Biogeosciences Discuss., 5, S3149–S3154, 2009
www.biogeosciences-discuss.net/5/S3149/2009/

Biogeosciences Discussions

BGD

5, S3149–S3154, 2009

Interactive Comment

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.

Received and published: 2 March 2009

Answer to Referee #3

Reviewer: A major question with this paper will be the use of domes. Although some researchers have championed the use of domes in the field, many other researchers doubt their appropriateness. As Figure 3 shows, the k values obtained using the dome provide values much higher than parameterizations from the literature, some of which are obtained using less intrusive methods.

Author comment: We are aware that there are some concerns regarding the use of the dome technique as we pointed out in our manuscript (p4215, lines 7-28). However, and despite discrepancies described in the manuscript, there are recent studies verifying that results using this method are consistent with those from other methods

(Borges et al., 2004b, Guérin et al., 2007). We agree that the gas transfer velocities obtained using the chamber technique are consistently higher than those predicted from wind speed using non-intrusive methods that average the gas exchange process over large time and spatial scales, such as the one from Wanninkhof (1992). We believe that the reason for the difference in magnitude between the gas exchange coefficients reported here and those in the literature is that those refer to the average conditions over large spatial and temporal scales, whereas the floating chamber technique yields estimates applicable to parcels of waters < 1 m2 over time scales < 1 h. Hence, the gas exchange coefficient reported here represents apparent values, which cannot be extrapolated outside the small scales applicable to the rates. This is why in our work we argue that the gas exchange coefficients derived from the floating chamber method are considered to be apparent rates, since their values cannot be directly compared with the absolute values from the widely used k-wind parameterizations, and cannot be extrapolated to open waters. On the other hand, for the purpose of this work, exchange rates estimated from short time scale variations were necessary, as the organic carbon content at the top centimeters could vary widely with the roughness conditions and with biological processes changing along the day and across space. Thus non-intrusive methods that average the gas exchange process over hours or days and large spatial scales to provide reliable estimates of the gas transfer velocity were not appropriate for this goal. Instead, floating chambers, allowing measurements over very short time (minutes) and spatial (m2) scales and delivering estimates of apparent k, were required for this study. In the new version of the manuscript we state clearly that this study is not particularly concerned with the absolute magnitude of the gas transfer velocity estimates obtained, but, rather, with resolving TOC effects on the apparent gas transfer velocity.

Reviewer: In fact in figure 3, the authors fit their points using a power curve, which completely misses their last point at wind speeds of 15 (the data points actually look exponential). The measured values, being much larger than Publisher relationships are a red flag to me.

BGD

5, S3149–S3154, 2009

Interactive Comment

Author comment: In figure 3 we didn't consider the last point at wind speed 15m/s because this is the only one obtained at these high wind speeds (15 ś 2m/s). All other points shown in this figure represent k values estimated from 3 or more observations (N=3-11), but at high wind speeds (15 ś 1m/s) we could just estimate that one point (it was not easy to deploy a small boat on the open ocean at that wind speed), so this represent a data point, rather than an average of 3 or more independent observations as the other data points are. Also, previous estimates of k related to wind speed show how that the uncertainty in k for any given wind speed increases greatly with increasing wind speed. For this reason, and to avoid strong bias derived from a single observation, that data point was not considered in the fit. We believe that this is providing us a more conservative relationship. We now provide these arguments in the revised version.

Reviewer: An intercept of 13cm hr-1 is very difficult to believe.

Author comment: Is true that we found a quite high intercept at zero wind speed (13.33cm h-1). However, as we pointed out in the manuscript, this value does not deviate that much from that reported by McGillis et al. (2004) during the Gas-Ex 2001 experiment in the Equatorial Pacific, where they also observed a very weak dependence of the gas transfer on wind velocity at wind speed below 6m s-1, and a high gas transfer value at zero wind (8.2 cm h-1). Hence, whereas the intercept is high it is not inordinate with previous, independent experimental assessments in the open ocean.

Reviewer: Also remember that the Kremer paper referenced here cautions against using the dome in areas with a large fetch yet this is not mentioned.

