 2008.

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

Prieto, L., Ruiz, J., Echevarría, F., García, C. M., Bartual, A., Gálvez, J. A., Corzo, A., and Macías, D.: Scales and processes in the aggregation of diatom blooms: high time resolution and wide size range records in a mesocosm study, Deep Sea Research Part I: Oceanographic Research Papers, 49, 1233-1253, 2002.

Quinn, P. K. and Bates, T. S.: The case against climate regulation via oceanic phytoplankton sulphur emissions, Nature, 480, 51-56, 2011.

Quinn, P. K., Bates, T. S., Schulz, K. S., Coffman, D. J., Frossard, A. A., Russell, L. M., Keene, W. C., and Kieber, D. J.: Contribution of sea surface carbon pool to organic matter enrichment in sea spray aerosol, Nature Geosci, 7, 228-232, 2014.

Reinthaler, T., Sintes, E., and Herndl, G. J.: Dissolved organic matter and bacterial production and respiration in the sea-surface microlayer of the open Atlantic and the western Mediterranean Sea, Limnol. Oceanogr., 53, 122-136, 2008.

Riebesell, U., Kortzinger, A., and Oschlies, A.: Tipping Elements in Earth Systems Special Feature: Sensitivities of marine carbon fluxes to ocean change, Proceedings of the National Academy of Sciences, 106, 20602-20609, 2009.

Russell, L. M., Hawkins, L. N., Frossard, A. A., Quinn, P. K., and Bates, T. S.: Carbohydrate-like composition of submicron atmospheric particles and their production from ocean bubble bursting, Proceedings of the National Academy of Sciences, 107, 6652-6657, 2010.

Salter, M. E., Upstill-Goddard, *R.* C., Nightingale, P. D., Archer, S. D., Blomquist, B., Ho, D. T., Huebert, B., Schlosser, P., and Yang, M.: Impact of an artificial surfactant release on air-sea gas fluxes during Deep Ocean Gas Exchange Experiment II, Journal of Geophysical Research: Oceans, 116, C11016, 2011.

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. Microbiol., 78, 2066-2069, 2012.

Schlitzer, *R.*: Ocean Data View. 2013.

Schulz, K. G., Bellerby, *R.* G. J., Brussaard, C. P. D., Büdenbender, J., Czerny, J., Engel, A., Fischer, M., Koch-Klavsen, S., Krug, S. A., Lischka, S., Ludwig, A., Meyerh√∂fer, M., Nondal, G., Silyakova, A., Stuhr, A., and Riebesell, U.: Temporal biomass dynamics of an Arctic plankton bloom in response to increasing levels of atmospheric carbon dioxide, Biogeosciences, 10, 161-180, 2013.

Sieburth, J. M.: Microbiological and organic-chemical processes in the surface and mixed layers - Air-Sea exchange of Gases and Particles, D.Reidel Publishing Company, 1983.

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, United Kingdom and New York, NY, USA, Cambridge University Press, 2007.

Steinfeldt, R., Sültenfuß, J., Dengler, M., Fischer, T., and Rhein, M.: Coastal upwelling off Peru and Mauritania inferred from helium isotope disequilibrium, Biogeosciences Discuss., 12, 11019-11059, 2015.

Stolle, C., Nagel, K., Labrenz, M., and Jürgens, K.: Bacterial activity in the sea-surface microlayer: in situ investigations in the Baltic Sea and the influence of sampling devices, Aquatic Microbial Ecology, 58, 67-78, 2009.

Stramma, L., Johnson, G. C., Sprintall, J., and Mohrholz, V.: Expanding Oxygen-Minimum Zones in the Tropical Oceans, Science, 320, 655-658, 2008.

Sugimura, Y. and Suzuki, Y.: A high-temperature catalytic oxidation method for the determination of non-volatile dissolved organic carbon in seawater by direct injection of a liquid sample, Marine Chemistry, 24, 105-131, 1988.

Tarazona, J. and Arntz, W.: The Peruvian Coastal Upwelling System. In: Coastal Marine Ecosystems of Latin America, Seeliger, U. and Kjerfve, B. (Eds.), Ecological Studies, Springer Berlin Heidelberg, 2001.

Upstill-Goddard, R. C., Frost, T., Henry, G. R., Franklin, M., Murrell, J. C., and Owens, N. J. P.: Bacterioneuston control of air-water methane exchange determined with a laboratory gas exchange tank, Global biogeochemical cycles, 17, 1108, 2003.

Verdugo, P., Alldredge, A. L., Azam, F., Kirchman, D. L., Passow, U., and Santschi, P. H.: The oceanic gel phase: a bridge in the DOM–POM continuum, Marine Chemistry, 92, 67-85, 2004.

Wallace, G. T. and Duce, R. A.: Transport of particulate organic matter by bubbles in marine waters 1, Limnology and Oceanography, 23, 1155-1167, 1978.

Wilson, T. W., Ladino, L. A., Alpert, P. A., Breckels, M. N., Brooks, I. M., Browse, J., Burrows, S. M., Carslaw, K. S., Huffman, J. A., Judd, C., Kilthau, W. P., Mason, R. H., McFiggans, G., Miller, L. A., Najera, J. J., Polishchuk, E., Rae, S., Schiller, C. L., Si, M., Temprado, J. V., Whale, T. F., Wong, J. P. S., Wurl, O., Yakobi-Hancock, J. D., Abbatt, J. P. D., Aller, J. Y., Bertram, A. K., Knopf, D. A., and Murray, B. J.: A marine biogenic source of atmospheric ice-nucleating particles, Nature, 525, 234-238, 2015.

Wood, R., Mechoso, C. R., Bretherton, C. S., Weller, R. A., Huebert, B., Straneo, F., Albrecht, B. A., Coe, H., Allen, G., Vaughan, G., Daum, P., Fairall, C., Chand, D., Gallardo Klenner, L., Garreaud, R., Grados, C., Covert, D. S., Bates, T. S., Krejci, R., Russell, L. M., de Szoeke, S., Brewer, A., Yuter, S. E., Springston, S. R., Chaigneau, A., Toniazzo, T., Minnis, P., Palikonda, R., Abel, S. J., Brown, W. O. J., Williams, S., Fochesatto, J., Brioude, J., and Bower, K. N.: The VAMOS Ocean-Cloud-Atmosphere-Land Study Regional Experiment (VOCALS-REx): goals, platforms, and field operations, Atmos. Chem. Phys., 11, 627-654, 2011.

Wurl, O., Miller, L., Röttgers, R., and Vagle, S.: The distribution and fate of surface-active substances in the sea-surface microlayer and water column, Marine Chemistry, 115, 1-9, 2009.

