

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

Anonymous Referee #3

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Overview:

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

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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.

General comments:

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.

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.

The lack of data also on surfactants/surface active substances (Croot et al., 2007; Frew et al., 1990; Gašparović et al., 1998) in the SML or ULW also weakens the paper as at least for these parameters, unlike TEP or CSP, there are data on the impact they have on air sea gas exchange (Salter et al., 2011).

It would also have been useful to have data on the bacterial attachment to TEP and CSP as this has been used as an indicator for different processes previously.

Air-Sea Gas exchange (3) – 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).

Glass plate sampling:

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 placed it at around 50 μm 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 50 μm 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. The authors are also referred to the recent work on the storage of such samples (Schneider-Zapp et al., 2013).

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). 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)

Comparisons between samplers also indicate that the glass plate is not ideal for bacte-

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rial sampling, with either metal screen (García-Flora 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.

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.

Analytical precision and accuracy: 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.

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 its 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).

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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.

Specific comments:

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: 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. 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). P10583, L18: You mean upwind of the vessel? P10583, L25: From where and how was this seawater obtained? This is important for cross-contamination of the samples. 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). 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. 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. P10585, L25: Were any standards or CRMs run for the amino acids? How was the concentration in seawater determined? P10586, L10: As above, were any standards or CRMs run for the carbohydrates? How was the concentration in seawater determined? P10586, L21: How were the errors determined in these measurements? How can the reader assess

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if there are significant differences between the values. 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. 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). P10587, L7: Please provide information on how errors were estimated for these parameters. P10587, L22: How were *Prochlorococcus* cells distinguished from bacteria in this work? Presumably *Prochlorococcus* was abundant but only had very low amounts of chlorophyll. P10588, 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? 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. P10589, L20: Does this include *Prochlorococcus*? P10589, L25: Does this number include misidentified *Prochlorococcus*? P10590, L15: Was the DHCHO really determined to this level of precision (implies 1 in 2668)? 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. 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? 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). 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? 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

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comment on this above. P10592, L26: This could also indicate a lower recovery of bacteria using a glass plate as has been observed previously (Cunliffe et al., 2009). P10592, L28: Or as above it could just mean the glass plate does not collect particles as well as a bottle. 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 δ 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? P10593, L13: Given the equation used to estimate D1 this could have been predicted from the onset, so what is the relevance of this? P10593, L19: Again this could be a sampling issue due to issues with glass plate sampling under higher wind speeds. 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. 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? P10595, L10: As noted earlier this result could be simply due to the glass plate undersampling bacteria. 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. P10595, L27: (sp) sea P10595, L10: Again the sampling method may also explain these results (Falkowska, 1999). P10596, L6: By this mechanism the insertion of a glass plate would also facilitate the production of TEP. 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. 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

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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. P10598, L8: What is meant by a discontinuous concentration? Do you mean a strong gradient across the SML? Please rephrase this. P105998, L24-28: An amino acid is described as phenylalanine – there is no such amino acid – I can only assume the authors are referring to phenylalanine. This should be corrected throughout the manuscript. 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. P10599, L10: There are no productivity measurements or chlorophyll measurements reported in this work so there is no evidence provided to support this statement. Please remove or provide supporting data for this statement. P10599, L19: Please see also the recent work published in Nature this year on aerosol production (Wilson et al., 2015). P105600, L2-16: These two paragraphs don't actually address anything specific with regard to organic aerosol production and therefore could simply be removed.

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