Review of
"Changes in optical characteristics of surface microlayers hint to photochemically and microbially-mediated DOM turnover in the upwelling region off Peru."
by L. Galgani & A. Engel, manuscript number **bg-2015-559**

1. General comments

This manuscript adds some very valuable data on the nature and occurrence of organic matter fractions in the sea surface microlayer (SML). The importance of the SML for marine biogeochemistry and gas exchange is now increasingly recognised. However, our knowledge of the composition of surface active organics and their biogeochemical cycling in the SML remains rather limited to date. The manuscript addresses these knowledge gaps by reporting a variety of bulk characteristics (DOC, DHAA, TEP and CSP abundance, and CDOM spectral absorbance and fluorescence characteristics) obtained by sound methodology. In this approach, spectral characteristics seem particularly useful for probing CDOM origins and transformations, although the somewhat ambiguous nature of spectral indices may need a more careful discussion at times. In the following I highlight some areas where the authors could improve their discussion.

I do understand that this manuscript is part of a special issue in Biogeosciences, and that some ancillary data are presented elsewhere [*Engel and Galgani*, 2015]. This, however, does make it quite difficult to relate observations to hydrography: for example both sea surface temperature (SST) and salinity are invoked in section 3.1 ff. in order to explain CDOM distribution patterns and their relation to coastal upwelling and terrestrial inputs, but the manuscript itself contains neither SST nor salinity. Including an overview of SST and sea surface salinity here would really help. This may also help support the authors statement that high CDOM absorption coefficients at stations S10_1 to S10_4 were "*probably due to an input of terrestrial material*" (page 19385, top paragraph). These high CDOM absorbance values seem to fall into a patch of upwelled water (see Fig 2, [*Engel and Galgani*, 2015]), and it remains unclear if SST and salinity characteristics at S10_1 to 4 are consistent with terrestrial inputs.

I do believe that the authors' analytical methodology, including CDOM fluorescence analysis, is sound. Unfortunately, however, neither section 2 (Materials and methods) nor section 3.2 (PARAFAC analysis for CDOM fluorophores) includes any details on the PARAFAC modelling and the verification of the final 5 component model chosen by the authors. It remains unclear, if their PARAFAC analysis tested for different numbers of components, and on what basis they identified the appropriate number of components in their model, e.g. residuals, split half analysis, Tucker congruency, … ? It is worth noting that such detail is usually provided in publications presenting PARAFAC models, although at times in a concise manner [*Dainard et al.*, 2015; *Murphy et al.*, 2008; *C. A. Stedmon and Bro*, 2008].

The discussion of spectral CDOM absorbance leans heavily on a paper by Helms et al [*Helms et al.*, 2008], which is based on an analysis of a coastal DOM gradient from high DOC swamp waters into the northwestern Atlantic off Georgia. As such, results in Helms et al [*Helms et al.*, 2008] are heavily weighted towards terrestrial (allochthonous) DOM. There is nothing wrong per se with applying CDOM spectral slopes and slope ratios as defined in Helms et al [*Helms et al.*, 2008] to a contrasting study are such as the Peruvian upwelling. However, DOM spectral signatures alone do not unambiguously define terrestrial (allochthonous) origin. For example, low spectral slope coefficients may also result from autochthonous CDOM production *in situ* [*Kitidis et al.*, 2006]. Furthermore, freshwater DOM inputs into the study area are conceivably small. Therefore, it might be useful to revisit the wording used for describing CDOM characteristics, in order to clarify that spectral signatures similar to those of allochthonous/terrestrial DOM don't necessarily suggest the presence of terrestrial material in the Peruvian upwelling. This recommendation also extends to the discussion of PARAFAC components of DOM fluorescence, where any attribution of terrestrial sources would need to be underpinned by further supporting evidence, e.g. observations of decreasing load with increasing salinity [*Murphy et al.*, 2008]. However, no such further analysis is presented.

Finally, I am somewhat concerned about the authors' conclusions from Fig. 8, which depicts correlations of PARAFAC component F1 (tryptophane-like) and socalled SUVA with the instantaneous global irradiance at the sea surface. Their statement in section 3.3 concludes that Fig. 8 provides evidence for “DOM photobleaching”. I disagree on the following grounds.
Firstly, the field data shown in Fig. 8 only show the net, overall change in F1 and SUVA, but do not allow identification of individual processes. Identification of photodegradation as the process responsible would require an experimental setup able to isolate photochemical effects from other factors including microbial production and consumption occurring simultaneously. This can be done in controlled irradiations [*Dainard et al.*, 2015; *C.A. Stedmon et al.*, 2007], but not with field observations alone.
Secondly, comparing indicators of CDOM abundance to instantaneous irradiance neglects the effects of photodegradation kinetics. For example, let's assume that any processes other than photodegradation may be neglected over the diel cycle (sampling occurred between sun rise and sun set). Then, CDOM bleaching would be expected to continue throughout the entire photoperiod, leading to monotonically decreasing F1 and SUVA during the day. That is, the highest CDOM levels should be present at sunrise (i.e. at lowest global irradiance) and the lowest CDOM levels should be present at sunset (i.e. **also** at lowest global irradiance). If anything, it would have made more sense to plot CDOM indicators against time-integrated global irradiance, starting from the point of first sampling on the day. There are of course cases where tightly coupled production & consumption kinetics result in diurnal cycles (e.g. CO photoproduction and microbial consumption [*Doney et al.*, 1995], but these also show the maximum impact of photochemistry in the late afternoon. Regarding CDOM, however, reported photobleaching half lives in the order of days to weeks [*Dainard et al.*,

2015; *Moran et al.*, 2000] argue against a pronounced diel cycle.
I suggest that Fig. 8 should be removed, and that results and discussion sections are amended accordingly.