Wurl, O., Miller, L., and Vagle, S.: Production and fate of transparent exopolymer particles in the ocean, J. geophys. Res., 116, C00H13, 2011.

Yu, H. and Mou, S.-F.: Effect of temperature on the retention of amino acids and carbohydrates in high-performance anion-exchange chromatography, Journal of Chromatography A, 1118, 118-124, 2006.

Zhang, Z.: Studies on the sea surface microlayer II. The layer of sudden change of physical and chemical properties, Journal of Colloid and Interface Science, 264, 148-159, 2003.

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 Interface Sci., 204, 294-299, 1998.

Zhou, J., Mopper, K., and Passow, U.: The role of surface-active carbohydrates in the formation of transparent exopolymer particles by bubble adsorption of seawater, Limnology and Oceanography, 43, 1860-1871, 1998.

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

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

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

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

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

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

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Figure 7a, b: Influence of wind speed (m s^{-1}) on the total area concentration of TEP (mm^2 L^{-1}) in the SML at all stations (a) and relationship between TEP enrichment factors (EF) and wind speed

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(m s^{-1}) for only those stations ~~of~~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.

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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.

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

~~References:~~

~~Agogue, H., Joux, F., Obernosterer, I., and Lebaron, P.: Resistance of marine bacterioneuston to solar radiation, Applied and Environmental Microbiology, 71 (9), 5282-5289, 2005.~~

~~Andreae, M. O., and Crutzen, P. J.: Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry, Science, 276, 1052-1058, doi: 10.1126/science.276.5315.1052, 1997.~~

~~Azetsu-Scott, K. and Passow, U.: Ascending marine particles: significance of transparent exopolymer particles (TEP) in the upper ocean, Limnology and Oceanography 49, 741-748, 2004.~~

~~Bange, H. W., Rapsomanikis, S., and Andreae, M. O.: Nitrous oxide cycling in the arabian sea, Journal of Geophysical Research: Oceans, 106, 1053-1065, doi: 10.1029/1999jc000284, 2001.~~

~~Bange, H. W.: Surface Ocean - Lower Atmosphere Study (SOLAS) in the upwelling region off Peru, Cruise No. M91, 1-26 December 2012, Callao (Peru) – Callao (Peru) Rep., 69 pp., Bremen, Germany, 2013.~~

~~Bar-Zeev, E., Berman-Frank, I., Girshevitz, O., and Berman, T.: Revised paradigm of aquatic biofilm formation facilitated by microgel transparent exopolymer particles, Proceedings of the National Academy of Sciences, 109 (23), 9119-9124, 2012.~~

~~Benner, R.: Chemical composition and reactivity. In (Eds.): Hansell, D. A. and Carlson, C., Biogeochemistry of marine dissolved organic matter. pp. 59-90. Academic Press. Elsevier Science, 2002.~~

~~Bigg, K. E., Leck, C., and Tranvik, L.: Particulates of the surface microlayer of open water in the central Arctic Ocean in summer, Marine Chemistry, 91(1-4), 131-141, 2004.~~

~~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, The Journal of Chemical Physics, 140, 144304, doi: http://dx.doi.org/10.1063/1.4870516, 2014.~~

~~Carlson, D. J.: The early diagenesis of organic matter: reaction at the air–sea interface, in Organic Geochemistry, edited by M. H. Engel and S. A. Macko, pp. 255-268, Plenum Press, New York, 1993.~~

Formatiert: Schriftart: 12 Pt., Fett

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~~Carlucci, A.F., Craven, D.B., and Henrichs, S.M.: Surface-film microheterotrophs: amino acid metabolism and solar radiation effects on their activities, Marine Biology 85, 13-22, 1985.~~

~~Carlucci, A. F., Wolgast, D. M., and Craven, D. B.: Microbial populations in surface films: Amino acid dynamics in nearshore and offshore waters off southern california, Journal of Geophysical Research, 97, 5271-5280, doi: 10.1029/91jc02614, 1992.~~

~~Chin, W.-C., Orellana, M. V., and Verdugo, P.: Spontaneous assembly of marine dissolved organic matter into polymer gels, Nature, 391(6667), 568-572, 1998.~~

~~Chow, J. S., Lee, C., and Engel, A.: The influence of extracellular polysaccharides, growth rate, and free coccoliths on the coagulation efficiency of Emiliania huxleyi, Marine Chemistry, doi: 10.1016/j.marchem.2015.04.010, 2015, in press/accepted.~~

~~Cisternas-Novoa, C., Lee, C., and Engel, A.: Transparent exopolymer particles (TEP) and coomassie stainable particles (CSP): Differences between their origin and vertical distributions in the ocean, Marine Chemistry . doi: 10.1016/j.marchem.2015.03.009, 2015, in press/accepted.~~

~~Cunliffe, M., and Murrell, J. C.: The sea-surface microlayer is a gelatinous biofilm, The ISME journal, 3(9), 1001-1003, doi: 10.1038/ismej.2009.69, 2009.~~

~~Cunliffe, M., Upstill-Goddard, R. C., and Murrell, J. C.: Microbiology of aquatic surface microlayers, FEMS microbiology reviews, 35(2), 233-246, 2011.~~

~~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, Progress in Oceanography, 109, 104-116, 2013.~~

~~Davies, J.T.: The effect of surface films in damping eddies at a free surface of a turbulent liquid,Proceedings of the Royal Society A, 290, 515–526, 1966, doi: http://dx.doi.org/10.1098/rspa.1966.0067~~

~~Dickson, A. G., Sabine, C. L., and Christian, J. R. (Eds.): Guide to best practices for ocean co2 measurements, in: PICES Special Publication 3, 191 pp., 2007.~~

~~Dittmar, T., Cherrier, J., Ludwichowski, K.: The Analysis of Amino Acids in Seawater, in: Practical Guidelines for the Analysis of Seawater, edited by: Wurl, O., CRC Press, 67 – 76, 2009.~~

~~Engel, A., and Schartau, M.: Influence of transparent expolymer particles (TEP) on sinking velocity of Nitzschia closterum aggregates, Marine Ecology Progress Series, 182, 69-76, doi: 10.3354/meps182069, 1999.~~

~~Engel, A.: The role of transparent exopolymer particles (TEP) in the increase in apparent particle stickiness (α) during the decline of a diatom bloom, Journal of Plankton Research, 22, 485-497, 2000.~~

~~Engel, A., Thoms, S., Riebesell, U., Rochelle-Newall, E. and Zondervan, I.: Polysaccharide aggregation as a potential sink of marine dissolved organic carbon, Nature, 428 , 929-932, 2004.~~

