

## ***Interactive comment on “Improved routines to model the ocean carbonate system: mocsy 1.0” by J. C. Orr and J.-M Epitalon***

**J. C. Orr and J.-M Epitalon**

james.orr@lsce.ipsl.fr

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### **Response to Referee, Prof. Andrew Dickson**

We thank Prof. Dickson for his insightful comments. In addressing his concerns, we think the revised manuscript will be improved substantially. His comments are repeated below in gray, while our responses follow in black.

The existence of carefully evaluated computer code for use in ocean carbon cycle models is clearly desirable, and this code goes beyond that used in the Ocean Carbon Model Intercomparison Project (OCMIP) both in terms of the number of carbonate system variables it computes, and in the careful evaluations provided by this manuscript. I thus feel it is appropriate for publication. Nevertheless, I feel it can be improved in a

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few key areas.

As with the companion paper (Orr et al., Biogeosciences Discussions 11, 5327–5397, 2014) this manuscript looks carefully at a number of potential discrepancies that arise when computing ocean carbonate chemistry. However, it too seemingly ignores the elephant in the room: the calculations themselves can, in principle, be done as accurately as machine precision allows, however, the real uncertainties in the various calculations are due to uncertainties in the input data – in this context, the various equilibrium constants and estimates of salinity-dependent concentrations.

As the manuscript notes, both in praising the work of Lewis & Wallace (1998) and in commenting on the paper by Millero (2010), these are all susceptible to error. Such errors take two potential forms: errors (typographical?) in the values for the various coefficients in the fitting equations representing the equilibrium constants, and uncertainties in the original data that is being represented. Although, it may well be that such uncertainties are not the largest contribution to the overall uncertainty in ocean carbon cycle models, I feel it might be useful for the authors to consider the implications of such errors on the calculated quantities such as  $p\text{CO}_2$  or even  $\Omega_{\text{arag}}$ , possibly in the way they have considered the implications of choosing alternate total boron estimates.

The last sentence above appears to suggest in part that we make sensitivity tests with mocsy to quantify how much computed variables differ when using different sets of constants. In the Discussion paper, we already showed that there was a large difference in computed  $p\text{CO}_2$  when switching between formulations for  $K_1$  and  $K_2$  from Lueker et al. (2000) and those from Millero (2010). Additionally, our companion paper (Orr et al., 2014, Figure 1) demonstrated that very small differences result when switching between formulations for  $K_1$  and  $K_2$  from Dickson and Millero (1987) and Lueker et al. (2000). We did not compare other formulations for  $K_1$  and  $K_2$  because they are not offered by mocsy. That is a design choice to encourage modelers to use the sets of constants recommended for best practices (Dickson et al., 2007) or perhaps a more recent formulation. Nor did we make similar tests for other key constants, despite known

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sensitivities of some computed variables (Orr et al., 2014, Table 9) including  $p\text{CO}_2$  to  $K_0$ ,  $\text{CO}_3^{-2}$  to  $K_B$ , and the  $\Omega$ 's to  $K_{spA}$  and  $K_{spC}$ . The reason is that today there is not a wide choice of up-to-date formulations for these constants. Indeed, community members typically use the same single formulation for each constant, as recommended for best practices.

Nonetheless, we are now considering making more sensitivity tests with various formulations of the different constants in the revised version of our companion manuscript (Orr et al., 2014), but with with other packages besides mocsy, which will never offer a wide choice.

Moreover, we do eventually plan to add an important feature to mocsy: propagation of errors. Yet implementation has been slowed by results from preliminary tests that indicate substantial covariance between some of the input variables (i.e., the equilibrium constants). Proper implementation that includes covariances will have to wait until after the revised manuscript is submitted. Error propagation may be the correct way to address unknown "typographical" errors, if one assumes they are numerous and randomly distributed. We hope though that after years of extensive community use and review, there remain no typographical errors in the set of constants recommended currently for best practices.

#### *Other more specific comments*

The discussion throughout refers to the  $p\text{CO}_2$ . Insofar as the Weiss (1974) formulation relates  $[\text{CO}_2]$  to the  $\text{CO}_2$  fugacity, rather than to its partial pressure I was wondering just how the one was converted to the other? (Of course it is practical to use the alternate coefficients in Weiss & Price (1980) to get an equilibrium constant that relates directly to  $p\text{CO}_2$ .)

In mocsy, we use  $K_0$  from Weiss (1974) to compute  $f\text{CO}_2$  from  $\text{CO}_2^*$  and the fugacity coefficient  $C_f$  (Weiss, 1974; Dickson and Goyet, 1994; Dickson et al., 2007) to compute

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$p\text{CO}_2$  from  $f\text{CO}_2$ .

$$[\text{CO}_2^*] = K_0 f\text{CO}_2 = K_0 C_f p\text{CO}_2 \quad (1)$$

In the revised manuscript we will mention these details. We prefer not to use the equivalent, more practical "combined" coefficient  $F$  from Weiss and Price (1980) in order to do calculations in a stepwise fashion. Furthermore that combined coefficient

$$F = K_0 C_f (1 - p\text{H}_2\text{O}) \quad (2)$$

includes a wet-to-dry air conversion (term in parentheses), which is not appropriate for the conversions in equation 1 above; rather, it is used only when converting between  $p\text{CO}_2$  and  $x\text{CO}_2$ . The latter is not yet computed in mocsy (see below).

