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Discussions

Interactive comment on "Thermal and haline effects on the calculation of air-sea CO_2 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.

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

1) The authors base their discussion on p(CO2) or f(CO2). However, these are usu-

ally quantities derived from measurements of the CO2 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.

2) Gas-exchange parameterisations based on radiocarbon (14C) 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.

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).

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.

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.

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 commenting on this paper as well.

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.

References:

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