~~Engel, A.: Determination of Marine Gel Particles. In (Ed.): Wurl, O., Practical Guidelines for the Analysis of Seawater, CRC Press, 2009.~~

~~Engel, A., and Händel, N.: A novel protocol for determining the concentration and composition of sugars in particulate and in high molecular weight dissolved organic matter (HMW-DOM) in seawater, Marine Chemistry, 127(1-4), 180-191, 2011.~~

~~Engel, A., Borchard, C., Piontek, J., Schulz, K. G., Riebesell, U. and Bellerby, R.: CO2 increases 14C primary production in an Arctic plankton community, Biogeosciences, 10(3), 1291-1308, 2013.~~

~~Engel, A., Borchard, C., Loginova, A. N., Meyer, J., Hauss, H., and Kiko, R.: Effects of varied nitrate and phosphate supply on polysaccharidic and proteinaceous gel particles production during tropical phytoplankton bloom experiments, Biogeosciences Discussions, 12 (8), 6589-6635, doi: 10.5194/bgd-12-6589-2015, 2015.~~

~~Frew, N. M., Goldman, J. C., Dennett, M. R., and Johnson, A. S.: Impact of phytoplankton-generated surfactants on air-sea gas exchange, Journal of Geophysical Research: Oceans, 95, 3337-3352, doi: 10.1029/JC095iC03p03337, 1990.~~

~~Frew, N.M.: The role of organic films in air-sea gas exchange. In (Eds.): Liss, P. S. and Duce, R. A., The Sea Surface and Global Change, Cambridge University Press, UK, 121–172, 1997.~~

~~Fuhrman, J. A., and Ferguson, R. L.: Nanomolar concentrations and rapid turnover of dissolved free amino acids in seawater: Agreement between chemical and microbiological measurements, Marine Ecology Progress Series, 33, 237-242, 1986.~~

~~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, Journal of Geophysical Research - Oceans, 119 (11). pp. 7911-7924, 2014.~~

~~Gao, Q., Leck, C., Rauschenberg, C., and Matrai, P. A.: On the chemical dynamics of extracellular polysaccharides in the high Arctic surface microlayer, Ocean Science 8, 401-418, 2012.~~

~~GESAMP: The sea-surface microlayer and its role in global change, in, Reports and Studies, WMO, 92, 1995.~~

~~Goldman, J. C., Dennett, M. R., and Frew, N. M.: Surfactant effects on air-sea gas exchange under turbulent conditions, Deep Sea Research Part A. Oceanographic Research Papers, 35, 1953-1970, doi.org/10.1016/0198-0149(88)90119-7, 1988.~~

~~Gutknecht, E., Dadou, I., Marchesiello, P., Cambon, G., Le Vu, B., Sudre, J., Garçon, V., Machu, E., Rixen, T., Kock, A., Flohr, A., Paulmier, A., and Lavik, G.: Nitrogen transfers off walvis bay: A 3-d coupled physical/biogeochemical modeling approach in the namibian upwelling system, Biogeosciences, 10, 4117-4135, doi: 10.5194/bg-10-4117-2013, 2013.~~

~~Harlay, J., De Bodt, C., Engel, A., Jansen, S., d'Hoop, Q., Piontek, J., Van Oostende, N., Groom, S., Sabbe, K. and Chou, L.: Abundance and size distribution of transparent exopolymer particles (TEP) in a coccolithophorid bloom in the northern Bay of Biscay, Deep Sea Research Part I-Oceanographic Research Papers, 56 (8). pp. 1251-1265, 2009.~~

~~Harvey, G. W., and Burzell, L. A.: A simple microlayer method for small samples, Limnology and Oceanography, 11, 608-614, 1972.~~

~~Henrichs, S. M., and Williams, P. M.: Dissolved and particulate amino acids and carbohydrates in the sea surface microlayer, Marine Chemistry, 17,141-163, 1985.~~

~~Hunter K.A., and Liss P.S.: Organic sea surface films. In (Eds): Duursma, E. K. and Dawson, R., Marine organic chemistry, Elsevier, Amsterdam, The Netherlands, 259-298, 1981.~~

~~Jähne, B., and Haußecker, H.: Air-water gas exchange, Annual Review of Fluid Mechanics, 30, 443-468, doi:10.1146/annurev.fluid.30.1.443, 1998.~~

~~Keeling, R. F., Körtzinger, A., and Gruber, N.: Ocean deoxygenation in a warming world, Annual Review of Marine Science, 2, 199-229, doi:10.1146/annurev.marine.010908.163855, 2010.~~

~~Keil, R. G., and Kirchman, D. L.: Bacterial hydrolysis of protein and methylated protein and its implications for studies of protein degradation in aquatic systems, Applied and Environmental Microbiology, 58, 1374-1375, 1992.~~

~~Kuznetsova, M., and Lee, C.: Enhanced extracellular enzymatic peptide hydrolysis in the sea-surface microlayer, Marine Chemistry, 73, 319-332, 2001.~~

~~Kuznetsova, M., and Lee, C.: Dissolved free and combined amino acids in nearshore seawater, sea surface microlayers and foams: Influence of extracellular hydrolysis, Aquatic Sciences - Research Across Boundaries, 64, 252-268, doi: 10.1007/s00027-002-8070-0, 2002.~~

~~Kuznetsova, M., Lee, C., Aller, J., and Frew, N.M.: Enrichment of amino acids in the sea-surface microlayers at coastal and open ocean sites in the North Atlantic Ocean, Limnology and Oceanography, 49, 1605-1619, 2004.~~

~~Kuznetsova, M., Lee, C., and Aller, J.: Characterization of the proteinaceous matter in marine aerosols, Marine Chemistry, 96, 359-377, doi: 10.1016/j.marchem.2005.03.007, 2005.~~

~~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.~~

~~Leck, C., and Bigg, E. K.: Source and evolution of the marine aerosol – A new perspective, Geophysical Research Letters, 32(19), L19803, 2005.~~

~~Lindroth, P., and Mopper, K.: High performance liquid chromatographic determination of subpicomole amounts of amino acids by precolumn fluorescence derivatization with o-phthaldialdehyde, Analytical Chemistry, 51(11), 1667-1674, 1979.~~

~~Liss, P. S.: Gas transfer: Experiments and geochemical implications. In (Eds): Liss, P. A. and Slinn, W. G., Air-sea exchange of gases and particles, Nato asi series, Springer Netherlands, 241-298, 1983.~~

~~Liss, P. S., and Duce, R. A.: The Sea Surface and Global Change, Cambridge University Press, 2005.~~

