

## ***Interactive comment on “Thermal and haline effects on the calculation of air-sea CO<sub>2</sub> fluxes revisited” by D. K. Woolf et al.***

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This paper describes a host of issues involved in proper boundary conditions for estimating the air-sea flux of CO<sub>2</sub>. The emphasis is on the impact of near-surface gradients in water temperature and salinity associated with so-called cool-skin/warm-layers driven by the net interfacial heat flux and salty skin driven by evaporation. The paper synthesizes recent literature on the topic and corrects (I think) the notion that the cool skin effects are significantly reduced by the thinness of the CO<sub>2</sub> diffusion layer. The authors attempt to settle the issue of errors associated with using bulk water temperature (say m deep) verses skin or radiative temperature. A considerable effort is devoted to the carbon-chemistry effect and how the time scale of those reactions adds uncertainty.

We thank the reviewer for his comments. We think this is a fair summary, except it does  
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not cover our contributions to dealing with the variability in the upper ocean carbonate parameters and discrepancies between climatological temperatures and the inferred in situ temperatures concurrent to CO<sub>2</sub> measurements. We point this out since it relates to the next comment on “how much we add” and to the later comment about whether the discussion of whether “monthly/seasonal variations is a distraction”.

The paper is fairly long and wordy and reviews a lot of basic material about the layered structure of the upper ocean. Most of this review is well-known to physical oceanographers, but considering the BiogeoDisc audience, it is likely appropriate. The paper draws heavily on McGillis and Wanninkhof (2006), so its length is excessive considering how little it adds to that paper.

We admit it can be wordy, but our response to this and similar comments is that a rather pedantic and careful description is necessary to avoid repeating errors of the past or making new mistakes. It is not going to be “an easy read” but a definitive description is needed to go forward. The “layered structure of the upper ocean” is to us also “old ground” and we do not claim any originality here, but it is less familiar to other communities and therefore we think it needs to be explained quite laboriously.

We think “how little it adds” is rather harsh, as we can show by providing our own brief review. Most of the topic and most of the material in Section 2 is derived from McGillis and Wanninkhof (2006) though the latter part adds to that paper in discussing the most appropriate use of actual equilibrator measurements. Section 5 revisits territory covered by McGillis and Wanninkhof, but corrects their mistake. Sections 3, 4, 6 and 7 have little or no overlap with McGillis and Wanninkhof. Sections 3 and 4 contain novel contributions both on a rationale for using equilibrator measurements in the context of climatology and on the profile of fugacity (as dictated by the kinetics of carbonate temperature). Section 6 is similar to Section 5, but is devoted to warm layers; in this case, we make only minor corrections to the formulae used by previous investigators. Section 7 is a fairly brief treatment of the analogous haline effects, which we think is useful to “round out” the paper and is an original contribution.

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One big finding is the error in MW06 about the effects of the cool skin. I find myself convinced by the authors arguments so I think that is a valuable contribution. Also, they make clear the uncertainties in several factors that make a definitive answer impossible at this time. The question of the balance of carbonate reaction time scales and the mixing time scale is new to me and should be resolved.

We are glad the reviewer is convinced. We note that the effects related to the concentration at the interface are unequivocally shown to be important, with the sensitivity of the solubility to temperature dominating. We show also that the correct calculation of the concentration at the base of the MBL certainly does not subtract from the interfacial effects. The unresolved issue is how much is added to the interfacial effects by the subsurface effect (which depends on carbonate chemistry).

On balance this is a worthy contribution and I recommend publication. I strongly urge the authors to tighten the text and make the MS much more readable. I consider myself an expert on the physical issues and I puzzled for days over the terminology and the figures. The multiple figure dealing with the same issue seemed to add more confusion than clarity.

We are disappointed that the paper has proved hard going for reviewers and other readers. Clearly we need to address that and have identified several actions that should result in a tighter and more readable version.

Personally I would like to see some discussion in terms of conservation principles, conserved variable, and turbulent-diffusive transport in a system with a source.

