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Discussions

Interactive comment on "Evidence for surface organic matter modulation of air-sea CO_2 gas exchange" *by* M. Ll. Calleja et al.

Anonymous Referee #4

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This paper presents the first dataset of gas transfer velocities (k) in the open ocean derived from chamber measurements, a technique that allows the investigation of small scale (time and space) k variations. The authors attempt to demonstrate that gas exchange is limited by the presence of organic matter in the surface layer, which can show much higher spatial heterogeneity than wind speed. According to Calleja and coll., this fact could have important consequences as in oligotrophic regions, the CO2 source might be higher than predicted from wind speed equations because k is weakly affected by organic matter. On the contrary, in highly productive region, high OM contents might significantly limit gas exchange and make the CO2 sink weaker than previously believed.

From my detailed reading of this manuscript, I am not convinced that the dataset of

Calleja et al. reveals a significant negative correlation between surface TOC and gas transfer velocity. I cannot trust data not shown, especially gas transfer velocity data derived from chamber in the open ocean at high wind speed and at low water-air delta pCO_2. Chamber are affected by a number of bias which cannot simply be ignored as made in this paper. Chambers can however give reasonable k relative values that could indeed be negatively correlated with TOC. The data presentation and analysis here is much too short and superficial and does not support the conclusions of the paper. In addition, the general style of the paper, the reference to the literature and the conclusion, are in some aspects incomplete and in some others very speculative. Also the paper is much too long in comparison with the amount of information it shows; a research note, removing long paragraphs of speculation, but showing and analysing the data, would be a more appropriate format. I recommend rejection or major revisions, depending on the quality of the data, when we will see them, and depending on the result of a detailed statistical analysis

Data presentation: only average CO_2 fluxes (fig2) and binned k data versus wind speed (fig 3) are shown. Please show the 40 individual points in a k-wind figure, so readers can have a better idea of the squatter in k data obtained with the chamber. I also miss a table with average,SD, ranges of: air and water pCO_2 and T, salinity, CO_2 fluxes, k, wind speed and TOC concentrations. In addition, error on the calculated k can be very high when the air-sea CO_2 gradient is below 200ppmv (Borges et al. 2004 L&O), what are the water pCO_2 values?

Data analysis: the statistical analysis is incomplete and should be better described. k vs wind speed relationships, as well as k-residual versus TOC were made on binned data only (7 points). What happens when using data? To demonstrate the dependence of k on TOC, raw data should be ranked by TOC concentration ranges and wind speed ranges and compared statistically. In addition, although the authors seem aware that the chamber method has some limits, in some cases they should moderate their conclusions and discuss their data in more details. I agree that analysing residuals

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is fair, because it suppress an eventual "average" bias in the method, but this is true only assuming the bias is constant. For example, the 2 data points at wind speeds of 9 and 11 m.s-1 are very high in comparison with other k parameterisation. Is it due to a significant (that is, demonstrated statistically) lower OM concentrations or to a bias in the method, like, for instance, changes in CO2 hydrostatic pressure in the chamber when waves start to form and break around the chamber? Discuss more deeply the data. A precise statistical analysis would allow a better understanding of the factors affecting their experimental k data, and separate what is due to OM from what is due to wind speed or to eventual biases with the chamber method.

General style: the effect of organic surfactants on air-sea gas exchange is known since 20 years. The present paper might indeed be the first direct evidence obtained experimentally in situ (if the dataset really allows it), but the process has already been described and discussed in some details. Reading only the title, the abstract and the introduction, as well as part of the discussion, one might believe that Calleja et al. demonstrate here a hitherto unknown process, which is not true. The relevant literature on organic surfactants is cited but superficially (see detailed comments). These citations appear at the end of the introduction although they should be its starting point. There are also little detailed (and superficial) references to this literature in the discussion. Instead, Calleja et al write long speculations for instance on the fetch effect, which presumably result from a bias in the chamber method (see below). Rewrite the abstract, the intro and part of the discussion, the latter being in addition much too long (one entire page on the fetch limitation can be removed, because of experimental limitation; see below).

Detailed but important comments: P4: the fact that wind is only a proxi of turbulence at the aquatic boundary layer (and thus of k) has been demonstrated by Zappa et al 2007 in GRL. There is abundant literature on the additional effects of waves, bubbles, rain and organic surfactants. Start with those ones.

P4L21-23 how was the relationship between surface active OM and k assessed in the

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previous studies? Detail the content of the cited references. P5 L3 write that tracers experiments are not able to describe the patchiness of OM in the ocean. For that reason the chamber method could be interesting. P6L21 how were pCO2 data corrected for water vapour pressure and temperature? Water vapour was not measured, air was dried in the chamber and there was no change in temperature in the equilibrator. What is corrected at the end and how? P8-9 description of the chamber method is too long. Place the last paragraph P9L15...P10 at the beginning. Refer to drifting measurement only once. The fact that chambers give higher results than gas tracers was indeed reported, but at low wind speed only. To my knowledge, these are the first chamber fluxes performed in the open ocean at such high wind speed. What do the authors think about potential problems caused by experimental conditions around and in the chamber? large waves movements, small waves breaking, etc... As a chamber user too, I am convinced that the 2 very high k data points at wind speeds of 9 and 11 m.s-1 might be affected by changes in hydrostatic pressure in the chamber, with wave movements. were pressure changes recorded in the chamber? Was there small wave breaking around the chamber? These two data points affect very much the slope of the linear regression; As result, part of the discussion (P19-20) on the fetch effect is speculative and must be removed.

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