~~Logan, B.E., Passow, U., Alldredge, A.L., Grossart, H.-P., Simon, M.: Rapid formation and sedimentation of large aggregates is predictable from coagulation rates (half-lives) of transparent exopolymer particles (TEP). Deep-Sea Research II 42, 203-214, 1995.~~

~~Long, R.A., and Azam, F.: Abundant protein-containing particles in the sea, Aquatic Microbial Ecology, 10, 213-221, 1996.~~

~~Mari, X., and Kiørboe, T.: Abundance, size distribution and bacterial colonization of transparent exopolymeric particles (TEP) during spring in the Kattegat, Journal of Plankton Research, 18(6), 969-986, 1996.~~

~~Mari, X. and Burd, A.: Seasonal size spectra of transparent exopolymeric particles (TEP) in a coastal sea and comparision with those predicted using coagulation theory, Marine Ecology-Progress Series, 163, 63-76, 1998.~~

~~Matrai, P. A., Tranvik, L., Leck, C., and Knulst, J. C.: Are high Arctic surface microlayers a potential source of aerosol organic precursors?, Marine Chemistry, 108(1-2), 109-122, 2008.~~

~~O'Dowd, C. D., Facchini, M. C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S. Fuzzi, S., Yoon, Y. J., and Putaud, J. P.: Biogenically driven organic contribution to marine aerosol, Nature, 431(7009), 676-680, 2004.~~

~~Orellana, M. V., Matrai, P. A., Leck, C., Rauschenberg, C. D., Lee, A. M., and Coz, E.: Marine microgels as a source of cloud condensation nuclei in the high Arctic, Proceedings of the National Academy of Sciences, 108(33), 13612-13617, 2011.~~

~~Passow, U.: Transparent exopolymer particles (TEP) in aquatic environments, Progress in Oceanography, 55, 287-333, 2002.~~

~~Paulmier, A., Ruiz-Pino, D., and Garcon, V.: The oxygen minimum zone (omz) off Chile as intense source of co2 and n2o, Continental Shelf Research, 28, 2746-2756, doi: org/10.1016/j.csr.2008.09.012, 2008.~~

~~Paulmier, A., and Ruiz-Pino, D.: Oxygen minimum zones (omzs) in the modern ocean, Progress in Oceanography, 80, 113-128, doi:org/10.1016/j.pocean.2008.08.001, 2009.~~

~~Paulmier, A., Ruiz-Pino, D., and Garçon, V.: CO_2 maximum in the oxygen minimum zone (omz), Biogeosciences, 8, 239-252, 10.5194/bg-8-239-2011, 2011.~~

~~Prieto, L., Ruiz, J., Echevarria, F., Garcia, C. M., Bartual, A., Galvez, J. A., Corzo, A., and Macias, D.: Scales and processes in the aggregation of diatom blooms: high time resolution and wide size range records in a mesocosm study, Deep Sea Research Part I 49(7), 1233-1253, 2002.~~

~~Quinn, P. K., and Bates, T. S.: The case against climate regulation via oceanic phytoplankton sulphur emissions, Nature, 480, 51-56, 2011.~~

~~Quinn, P. K., Bates, T. S., Schulz, K. S., Coffman, D. J., Frossard, A. A., Russell, L. M., Keene, W. C., and Kieber, D. J.: Contribution of sea surface carbon pool to organic matter~~

~~enrichment in sea spray aerosol, Nature Geoscience, 7, 228-232, doi: 10.1038/ngeo2092, 2014.~~

~~Reinthaler, T., Sintes, E., and Herndl, G.: Dissolved organic matter and bacterial production and respiration in the sea-surface microlayer of the open Atlantic and the western Mediterranean Sea, Limnolology and Oceanography, 53, 122-136, 2008.~~

~~Riebesell, U., Körtzinger, A., and A. Oschlies: Sensitivities of marine carbon fluxes to ocean change, Proceedings of the National Academy of Sciences, 106(49), 20602-20609, 2009.~~

~~Russell, L. M., Hawkins, L. N., Frossard, A. A., Quinn, P. K., and Bates, T. S.: Carbohydrate-like composition of submicron atmospheric particles and their production from ocean bubble bursting, Proceedings of the National Academy of Sciences, 107(15), 6652-6657, 2010.~~

~~Salter, M. E., Upstill-Goddard, R. C., Nightingale, P. D., Archer, S. D., Blomquist, B., Ho, D. T., Huebert, B., Schlosser, P., and Yang, M.: Impact of an artificial surfactant release on air-sea gas fluxes during Deep Ocean Gas Exchange Experiment II, Journal of Geophysical Research-Oceans, 116, C11016, 2011.~~

~~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, Applied Environmental Microbiology, 78, 2066-2069, doi: 10.1128/aem.06344-11, 2012.~~

~~Schlitzer, R., Ocean Data View, http://odv.awi.de, 2013.~~

~~Schulz, K. G., Bellerby, R. G. J., Brussaard, C. P. D., Büdenbender, J., Czerny, J., Engel, A., Fischer, M., Koch-Klavsen, S., Krug, S. A., Lischka, S., Ludwig, A., Meyerhöfer, M., Nondal, G., Silyakova, A., Stuhr, A., and Riebesell, U.: Temporal biomass dynamics of an Arctic plankton bloom in response to increasing levels of atmospheric carbon dioxide, Biogeosciences, 10(1), 161-180, 2013.~~

~~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, United Kingdom and New York, NY, USA, Cambridge University Press, 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.~~

~~Stolle, C., Nagel, K., Labrenz, M., Jürgens, K.: Succession of the sea-surface microlayer in the coastal Baltic Sea under natural and experimentally induced low-wind conditions. Biogeosciences 7: 2975-2988, 2010.~~

~~Sugimura, Y., and Suzuki, Y.: A high-temperature catalytic oxidation method for the determination of non-volatile dissolved organic carbon in seawater by direct injection of a liquid sample, Marine Chemistry, 24, 105-131, doi: org/10.1016/0304-4203(88)90043-6, 1988.~~

~~Tarazona, J., and Arntz, W.: The Peruvian Coastal Upwelling System. In (Eds): Seeliger, U. and Kjerfve, B., Coastal Marine Ecosystems of Latin America, Springer, Berlin Heidelberg, Germany, 229-244, 2001.~~

~~Upstill-Goddard, R. C., Frost, T., Henry, G. R., Franklin, M., Murrell, J. C., and Owens, N. J. P.: Bacterioneuston control of air-water methane exchange determined with a laboratory gas exchange tank, Global Biogeochemical Cycles, 17, 1108, doi: 10.1029/2003gb002043, 2003.~~

~~Upstill-Goddard, R. C.: Air-sea gas exchange in the coastal zone, Estuarine, Coastal and Shelf Science, 70, 388-404, doi:org/10.1016/j.ecss.2006.05.043, 2006.~~