Author comment: We agree that Kremer call for cautions against using the dome in large fetch areas. He suggests that the working range to be considered for the chamber method should be limited to cases of low to moderate winds (less than 10 m s-1) and limited fetch that reduces waves and no whitecaps. However, he also recall that this is a self-enforcing restriction since winds producing whitecaps inject sparging air bubbles, and waves break the seal of the chamber letting air enter. So the fetch length shouldn't be an impediment itself, but fetch along with wind speed, which is what determines the size of waves produced. In that respect, two considerations should be taken into account in the work presented here: first, the flux measurements were performed with the chamber including a weight to allow its walls to extend 3-5 cm into the water column, further avoiding the creation of turbulence, and preventing air to enter the chamber; second, 90% of our data encompasses wind speeds below 10 m s-1, so only 10% of our data would be out of the working range suggested by Kremer, and as pointed earlier, the observation derived at 15 m s-1 was not used in the fit. Also, results from previous works (Jähne et al. 1987) suggest that the chamber device would create less turbulence in the aquatic boundary layer, and measured fluxes would be more realistic, when they are performed over an area that is large enough relative to that influenced by the chamber, which is the case of the large fetch areas where the work was performed.

Reviewer: These high k values make it very difficult for a non dome believer like myself to move forward with this paper, but the relationship in figure 4b is still intriguing. I do have a little trouble of using the residuals of a power curve when the relationship in figure 3 looks more exponential or cubic. It also looks like the highest wind speed data point is not included as there are no residuals of +70 in figure 4, yet this is not stated.

Author comment: The reviewer should not, in our opinion, argue from any a priori believes, and focus solely on the evidence presented here and earlier. We believe that there are arguments for and against for and against the use of domes, as there are for other techniques, and that the appropriateness of the use of domes derives from the intent and conditions of the measurements and goals, as we argued above. We believe that there is no particular value in positioning oneself as believer of one or another method, but in appreciating the potentials and limitations of each as to be able to use the most suitable method for the application on hand. As indicated by reviewer #4, who is also critical of the dome method, "analysing residuals is fair, because it suppress an eventual average bias in the method". Figure 4 represents the relationship between the residuals of k and surface TOC concentrations but only at wind speeds

BGD

5, S3149–S3154, 2009

Interactive Comment

below or equal to 5 m s-1, the range of winds where we found a statistically significant dependence between k and TOC within the top cm. So wind speed data above 5 m s-1 is not included in the plot (is not that we excluded only the data point at 15 m s-1, but all the points at winds higher than 5 m s-1). Analysis of the relationship between the residuals and TOC was performed for all the data set, and also for different wind speed ranges. The residuals of k where found to decrease significantly with increasing TOC content only at these low wind regimes. This is stated in p. 4221, but may be is not clear enough. We apologize for the confusion, and have clarified this condition further in the revised manuscript.

Reviewer: That aside, on one hand this could be evidence that organic matter in the top layer can dampen DOC flux as the author contends and others have shown. On the other hand I worry a little that this is correlative but might not be evidence of a true mechanism but is a correlative relationship that is in-direct not direct. Possible indirect causes (methodological and real) aren't discussed, but should be. Is there any inherent physical difference in the high DOC sites that could be causing an in-direct effect?

Author comment: Our measurements encompass a wide range of oceanographic conditions, extending from nutrient-rich and highly productive waters in the Southern Ocean to very oligotrophic and unproductive waters in the Subtropical Atlantic gyre. We didn't find any specific pattern that could relate TOC concentration to different water masses, although there were large inherent physical differences (temperature and salinity) among the water masses sampled. We believe that the generality of our findings across these very contrasting conditions confers robustness to our results as the dependency observed seems to be independent of the different physical properties of water masses, but attributable to the organic matter concentration changes produced by short-term biological processes.

Reviewer: Figure 4 shows that DOC can cause a 40cm hr-1 difference in k over a rather modest range in DOC. This is rather large and therefore troubling. If we used any of the other curves available, a -20cm hr-1 correction to the gas transfer velocity would cause negative or extremely small ks over a wide range of wind speed. The paper cited by Frew et al. 2002 demonstrate that surfactant concentration can only change k by ˜10cm hr-1, over a DOC range 2-3x greater. This paper should discuss why the range found here (40 cm hr-1) is so much larger with smaller DOC ranges than ranges found previously. In summary, I do find figure 4b intriguing, yet some of the numbers and ranges obtained by k seem high and are troubling to me as a reviewer.

Author comment: Frew et al. 2002 demonstrated that the degree of k reduction is dependent on the excess microlayer surfactant relative to the underlying water rather than bulk surfactant concentration. Instead we found that reduction is not dependent on the excess, but on the bulk TOC concentration. In one hand, one should be aware that surfactants might be a percentage of the bulk TOC concentration and so the whole TOC effect that we see must be masking the pure surfactant effect and must also be accounting for the effects of other organics apart from surfactants. The multiple processes, in addition to that of surfactants investigated by Frew et al. (2002), possibly involved in the effect of TOC may explain why we find a larger difference in the magnitude and ranges affecting k obtained.

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

BGD

5, S3149–S3154, 2009

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper