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Interactive comment on "The organic sea surface microlayer in the upwelling region off Peru and implications for air–sea exchange processes" *by* A. Engel and L. Galgani

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We respond here to the main issues raised by 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 sea surface microlayer at the highly productive upwelling region off Peru and the 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: '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.'

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 sites, 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 observations 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 will refer to these publications in the revised version.

The referee 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 and limited to 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. Organic 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. None of these were collected 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 ÌÍAa-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 briefly 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 has referred to the study by Wurl et al. (2011) in another context. 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.

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<5%). We understand that the referee did not evaluate a major part of our results based on amino acid and carbohydrate analyses.

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.

Selected specific comments:

Referee: Bias due to variability of withdrawal rate during glass plate sampling.

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$\pm$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 $\sim$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 in 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: 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 this 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.

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