~~van Pinxteren, M., Müller, C., Iinuma, Y., Stolle, C., and Herrmann, H.: Chemical characterization of dissolved organic compounds from coastal sea surface microlayers (Baltic Sea, germany), Environmental Science and Technology, 46(19), 10455-10462, doi: 10.1021/es204492b, 2012.~~

~~Verdugo, P., Alldredge, A. L., Azam, F., Kirchman, D. L., Passow, U., and Santschi, P. H.: The oceanic gel phase: a bridge in the DOM–POM continuum, Marine Chemistry, 92(1-4), 67-85, 2004.~~

~~Wallace, G. T., and Duce, R. A.: Transport of particulate organic matter by bubbles in marine waters 1, Limnology and Oceanography, 23, 1155-1167, doi: 10.4319/lo.1978.23.6.1155, 1978.~~

~~Wurl, O., Miller, L., Röttgers, R., and Vagle, S.: The distribution and fate of surface-active substances in the sea-surface microlayer and water column, Marine Chemistry, 115, 1-9, 2009.~~

~~Wurl, O., Miller, L., and Vagle, S.: Production and fate of transparent exopolymer particles in the ocean, Journal of Geophysical Research, 116(C7), doi: 10.1029/2011JC007342, 2011.~~

~~Zhou, J., Mopper, K., and Passow, U.: The role of surface-active carbohydrates in the formation of transparent exopolymer particles by bubble adsorption of seawater, Limnology and Oceanography, 43, 1860-1871, 1998.~~

Tables

Table 1: Hydrographic conditions encountered during SML sampling off Peru in 2012 ~~(METEOR 91).~~

	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

(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

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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	mm² 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	mm² 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
~~bacteria~~	~~x10^{3} mL^{-1}~~	~~1955~~	~~2057~~	~~30~~	~~8538~~	~~36~~
~~phytoplankton~~NCPL	x10³ mL^{-1}	45	53	5.4	300	35
CPL	x10³ mL^{-1}	27	35	3.7	193	35
Het. bacteria	x10^{4} mL^{-1}	195	206	3	854	36

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Table 3: Correlation coefficients (r) between concentrations of various organic components in the SML and their concentration in the underlying seawater (~~xULW~~r_{ULW}), temperature (~~T~~r_T, °C), and wind speed (~~U~~r_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 NCPPL and CPPL from the ULW.

SML	~~xULW~~r_{ULW}	~~T~~r_T	~~U~~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