How is  $p\text{CO}_2$  calculated at pressure? Is the Weiss (1974) approach to high-pressure  $\text{CO}_2$  solubility used? (I don't think it is mentioned either in Millero (1995) or in Orr et al. 2014, Table 7.)

We confirm that neither Millero (1995) nor Orr et al. (2014) mention anything about pressure corrections for  $K_0$ , from which  $f\text{CO}_2$  is computed from  $[\text{CO}_2^*]$ . Prof. Dickson's remark has prompted us to take another look at the Weiss (1974) equations and at the  $K_0$  formula in all packages for which we have source code, including mocsy. All packages compute  $K_0$  with the same standard equation (Weiss, 1974, equation 12), but none of them make the exponential pressure correction (Weiss, 1974, equation 5):

$$[\text{CO}_2^*] = K_0 f\text{CO}_2 \exp[(1-P)v_{\text{CO}_2}/RT] \quad (3)$$

Thus the computed  $f\text{CO}_2$  refers only to potential values considering the pressure as that at the surface. As pointed out by Weiss (1974), that simplification is adequate down to about 100 m; below that the pressure correction is not negligible and should be included. We will discuss this systematic bias in the revised manuscript and remedy the problem in the next version of mocsy.

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Finally, does mocsy allow for computation of the more common form used for the atmosphere:  $x(\text{CO}_2)$  in dry air?

No, mocsy does not currently compute any atmospheric variables, neither  $x\text{CO}_2$ ,  $p\text{CO}_2$ , nor  $f\text{CO}_2$ . It only computes oceanic variables. That is, it is designed for ocean models, which do not assume air-sea equilibrium. Hence mocsy currently computes only the ocean side of the air-sea difference in  $p\text{CO}_2$  as well as other oceanic carbon system variables. Models compute the air-sea  $\text{CO}_2$  flux from the air-sea difference in  $p\text{CO}_2$ . Models do not carry oceanic  $p\text{CO}_2$  as a tracer but need to compute it from two passive tracers  $A_T$  and  $C_T$ . For the atmospheric side, the  $x\text{CO}_2$  does not usually need to be computed because models typically specify that a priori (or compute it from emissions and fluxes to and from a finite atmosphere). From atmospheric  $x\text{CO}_2$ , they compute atmospheric  $p\text{CO}_2$  via the standard formula that accounts for atmospheric pressure and humidity. The mocsy package does not yet provide these computed atmospheric variables because models already have procedures in place to make those standard calculations. Nonetheless, for completeness we may well provide routines to convert between  $p\text{CO}_2$  and  $x\text{CO}_2$  in the next version of mocsy.

The use of the particular chemical formulae  $\text{PO}_4^{3-}$  and  $\text{SiO}_2$  to represent the terms *total (dissolved inorganic) phosphate* and *total (dissolved inorganic) silicate* is potentially misleading, especially as a later discussion focuses on the contribution of various such species to total alkalinity. I recommend choosing an alternate notation.

In the revised manuscript, we will use  $\text{P}_T$  and  $\text{Si}_T$  following the guide for best practices (Dickson et al., 2007).

The decision to use an analytical expression for the Revelle Factor, whether that of Frankignoulle (1994) or of Egleston et al. (2010), implies – I believe – that the contributions of phosphate species and silicate to alkalinity are ignored. This may well explain the deviations from CO2SYS shown in Figs. 1 & 2.

We thank Prof. Dickson for this insight into the cause of differences in  $R$  shown in

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Figs. 1 and 2. His explanation appears correct. Indeed, the analytical expressions from Frankignoulle (1994) and Egleston et al. (2010) both ignore nutrient alkalinity, whereas the numerical solution from CO2SYS does not. We will test his idea and report on results in the revised manuscript. Based on these results we will also consider changing the formulation for the Revelle factor in mocsy, although differences remain small. Discrepancies could also derive from numerical issues.

It is – I feel – misleading to refer to the various equilibrium constants as apparent constants. This term appeared originally in the biochemical literature as a synonym for conditional constant (a concentration quotient that applies only when the concentration of one of more reactants or products is fixed at a particular constant value); it was then adopted by Pytkowicz in the 1960s to describe what had earlier been referred to as incomplete constants (as they were a combination of concentration terms and  $10^{-\text{pH}}$ : believed to be the activity of hydrogen ion). Thus it is not (as the m/s states on p. 2882) because “these equilibria use concentrations instead of activities”. I would prefer to say “concentration quotients” if I am making clear that these are not standard equilibrium constants (with a reference state of pure water), otherwise I feel that “equilibrium constants” is sufficiently correct and clear.

