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Biogeosciences Discussions

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

M. Ll. Calleja et al.

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Answer to Referee #4

Reviewer- Data presentation: only average CO2 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 pCO2 and T, salinity, CO2 fluxes, k, wind speed and TOC concentrations. In addition, error on the calculated k can be very high when the air-sea CO2 gradient is below 200ppmv (Borges et al. 2004 L&O), what are the water pCO2 values?

Author comment: In the new version of the manuscript a new figure 3 has been added where the 40 individual data points are shown so the reader can better visualize the

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Interactive Discussion
Discussion Paper

scatter in k data when plotted versus wind. Also, a table with average and SD of the pCO2 gradient between water and atmosphere, T, salinity, wind speeds, CO2 measured fluxes and k-estimates has now been added, as required (Table 1). The water pCO2 values ranged between 189μatm at the highly productive waters of the Southern ocean and 419μatm at the upwelling waters of the North West African coast. Air-water pCO2 gradients were always below 200ppmv. We agree that the lowest the gradient is the highest can the error on the estimated k be. However, this error can be retrieved by taking longer flux measurements. As recommended by Frankignoulle 1988, when the chamber technique was first described, the chamber measurements should be taken long enough to get a good linear correlation of pCO2 against time inside the chamber air volume. Ultimately the error of k is then derived from the error in the slope of pCO2 vs time (see figure 1). We were aware of this limitation and hence our flux measurements lasted from 2 to 5 times longer (between 10 and 20 minutes, as stated in p4215 of the manuscript), than those measured by Borges et al. 2004 (only 5 minutes). Also, the R2 of those linear regression curves were, on average, 0.93 ś 0.01, providing high precision on the estimates of k from its slope.

Reviewer- 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 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

BGD

5, S3155–S3159, 2009

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.

Author comment: We have simplified the figures to provide a more clear overview of the data set and the patterns investigated. We apologize if the manuscript was not clear enough in that sense, but data was statistically deeply analyzed: OM concentration ranges and wind speed ranges were compared statistically although this data was not shown. We ultimately focused our attention in the relationship between the residuals of k against OM when winds were below or equal to 5 m s-1 (figure 4), which was the relationship we wanted to test. We believe that the relationship between the residuals of k and OM is no longer significant for higher wind speeds ($>$ 5m s-1) because higher turbulence might be dominating gas transfer velocity at those wind regimes. In any case we are aware of the limitations of the chamber technique, which make measurements at higher wind speeds more difficult, thus causing possible biases due to potential changes in the CO2 hydrostatic pressure induced by the chamber presence. We used a binning approach following previous analysis of k vs wind speed, also based on binned data (e.g. Borges et al. 2004, Guérin et al, 2007). We now also show the raw data superimposed on the plots using binned data, to provide a full appreciation of the scatter (new figure 3). Indeed, whereas the R2 increases with the binning process, the overall precision of the predictions, as given by the SD of the estimates remains unchanged in the binning vs the raw data analysis (because of the changes in degreed of freedom). In the new manuscript we now provide additional statistic data for the relationship of k vs wind speed and also of residual k vs OM at different wind regimes, for both binned and raw data, in a new table (Table 2). We also discuss deeply the data analysis and possible explanations to the results observed. The text has been also edited to tone down the certainty about our claims and more thoroughly acknowledge the limitations of our analysis.

Reviewer- General style: the effect of organic surfactants on air-sea gas exchange is

BGD

5, S3155–S3159, 2009

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).

Author comment: It was, obviously, not our purpose to make readers believe that the role of organic matter affecting air-sea exchange is a new concept. We apologize for the strong statements which could be due to the fact that the first author and writer is not an English speaker and statements could sound stronger than they were intend to be. What we really want to remark and do believe is new and important is the fact that this is, as far as we know, the first direct evidence obtained experimentally under in situ oceanographic conditions for such effect with a quantitative assessment of its possible strength. We have reorganized the manuscript as recommended, and have edited carefully the revised version of the manuscript, including abstract, introduction and part of the discussion, to avoid too strong statements, and unnecessary speculations and better acknowledge the preceeding research on the role of organic matter films affecting air-sea exchange.

Reviewer- 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,

BGD

5, S3155–S3159, 2009

Interactive Comment

bubbles, rain and organic surfactants. Start with those ones. P4L21-23 how was the relationship between surface active OM and k assessed in the 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.

Author comment: All the detailed comments have been addressed and incorporated in preparing the revised version of the manuscript.

Interactive comment on Biogeosciences Discuss., 5, 4209, 2008.