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Eingefügte Zellen

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Figures

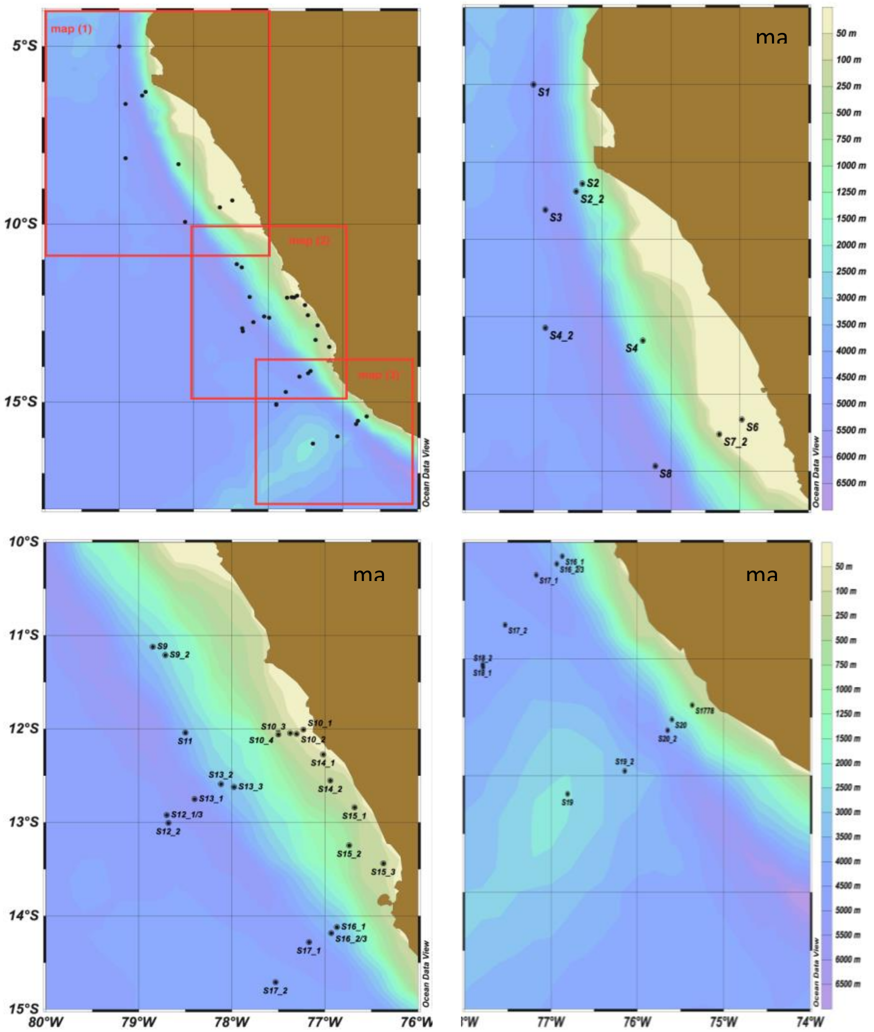


Figure 1

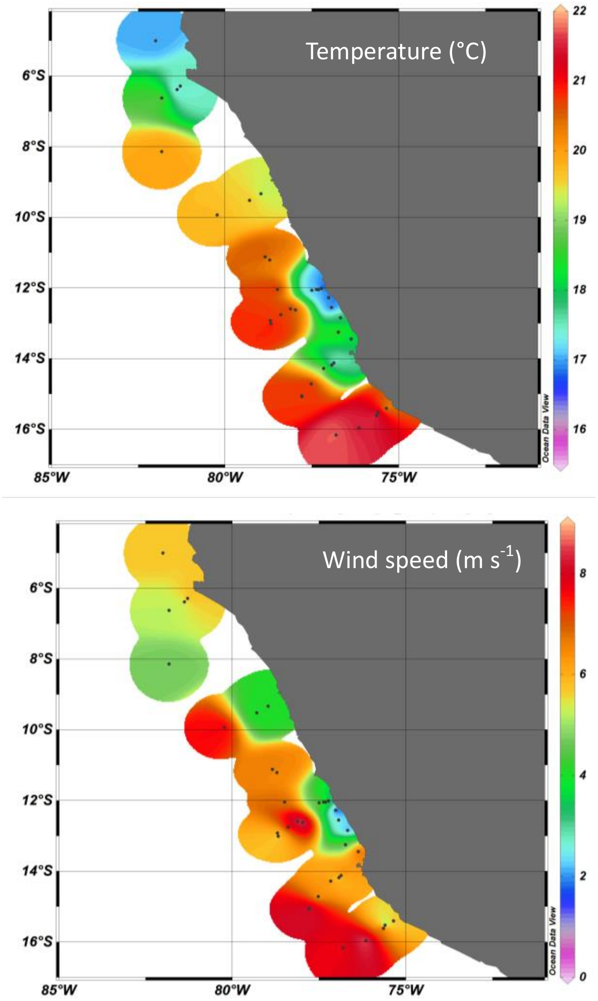

Temperature (°C)
6°S
8°S
10°S
12°S
14°S
16°S
85°W
80°W
75°W
22
21
20
19
18
17
16
Ocean Data View
Wind speed (m s-1)
6°S
8°S
10°S
12°S
14°S
16°S
85°W
80°W
75°W
8
6
4
2
0
Ocean Data View

