

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

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The paper by Woolf et al. is a technical discussion of the effect of thermal and haline gradients at air-sea interface on air-sea CO₂ fluxes. It would be useful if the often theoretical arguments could be related back to the actual experimental measurements (e.g., using shipboard equilibrators) and related calculations of air-sea fluxes. This was done in the paper by McGillis and Wanninkhof (2006), which is at the base of the analysis and criticism of the present paper. It would certainly make the present paper more accessible and usable.

We thank Jan and his students for their input. We do not agree that there is less connection to practical measurements than in McGillis and Wanninkhof (2006), indeed we devote much more effort to the practical problem of estimating the concentration at the

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base of the “skins” given that almost all measurements take water from much deeper. However, it is certainly fair comment that we did not devote much attention in the paper to explaining the future applications. (We devoted only a four line paragraph at the end of the Introduction to this issue). This study was motivated by the need to produce more accurate estimates of air-sea fluxes, with genuine uncertainty estimates and we can certainly explain that motivation. There are also specific topics tackled within the paper that are motivated by an informed reading of the existing literature. For example, section 6.4.4 of the latest Takahashi et al. *climatology* (2009, DSR II, 56, 554-577) describes a correction of up to $-0.28 \text{ Pg C yr}^{-1}$ related to temperature discrepancies between a standard climatological SST and SST measurements concurrent to oceanic pCO_2 measurements. That uncertainty motivates section 3 in particular, where we argue that the equilibrator measurements should be directly combined with climatological temperature (largely ignoring inferred values outside the hull of the ship). We should state clearly that we have no wish to lecture anyone on how to make equilibrator measurements, but there are interesting and important issues regarding how those measurements are applied to climatological calculations. We plan that those concerns will be more forcefully expressed in a revised version of our paper. The paper will remain primarily theoretical with the actual applications only outlined, but the motivation for the work clearly stated.

In particular, I would like to make the following comments:

1) The authors base their discussion on $\text{p}(\text{CO}_2)$ or $\text{f}(\text{CO}_2)$. However, these are usually quantities derived from measurements of the CO_2 mole fractions in an equilibrator headspace, which will have already been subject to certain corrections and temperature measurements. It is not clear whether these equilibrator corrections would counteract any suggested biases due to boundary layer effects.

We do rely on the accuracy of equilibrator measurements (though realistic estimates of biases and random errors can be built into climatologies). We are not experts on those measurements and do not presume to advise those that are. One of the important

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points of the paper (especially Section 3) is that the inferred temperature outside the ship's hull can be largely eliminated as a source of error (the lead author does have direct experience of the difficulty of estimating this temperature from participation in "ferry" measurements). Of course, all measurements may have unknown errors, but there does not seem to us to be any benefit on dwelling on unknown biases associated with the equilibrator. Instead we plan to remove known biases related to thermal and haline effects. We will state explicitly that we assume that there are no further biases.

2) Gas-exchange parameterisations based on radiocarbon (^{14}C) budgets (e.g., Wanninkhof, 1992; Sweeney et al. 2007) are based on the concentration gradient between ocean and atmosphere. They have ignored the suggested boundary layer effects so far. The radiocarbon-based value of k should be slightly smaller if the skin effect was included in the calculation of k . This would compensate for the enhanced gradient when this corrected value is used in "unknown" gas exchange calculations. Putting it differently, any user of these parameterisations in their present form should also disregard any boundary layer effects, to avoid introducing any biases.

This is an interesting point, which may deserve a more thorough treatment, but from a brief analysis we reason that any "compensation" will be small compared to the global effect of ignoring the skin effect in the calculation of the concentration difference. Strictly for the purposes of this response, we explain the underlying reasoning below.

Firstly, we do not have any firm attachment to any method or parameterisation for measuring or parameterizing transfer. All the methods at the root of estimates of k will have some potential biases related to temperature. One effect is related to the experimental Schmidt number being miscalculated (transfer velocities are usually assumed to scale as Sc^{-n} , where it is often also assumed $n=1/2$). The other important effect is due to the concentration difference being miscalculated. The effect on Schmidt number will always be small; we estimate an underestimate of predicted transfer velocities of the order of 0.5% or less due to ignoring the skin effect (and therefore underestimating the

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Schmidt number) in the original “k experiment”. The effect on concentration difference is only substantial if the k experiment was conducted in near-saturation conditions. (This is closely related to our explanation in the Introduction that the importance of the skin effect is largely due to the near balance of CO₂ between atmosphere and ocean; thus an implied underestimate of say $\sim 0.2\%$ in the gross invasive flux will translate to a $\sim 10\%$ underestimate of the net invasive flux). Most k experiments are deliberately conducted “off equilibrium” to ensure the net flux is large; thus the error in the net concentration difference due to the skin effect will be very small. The “Bomb 14C” method is unusual and the theoretical effect is relatively difficult to untangle, but again an $\sim 0.2\%$ underestimate of the interfacial concentration might be expected. This would translate to a $\sim 0.2\%$ overestimate of the transfer velocity immediately “post Bomb”, but that overestimate will increase progressively as more Bomb 14C penetrates the ocean. Even given a rather substantial penetration of Bomb 14C, we suggest the effect will be dwarfed by the O(10%) effect that we explain in the paper.

