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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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Response to Anonymous 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

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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.

Referee: 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 tech- niques. 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 $\sim$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 later 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.

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$\pm$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 $\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. We also like to emphasize that for field research, it is nearly impossible to sample the SML manually from a shaking zodiac at open sea with an exact rate. 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: 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: 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: 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: 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: 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.

Minor technical suggestions by referee 1 will be adopted when revising the manuscript.

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