Figure 2

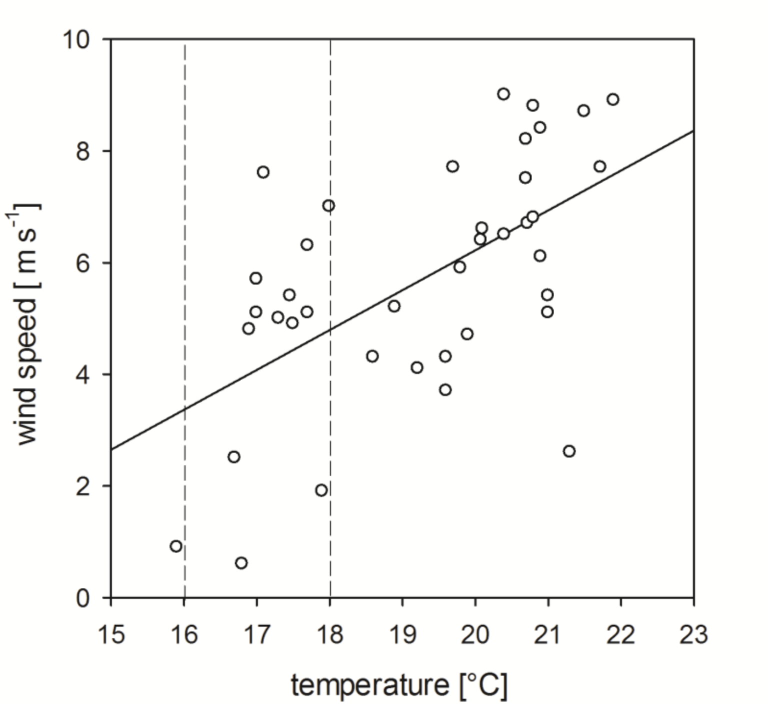


Figure 3

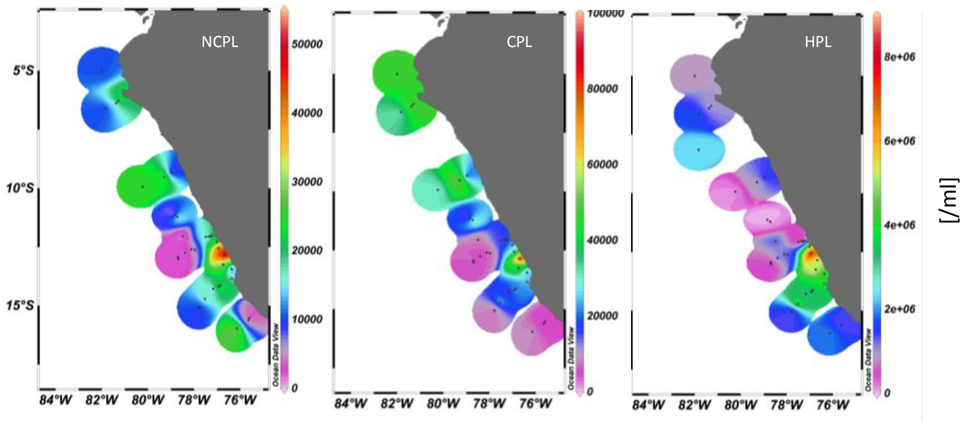


Figure 4

Figure 4

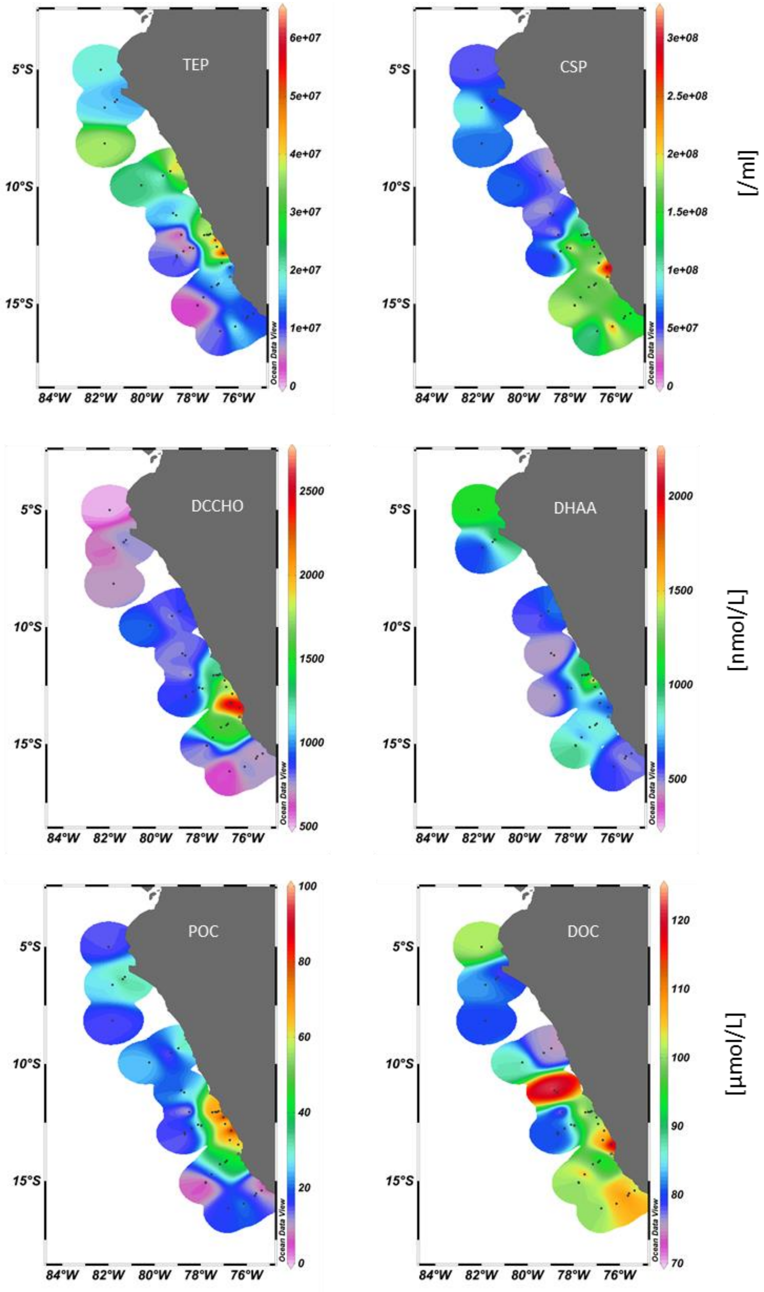
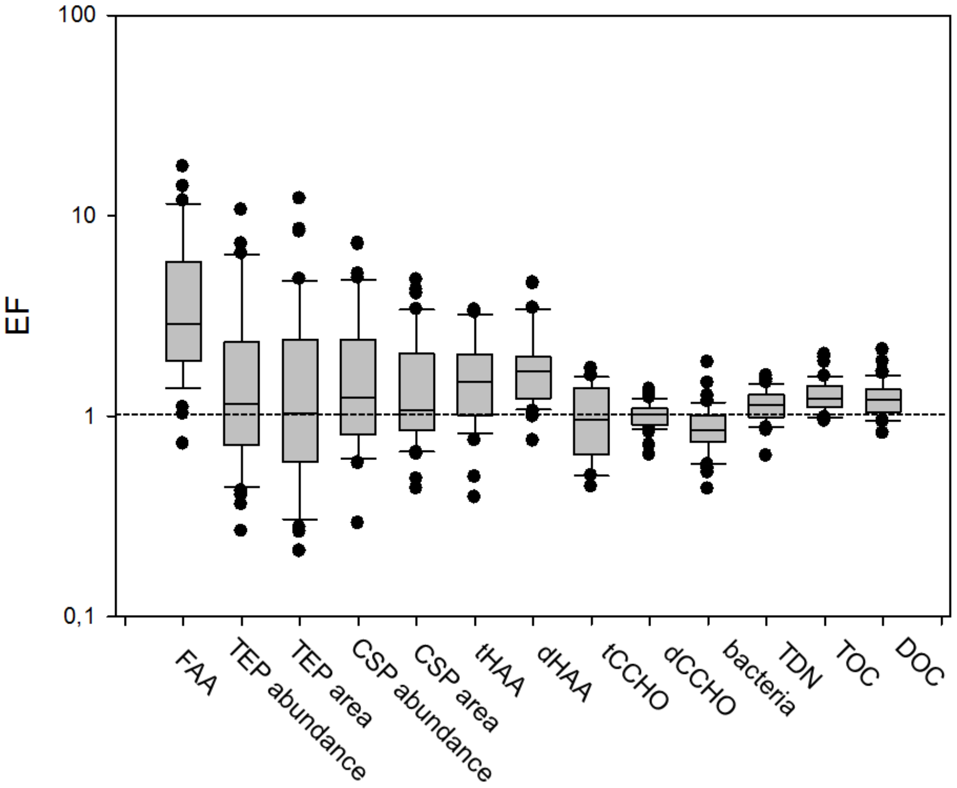

TEP
CSP
DCCHO
DHAA
POC
DOC
5°S
10°S
15°S
84°W
82°W
80°W
78°W
76°W
6e+07
5e+07
4e+07
3e+07
2e+07
1e+07
0
3e+08
2.5e+08
2e+08
1.5e+08
1e+08
5e+07
0
[/ml]
2500
2000
1500
1000
500
2000
1500
1000
500
[nmol/L]
100
80
60
40
20
0
120
110
100
90
80
70
[µmol/L]
Ocean Data View

Figure 5

1635


EF
100
10
1
0,1
FAA
TEP abundance
TEP area
CSP abundance
CSP area
tHAA
dHAA
tCCHO
dCCHO
bacteria
TDN
TOC
DOC

1636

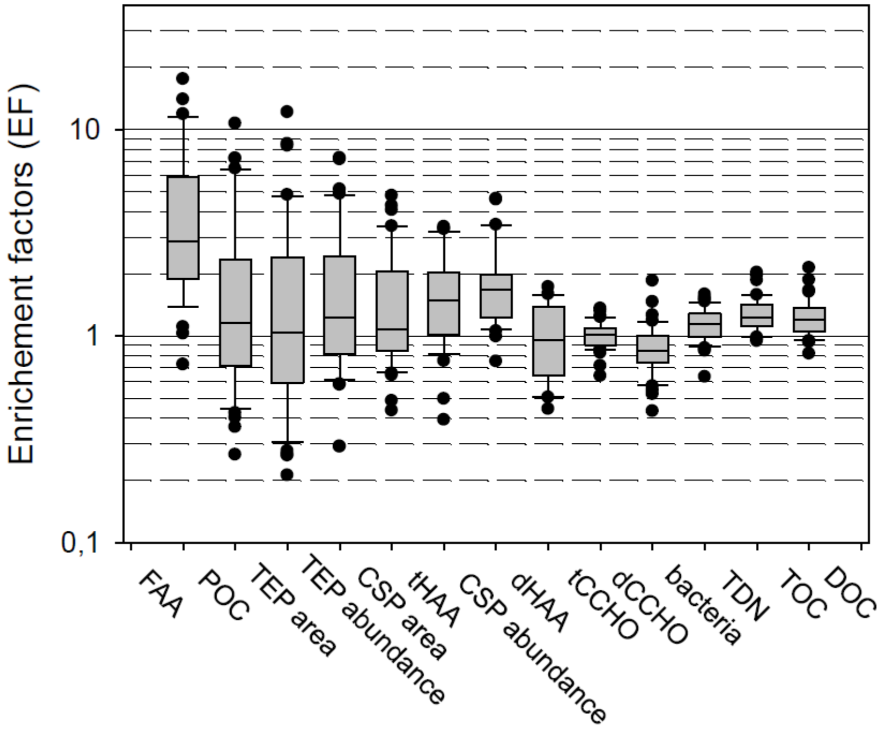


Figure 6 (revised)