3) It would be useful to separate the (iso)chemical effects more clearly from the error highlighted in McGillis and Wanninkhof’s (2006) paper, i.e. the assumption that the equilibrator concentration would be subject to a temperature correction that would cancel out the skin effect on the saturation concentration. Since the effects apply to any non-soluble gas, the skin effects should first be evaluated for a gas that is not subject to chemical equilibria (such as O₂).

We did limit ourselves to CO₂, but the effects are worth mentioning for any gas that is always, or on average, close to saturation. The most obvious examples are oxygen and the noble gases.

We start here by briefly explaining the situation for other (generally simpler gases). The situation is relatively complicated for carbon dioxide because it is a non-ideal gas (a very small effect) and due to the temperature sensitivity of the carbonate system (arguably a fairly significant effect). For an ideal and unreactive gas, two thermal mechanisms still remain; one due to the sensitivity of solubility to temperature, the other

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related to the miscalculation of saturated vapour pressure adjacent to the interface. A “-2.5%/K” solubility effect for CO₂ will need to be recalculated for other gases but the effect will usually be negative and the most significant effect. A “-0.2%/K” humidity effect is independent of the gas and will always apply.

We are not immediately sure how much to incorporate in a revised version. It need be only a small digression but would extend the scope of the paper and logically a separate section will be required.

4) The present paper mentions that CO₂ hydration reactions are slow, but this applies to the purely chemical case. In the presence of carboxylase (a ubiquitous enzyme with a very high turnover rate) the equilibration between the different DIC components may well be very rapid. Perhaps this should be discussed in the context of the "rapid" and "equilibrium" models.

Yes, we are familiar with this effect and recall experiments by Ben Matthews at UEA on the effect of this enzyme on transfer velocity. It is worth mentioning and we will add some text.

5) My colleague, Dr Martin Johnson, has recently written a review on uncertainties in air-sea gas exchange calculations, which states that the skin effect is small. The paper by Johnson et al. (2011) is called "A Rumsfeldian analysis of uncertainty in air-sea gas exchange" (<http://repository.kulib.kyoto-u.ac.jp/dspace/bitstream/2433/156156/13/06-04%2849%29.pdf>). Perhaps this paper should be cited and its findings appraised.

We are familiar with the paper by Johnson et al. (2011) and we discussed it with him even before publication. In our understanding the remarks on the skin effect in that paper are essentially derived from the analysis of McGillis and Wanninkhof (2006) without adding to it, in which case a citation is unnecessary.

6) Going beyond the theoretical aspects of the argument, Ward et al. (2004) claim to have experimental evidence that the skin effect is irrelevant. It might be worth com-

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menting on this paper as well.

We think that you have misread Ward et al. (2004) and there is nothing in that paper which contradicts us. Ward et al (2004) preceded McGillis and Wanninkhof (2006) and calculated (based on measuring the temperatures and fugacities) the magnitude of skin effects and warm layer effects on CO₂ flux in broadly the same way as other investigators before 2006. The following two quotes from the Conclusions of Ward et al., we think summarises what their calculations revealed and why: Page 12/14 paragraph [71]: “The relative increase in the CO₂ flux (i.e. $\Delta F/F$) from temperature in this study is quite small (Figure 3). This is a consequence of the large air-sea CO₂ fugacity difference in the equatorial Pacific. In other regions where the $\Delta f\text{CO}_2$ (and hence the flux) is smaller, the relative increase in the CO₂ flux is greater from temperature biases...” Page 13/14 paragraph [72]: “... the net effect from the warm layer biases tended to cancel each other. However, this conclusion should not be extrapolated to a global situation. ...” The first quote accords with the explanation in the Introduction and in answer to Comment 2 that the importance of these effects is largely due to the near balance of CO₂ between atmosphere and ocean. In local cases where the imbalance is large, the relative effect of each thermal or haline effect will be quite small. The second point accords with our discussion on warm layers (Section 6) that these will be very important and can cancel or even reverse the thermal skin effect in locations such as the equatorial Pacific, but will be less important on a global average.

7) My PhD students and I found the paper rather hard to understand, often vague and sometimes repetitive. A bit of editing, a structure with more subsections and a section that distinguishes physical effects (that would apply to all gases, see above) from chemical ones (as for CO₂), would allow people to recognise the significance of the paper more clearly.

This topic requires close attention to detail and thus it is going to be difficult to make it both definitive and easy to read. On the whole, we think it is necessary to be quite

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pedantic rather than risk misinterpretation. However, we did think that we had made it cogent and understandable and we are humbled that various reviewers and readers have protested that it is not. Clearly, we will need to try harder in a revised version.

The phrase “often vague” worries us most. There are a few issues that have to be left open (the accuracy of solubility formulae; “rapid model” vs “equilibrium model”; precise magnitude of the thermal skin anomaly) simply because knowledge is insufficient, but otherwise we thought that we had erred on the side of pedantry rather than vagueness. There are a few things that other reviewers have picked up as requiring explanation or referencing, but we would be grateful if you can identify others.

We will introduce subsections to Section 2. All the other sections are fairly short. We have covered “other gases” in response to Comment 3.

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