Recommendation:
I believe this MS presents very interesting data on DOM abundance and characteristics at the sea surface. Despite the issues raised by my comments above, I believe that thorough revision can produce a high quality manuscript that merits publication in BG.

Further specific and editorial comments are detailed below.

2. Specific and editorial comments

Abstract:

* Some tangible information should be added to the abstract, for example dates, and some quantitative information.

References:

* A number of references are missing from the bibliography, starting with GESAMP, 1995 (Page19376, line 3). Van Blough 2005 should be Blough 2005.

* Others:
  Engel 2015 (p 19380)
  Zsolnay et al 1999
  Bange et al 2013

* Please edit carefully throughout

Materials and Methods

* Page 19378, lines 20 ff Please clarify what was meant by “great care was taken that the sampling procedure was well standardized”.

* Page 19379, lines 14 ff. Not really a criticism: however, it might be worth stating that the SML thickness as sampled by the glass plate is less than that by e.g. the Garrett screen.

* Page 19382, lines 21 ff. CDOM absorbance is simply an optical characteristics and not a 'concentration'. Please do not use 'concentration' when describing CDOM optical characteristics.

* Page 19383, lines 14 ff. Effect of salinity on spectra slope. Please clarify that the variation of CDOM spectral characteristics in this context is simply reflecting 2 end member mixing along a salinity gradient, and not salinity effects per se.

* Page 19383, lines 15. Definition of SUVA: SUVA is defined in EPA Document #: EPA/600/R-09/122, “DETERMINATION OF TOTAL ORGANIC CARBON AND SPECIFIC UV ABSORBANCE AT 254 nm IN SOURCE WATER AND DRINKING WATER” (2009)

  SUVA (L/mg-M) = UVA(cm^{-1}) / DOC (mg/L) * 100 cm/M

  UVA Calculation: UVA = A /d

  where UVA = The calculated UV absorbance of the sample in absorbance units (cm^{-1}), A = The measured UV absorbance at 254 nm of the sample that is filtered through a 0.45-µm filter media, and d = The quartz cell path length in cm.

  Your DOC normalised absorption coefficient at 254 nm is **NOT** SUVA, so please do not call it that.

* Page 19384, lines 14 ff. HIX. Similarly, please use a distinct acronym for your modified HIX, as your wavelength ranges significantly depart from those in the original paper by Zsolnay et al 1999.

* Page 19385, lines 5 ff, Enrichment factors. Perhaps this is a matter of taste: Enrichment factors (EFs) usually refer to a difference in abundance between SML and ULW. However, HIX, spectral slopes and SR etc. are not measures of abundance, and therefore I personally would prefer using something other than 'EF' to denote differences in DOM properties between SML and ULW.

Results

* Page 19387, line 1 ff. Socalled SUVA values: 0.6 mg C L^{-1} m^{-1} is NOT “*comparable to riverine waters*”. This value was obtained with Pacific Ocean fulvi acids [*Weishaar et al.*, 2003]. Please correct your statement.

* Page 19388, lines 24 ff: Origin of PARAFAC component F2: Please clarify why you state that a positive correlation of F2 with SST and bacterial abundance might suggest “*a refractory DOM component of terrestrial origin*” ??? My hunch would be that bacterial abundance could well be related to primary production, which in your study area is likely to be

fuelled mainly by coastal upwelling? I also do not agree with your description of F2 as a “refractory DOM component” resulting from either photochemical or microbial DOM degradation. Please revise.

Furthermore, positive correlations between F2 on the one hand and F3 and F5 on the other does not necessarily support your statement that F2 is derived from these other two FDOM fractions. Either all 3 fractions are formed by the same underlying process (then I'd expect positive correlations between them), or F2 is formed from F3 & F5, that is an F2 increase must cause decreases in F3 & F5. Please revise.

* Page 19391, lines 19 ff, Mycosporine like amino acids: The authors try to link mycosporine like amino acids (MAAs) to their CDOM characteristics. This is rather speculative. Besides, MAAs are not of high molecular weight as stated here. This section does not add value to the results section and should be deleted.

Discussion

* Page 19393, lines 20 ff: SR, DHAA%, and “lability“: Please spell out how SR and DHAA% support the notion of a labile DOC fraction in the SML. Are you referring to lability with respect to microbial consumption or with respect to photochemical degradation?

* Page 19394, lines 16 ff, nitrous oxide binding to aromatic groups. The authors refer to Cao et al. (2015) who found evidence for the formation of complexes between nitrous oxide and some mono-aromatics. However, Cao's study was conducted in a Ne matrix using millimolar concentration, i.e. rather different from the conditions at the sea surface. In my view, this section is far too speculative and should be removed

* Page 19395, line 1 ff. Origin of F2. What is your evidence for your statement that “*F2 fluorescence appears to be related to DOM exposure to sunlight [...]*”?

* Page 19395, lines 23 ff. The discussion here speculates on the sunlight induced release of DOM fractions but cannot provide any supporting evidence from the field data shown. Please remove this section.

* Page 19396, line 1 ff. Section 4.3 Implications: This section is somewhat repetitive in that it repeats statements regarding the possible roles of photodegradation and UV-induced stress. Much of this section is highly speculative and either not well or not at all supported by the authors own observations. Some of the statements on fluorescent organic matter remain unclear and need thorough revision in the light of the observational evidence available here. For example, components F3 and F5 are described as high molecular weight and more humic and refractory, but at

the same time related to microbial cycling fuelled by the upwelling system. This seems a little confused, given that the currently accepted size-reactivity continuum model implies that HMW material is less complex and more bioavailable (i.e. labile) than low molecular weight DOM [*Benner and Amon*, 2015].

I recommend a rewrite of this section, focused on the less speculative aspects that can be gained from this interesting data set.

End of review

References

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