We will revisit the text on carbonate chemistry and make it clearer why assuming DIC and TA is conserved is sensible and powerful. The ultimate resolution of "rapid model vs equilibrium model" may need a "bulk layer model" (e.g., Fairall et al., 2000, *Boundary-Layer Meteorology*, 96, 63-105) with a carbonate chemistry model inserted. We will make this point in a revised version.

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Also, the discussion about monthly/seasonal variations is a distraction – I suggest essentially removing it and focusing on the vertical gradient issues.

We think this discussion is not a distraction but one of the most important contributions of this paper. However, we did fail to explain its importance in the paper. Its importance may be appreciated fairly immediately by referring to the construction of current CO<sub>2</sub> flux climatologies (e.g., Takahashi et al., 2009, *DSR II*, 56, 554-577). These studies require some difficult decisions on how to use the available measurements to construct the climatology. One key example can be seen in section 6.4.4 of Takahashi et al. (2009) where they describes a correction of up to -0.28 Pg C yr<sup>-1</sup> related to temperature discrepancies between a standard climatological SST and SST measurements concurrent to oceanic pCO<sub>2</sub> measurements. The related uncertainty (of 10% or greater) is similar in importance to the cool skin effect and warm layer effect and is thus one of the three thermal or haline effects that we think deserve the majority of attention.

Since we are interested in the flux, please give an equation for the flux at the interface with the proper variables from your discussion –with all temperature dependent factors including Schmidt number.

We agree that introducing the flux equation early in Section 2 is appropriate. Schmidt number variation with temperature is worth mentioning, but in our opinion this is one of a number of "<1%" effects and most attention should be devoted to the larger effects. (We substantiate this within our response to Jan Kaiser, but we will also cover it in the revised paper)

I suggest eliminating Fig. 1 and adding an additional line in Fig. 3 that shows the conservative carbonate chemistry variable.

After reading all the reviews and taking various opinions, our mistake with figure 1 is not to make it more explicitly a pictorial guide to the terminology we use and the standard "GHRSSST terminology". Thus we prefer to strengthen figure 1 rather than remove it.

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In the current version of figure 3, we label shallow and deep waters as “iso-chemical ..” and “chemically distinct”. May be this does not work and we should show typical profiles of DIC and TA. We are not clear about this and probably need to try alternative versions of the figure on willing volunteers.

I think I understand Fig. 4 but Fig. 5 is confusing and does not seem to add. Also, Fig. 4 is poorly representative. Should not the rapid and equilibrium lines approach each other as you go down the water column. Why are there two scales with  $C_m$ ,  $C_t$ ,  $C_i$ , etc? Please put horizontal marks at the appropriate depths.

In figure 4 we deliberately displaced the two concentration scales (for the rapid model and the equilibrium model), but clearly this has caused some confusion. Also the “CM” for the rapid model is different than the “CM” for the equilibrium model). We will redraw the two concentrations on an identical scale showing that they converge at “I” and “T” but differ in between. We will ask some willing volunteers whether any version of figure 5 helps more than hinders!

I suggest combining Figs. 2 and 6 and adding a curve for  $Sc \propto E_t^{-1/2}$  if appropriate. I think the temperature dependence of  $Sc \propto E_t^{-1/2}$  is comparable to that for solubility. MW06 dismiss this, but do not explain why. I note the standard  $k$  coefficient used in these applications represents an integral over the diffusion sublayer, so it isn't obvious what temperature to use.

Figure 2 and figure 6 are “a pair” but logically figure 2 belongs in section 2 and figure 6 in Section 7, therefore separating them seems sensible to us. It is true that the temperature dependence of  $Sc$  and Solubility ( $K_0$ ) “cancel”; that is  $K_0 Sc^{-0.5}$  barely varies, but this misses the point. The importance of the alteration in calculated concentration resulting from cool skins and warm layers is magnified  $\sim x50$  by the fact that oceanic and atmospheric  $CO_2$  are near equilibrium, while the  $Sc^{-1/2}$  effect is not magnified. Again (as discussed above) we can show that the  $Sc^{-1/2}$  effect is less than 1% for a typical thermal skin. That needs to be mentioned and explained, but we are not convinced it

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is worth adding a figure.

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