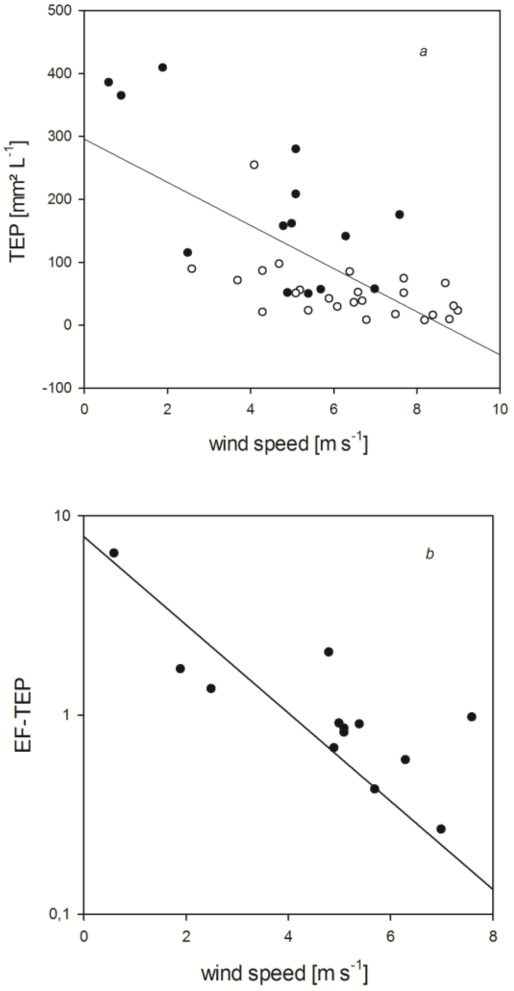

a
TEP [mm² L-1]
500
400
300
200
100
0
-100
0
2
4
6
8
10
wind speed [m s-1]
b
EF-TEP
10
1
0,1
0
2
4
6
8
wind speed [m s-1]

Figure 7a, b

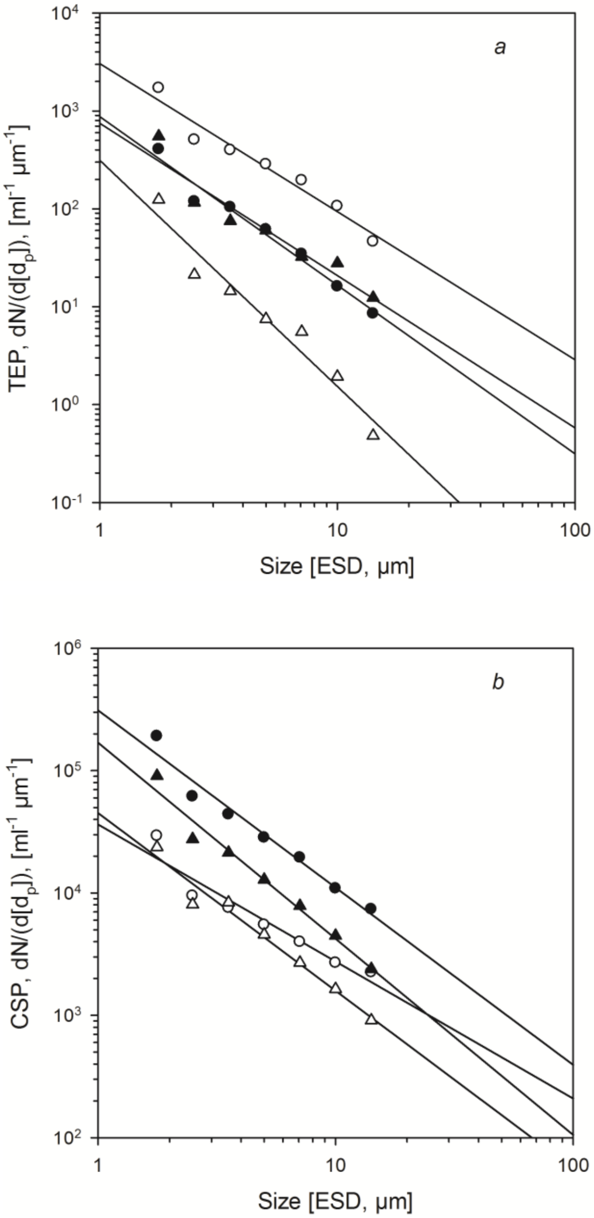

a
TEP, dN/(d[d_p]), [ml^-1 µm^-1]
10^4
10^3
10^2
10^1
10^0
10^-1
1
10
100
Size [ESD, µm]
b
CSP, dN/(d[d_p]), [ml^-1 µm^-1]
10^6
10^5
10^4
10^3
10^2
1
10
100
Size [ESD, µm]

Figure 8a, b

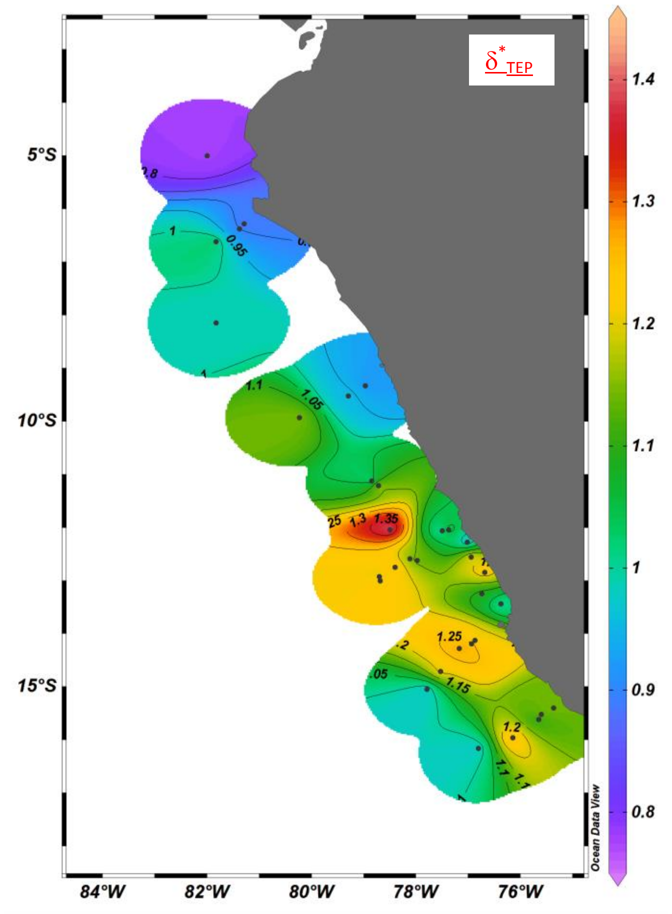


Figure 9 (new)

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