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Interactive comment on "Thermal and haline effects on the calculation of air-sea CO₂ fluxes revisited" by D. K. Woolf et al.

Anonymous Referee #1

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1 General Comments

This article is concerned primarily with the issue of the thermal skin effect on the airsea exchange of carbon dioxide. There is also discussion on the effect of diurnal warm layers, as well as the impact of a salinity skin on the air-sea fluxes of CO_2 .

This article criticizes the paper from McGillis and Wanninkhof (2006), who showed that the differences in the thicknesses of the thermal and mass boundary layers had not been properly considered in previous results, and this led to an over-estimate of thermal effects on gas fluxes. This article argues that the existence of the cool-skin temperature deviation can in fact influence the oceanic uptake of CO_2 by up to 0.6 CC_2 GtCyr $^{-1}$.

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This paper was long and difficult to read and I think it has several issues. In general there are several missing references, which would indicate that the authors are not familiar with the literature (or they are being too selective). There are also some fundamental flaws with their argument which I have described below.

2 Specific Comments

Section 2 describes the three mechanisms mentioned in the introduction. It would make it easier to read if the authors were to provide a few sentences at the beginning of the section, and then describe each mechanism in subsections.

The discussion around Figure 1 does not include the haline boundary layer, even though this is in the title of the article. The authors should include discussion of the salt boundary layer here. There are also several different temperatures being introduced, and it would be useful to have an explanation of these in the figure caption. Also, there are a lot of different temperatures, concentrations, etc. (e.g. T_B, T_M), and it would be useful if these could be summarized in figure 1 which could be used as a reference when reading the paper.

It would be useful to know that the authors are at least aware of how XCO_2 is determined in equation (1), and therefore it would be very useful to have a brief description of measurement techniques.

Equation (2) introduces solubility and the authors describe how different solubility formulas introduce uncertainties. However, they do not indicate which formula they follow. Can the authors recommend one over the other? In figure 2 they present the formula by Weiss (1974) - please explain the arguments for accepting the Weiss formula? With respect to figure 2, I think the authors should plot the temperature sensitivities for salinities of 30-35 ppt, as I think (in general), there is less attention given to salinity than temperature.

The discussion regarding the calculation of C_M : I agree that it is possible to determine C_B with the measurements from a shipboard system. However, I cannot possibly understand how the authors propose to have a measurement of the temperature and salinity at the base of the mass boundary layer i.e. T_M and S_M . Can they describe how such a determination can be made?

I also have a hard time accepting the assumption that the DIC and TA will remain unchanged between a depth of several meters and z_M (about 100 μ m). I would like to see a justification of this statement here (rather than later as they suggest).

Please add the reference Wanninkhof and Thoning (1993) to P16388 L25 (i.e. correct shipbased measurements using an equilibrator).

The authors state that the temperature of interest for measurements is the "climatological" temperature at the base of the MBL. They also state that if there is a discrepancy between the measured temperature and the "temperature of interest" (arbitrarily a climatological one), then "the same equation can be applied". I don't understand this argument or its relevance. Can the authors kindly explain? Also, once again, the authors postpone a discussion (P16389 L1) which only adds to the confusion.

The sentence "but importantly any error in the in situ data is otherwise irrelevant to the calculation" does not make any sense. If there are errors, then surely these would be relevant? Am I missing something?

Figure 3 is a "common example" of vertical temperature structure. Can the authors provide some references? It's also described as a "common but minority situation", which doesn't make sense.

I'd like to see the following statements backed up with some citations:

- Therefore, some sea surface temperature climatologies use only nighttime data to calculate a foundation temperature.
- Since changes in total DIC and alkalinity within one day are usually 10 miniscule it is

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usually reasonable to assume that these properties are uniform within this layer. - A very thin layer at the sea surface largely controls gas transfer due to the suppression of turbulence in that layer.

Figure 4 is not drawn to scale (P16395 L9), but should be. The depth axis can be drawn with a log scale. I think it's important to show the different scales we are dealing with for temperature and mass. Do we know that the temperature profile with the thermal boundary layer has the shape which is shown in Figure 4? Can the authors provide a reference for this? Also the caption in figure 4 should indicate what each of the various temperatures and concentrations represent (see earlier comment). I would like to see lengthscales added to Figure 4, which will require an estimate of the various boundary layers (for estimates of the thermal boundary layer thickness, see Ward, Air—Water Interfacial Temperature Measurements in "C.S. Garbe, R.A. Handler, B. Jähne (eds.): Transport at the Air-Sea Interface pp. 191-201, 2007, Springer-Verlag Berlin, Heidelberg 2007").

For the discussion of T_{Rad} , the article by Donlon et al. (2002) should be cited ("Toward Improved Validation of Satellite Sea Surface Skin Temperature Measurements for Climate Research"). This Donlon paper also introduces the nomenclature SST_{skin} , so I don't understand why the authors chose to omit this from their list of references.

The authors make the point that T_{Rad} should not be used as a substitute for T_M , but instead T_B should be used. This is not correct. It is often the case that $T_M << T_B$ (where T_B is measured at several meters below the surface) e.g. under conditions of diurnal warming. The authors should refer to Ward (2006, JGR, doi:10.1029/2004JC002689)

The authors go on to discuss the concentration profile in Figure 4, and state that the water below the depth M is well-mixed. Further down they state that "below the base of the mass boundary layer, turbulence will be substantial and therefore transport faster than by molecular diffusion alone". This is thoroughly inaccurate. There is no turbulence available for mixing at this depth, as it is embedded within the viscous sublayer

where turbulent diffusion is damped, and where molecular viscosity ν is the dominating momentum transport mechanism. However, the rate of strain of the concentration fields results in enhanced mixing rates of gases by molecular diffusion. The authors do not seem to understand the issues here.

The nomenclature $SST_{subskin}$ is used further in the paper, but the source of this term is not cited - Donlon et al. (2002).

Equation (6) is simplified to equation (7) by assuming that $C_I \sim C_M$. The same is assumed in equation (12). If I look at Figure 4, I see a concentration (rapid) profile where the only variability that exists with depth is the gradient between the depths I and M. But here the authors now assume that there is no gradient. Does this not eliminate their whole argument?

Add a reference by Ward et al. (2006, JGR, doi:10.1029/2003JC001800) at P.16400 L.24 (observations of warm layers).

I'd like to see a diagram showing the warm layer situation described on P16401.

There is no reference to Olsen et al. (2004, GRL, doi:10.1029/2004GL020583) when discussing the effect of the warm layer on gas transfer.

There is no reference to Turk et al. (2010, GRL, doi:10.1029/2010GL045520) when discussing rain on P16405 L27.

The conclusions section has the sentence: "Where a deep or nighttime temperature is applied when a warm layer is in place, the interfacial concentration will be overestimated and the concentration at the base of the MBL will be underestimated". I don't get this, and I would need to see a diagram for this to be adequately explained. Please provide such a diagram.

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3 Technical Corrections

P16383, L25: it would be useful if the authors could list the three mechanisms here in the introduction, so that the reader knows what to expect.

P16385, L5: remove "or Molecular Boundary Layer" and please refer to this layer as the mass boundary layer

P16385, L13: delete "of the volatile"

P16386, L9: an sensitivity should be a sensitivity

P16387 L19: A new paragraph at "We now consider"

P16395 L6: The following text is very unclear and should be re-written: "will be curved as the hand over to turbulent transport progresses further as the interface recedes"

Interactive comment on Biogeosciences Discuss., 9, 16381, 2012.