

Interactive comment on “Surfactant control of gas transfer velocity along an offshore coastal transect: results from a laboratory gas exchange tank” by R. Pereira et al.

Anonymous Referee #3

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General comments:

The authors present results on surfactant control over gas transfer velocities across the sea-air interface. These results arise from seasonal field sampling of sea-surface microlayer and subsurface water along an offshore coastal transect combined with laboratory experiments using a custom-designed air-sea gas exchange tank (Schneider-Zapp et al., 2014). The comparison of field and laboratory study was applied to derive k_w from natural samples. The field parameters analysed were surfactant activity (SA) and coloured dissolved organic matter (CDOM). In the laboratory, CH_4 partial pressure was monitored to derive gas transfer velocity k_{660} (k_w for CO_2 in seawater). The authors conclude that surfactant activity in the SML can lead to a k_{660} suppression

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between 14 and 51% with strong seasonal and spatial gradients in coastal waters.

The topic presented here is indeed very interesting and of great importance for ocean and atmospheric scientists, and can make a significant contribution to the present understanding of oceanic control over atmospheric gases concentration. However, despite the relevance of the topic and its link to climate change, the aims of the study as well as potential biological implications are poorly presented. Since the study deals with biogenically organics produced, I would expect some more discussion in this respect that would expand the perception of this work across disciplines. I also think that the authors should mention how their study contributes to the understanding of air-sea gas exchange in relation to expanding oxygen minimum zones and ocean acidification, in the introduction as well as in the implications section. As an example, a recent special issue “Biogeochemical processes, tropospheric chemistry and interactions across the ocean–atmosphere interface in the coastal upwelling off Peru” (BG/ACP/AMT/OS inter-journal SI) deals with trace gases emission from coastal upwelling regimes characterized by high biological productivity. It is a totally different marine system but worth mentioning. I think the discussion shall be rewritten. It is hard to follow the authors’ argumentation, especially concerning CDOM. Results of SA and CDOM should be better linked to the gas-exchange tank experiment. Finally, I think some sentences in the introduction should refer to Eddy covariance measurements of sea-air fluxes of gases such as CO_2 as comparison to the presented data and technique.

Based on these considerations, the manuscript needs major improvement; therefore I would suggest publication after major revisions.

Specific comments:

Abstract: I agree with the first referee that abstract should be expanded, and I suggest including the aims of the study. Page 1, line 14: please revise. There is not enough information to state that terrestrially-derived CDOM can be biogeochemically processed in North-Sea coastal waters. Page 1, line 15: k_{660} isn’t it for CO_2 in seawater (and not

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freshwater?)

Introduction: Page 1, line 24: which sources and sinks? Please be more specific Page 1, line 25: which are the “environmental controls” for CO₂? Please specify. Please make a short introduction to the sea-surface microlayer and the nanolayer (e.g. Lass et al. 2013, Biogeosciences, 10, 5325–5334) as at line 35, page 1 you refer to the “monolayer”. Page 2, lines 38-40: please specify what are natural surfactants and explain why you choose to use CDOM as a tracer in this particular study, and what has been previously shown for CDOM in the SML. Also, some more details are needed in describing “procedural difficulties”.

Methods and results: Since you sampled a transect of the Dove Time Series, I suppose there should be more parameters available to describe the physical and biological environment. It would be useful to have temperature, wind speed, DOC, chlorophyll data, as an example. Also, what was the estimated thickness of the SML you collected? How did you avoid ship-contamination while sampling from the RV Princess Royal? Please shortly introduce the enrichment factor. In the results you present a mean EF. I think a median EF is more suitable than a mean EF to avoid excess weighting of a few high-enriched samples that shift EFs towards higher values. Page 2, line 66: why did you use the mean value for CDOM (250-450 nm)? Please explain. I suppose (from table 2) that the mean value is calculated between 250 and 450 nm, please expand the method section. How were CDOM samples treated? Did you filter through GF/F, or PES 0.45 μm .? For how long were the samples stored before analysis? Are these samples the same from Schneider-Zapp et al. 2013? If so, make a specific reference. Page 3, lines 84-86: it is a long sentence, please rephrase. Page 3, line 11: which one was higher, spatial or temporal variability? This sentence is opposite to the abstract. Line 112: please give some reference values for SA in the SML from the literature. Page 4, line 1: why do you expect a relationship between SML and SSW? Please explain. A variation in EF from 1 to 1.9 means no enrichment or relatively high enrichment. Are these mean/min/max values? It is hard to understand EFs is no error estimation on EF

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is given, either. For example, assuming a 10% error on EFs calculation, would you consider EF = 1.1 being enriched in the SML and EF = 0.9 or 0.89 (for SA, for instance) being rather enriched in the SSW? You could apply the Gaussian error propagation analysis to EFs as well to obtain a clearer enrichment/depletion. Page 4, line 123: I would first describe CDOM and then SR, as it derives from CDOM. Please give some reference values for SR. What does a number close to 1 or to 2 means? Compare to the literature. Page 4, line 135: please specify what do you mean by marine endmembers. Line 146: why dilution with marine LMW-DOM? Could it just be a photochemical degradation over HMW-DOM terrestrially derived? Line 148: please specify why an in-situ supply of LMW DOM should take place. By what process? I think more data are needed to support this hypothesis, as well as more reference to the existing literature. Lines 149-151: please specify what do you mean by clear compositional distinction between SML and SSW. Only in terms of MW or also of origin? Autochthonous marine DOM can be HMW-DOM as well. If no data on biological production are presented, it is hard to support this statement. Page 5, line 169: you filled the gas-exchange tank with SSW. I think you should introduce processes that lead to the establishment of a SML from SSW components, since you saw a relationship for SA in the two compartments. In particular, you should describe processes leading to higher SA and CDOM in the SML. However, you also state that SML and SSW are compositionally distinct. I think this may be contradictory here unless you specify/introduce enrichment and modification processes leading to different organic composition of the two compartments. Line 175: why don't you try specific CDOM $a(\lambda)$ to check for correlation to R660 instead of a mean value over a large wavelength range? Line 193: which correlation? Between R660 in the tank and SA of SML in situ? Page 6 line 195: I think this second argument does not add relevant information to your data and there is a lack of arguments to explain your observed correlation (that I suppose being between R660 and SA in field SML). You should instead refer to studies linking the composition and/or temporal dynamics of SML with SSW and processes leading to the enrichment of DOM in the SML. You could rather emphasize that you saw a correlation in SA between SML and

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SSW, which has been shown in many studies, and make references to those. Line 203: please give examples with the aid of the literature of what kind of organic components, both from biological and anthropogenic sources, can be part of the surfactant fraction of the SML.

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