For simplicity, we will only use the term “equilibrium constants” in the revised manuscript. We will not refer to apparent constants, but may mention “concentration quotients”, a term that we were unfamiliar with previously.

I note the authors say both “total boron” (p. 2882 line 16) and “total borate” (p. 2882 line 24), I’d prefer they used one only.

In the revised manuscript, we will use *total boron* and avoid the term *total borate*.

The authors choose to talk about discrepancies both in relative terms (Figs. 1 & 2) as well as in absolute terms (other figures). I found this confusing, and wonder at the value of using absolute discrepancies without, at least, indicating how large the original number is.

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In the revised manuscript if we continue to show absolute differences, we will also indicate sizes of the original numbers.

On p. 2886 the authors write “Hence the  $A_T$  minus  $C_T$  increases, as must then the buffer capacity.” I am not sure that this is very clear. I assume this is referring to the fact that the Revelle factor has a maximum when  $A_T \approx C_T$  and thus as one moves away from this the Revelle factor decreases.

We thank Prof. Dickson for flagging this sentence. Not only is it unclear, it is wrong. It is incorrect because it is based on the idea that  $C_T$  decreases. Earlier in the same paragraph, we correctly pointed out that  $A_T$  and  $C_T$  are unaffected by the boron formulation because both are input variables (in this case). Hence the  $A_T - C_T$  difference remains constant. In the revised manuscript, we will explain the reduction in the Revelle factor in simpler terms after rearranging its equation:

$$R = \frac{\partial p\text{CO}_2 / p\text{CO}_2}{\partial C_T / C_T} = \frac{\partial p\text{CO}_2}{\partial C_T} \left( \frac{C_T}{p\text{CO}_2} \right) \quad (4)$$

On the right hand side, the partial derivative increases by roughly 1% when the new boron formulation (Lee et al., 2010) is used in place of the standard (Uppström, 1974). However the adjacent concentration ratio (in parentheses) decreases by relatively more, about 1.4%. Hence  $R$  decreases because  $p\text{CO}_2$  increases ( $C_T$  remains constant).

Although I think it was Zeebe & Wolf-Gladrow who coined the phrase “practical alkalinity” I am not sure it bears repeating here. If the contribution of phosphate and silicate alkalinity is larger than the likely error in alkalinity, then it is not strictly either practical or an alkalinity.

In the revised manuscript, we will avoid the use of the term practical alkalinity.

It is incorrect to write the water alkalinity as is done in (4); rather it should include the hydrogen sulfate and hydrogen fluoride terms – which should be removed from (7):

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$$A_W = [\text{OH}^-] - [\text{H}^+]_F - [\text{HSO}_4^-] - [\text{HF}].$$

The grouping  $([\text{H}^+]_F - [\text{HSO}_4^-] - [\text{HF}])$  is a form of total concentration of hydrogen ion in the seawater; and the water alkalinity is a measure of the difference from acid-base neutrality. Note that in many representations this grouping is represented as  $[\text{H}^+]$ , strictly this should be thought of as being on the so-called sea water scale.

Thank you for these corrections. In the revised manuscript, we will correct equations (4) and (7) and add sentences about the meaning of  $A_W$  and the grouping of the seawater scale.

Fig. 1: The close correspondence between the relative deviation in  $[\text{H}^+]$  and in  $[\text{CO}_2^*]$  suggests a slight discrepancy in  $K_1$ ; the mismatch between the error in  $[\text{CO}_2^*]$  and that in  $p\text{CO}_2$  suggests a slight discrepancy in  $K_0$ . As was noted above, the growing discrepancy in the Revelle factor suggests to me that nutrients may not have been considered when calculating it (either in CO2SYS or in mocsy).

We will report on further investigation of these discrepancies and elaborate in the revised manuscript. For now we can say that study of the CO2SYS and mocsy code reveals that the small mismatch in discrepancies between  $[\text{CO}_2^*]$  and  $p\text{CO}_2$  is not due to  $K_0$ ; rather it is due to slightly different fugacity coefficients  $C_f$ , in particular a minor bug in mocsy (incompatible units between the gas constant and atmospheric pressure). That will be corrected in the revised manuscript. Secondly, we already confirmed above that nutrients were neglected in the analytical equations of  $R$  from Frankignoulle (1994) as used by mocsy; conversely, they were not neglected in the numerical solution of  $R$  implemented by CO2SYS.

Why is a mean a useful parameter to plot in Figs. 1 and 2? I would have thought that the maximum discrepancy would have been the one most of interest.

It is a good idea to show the maximum. But we think that the mean is also of interest because by definition it is more typical. We will explore options of how to represent

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both in the revised manuscript.

Fig. 3: I am not sure that absolute deviations are superior to relative ones here. Certainly I found the scale difference between  $p\text{CO}_2$  and the corresponding concentration of unionized  $\text{CO}_2$  to be odd.

The point is well taken against using absolute differences (as in the Discussion paper) and the benefit of showing relative differences instead. With the latter, which we will adopt in the Revised manuscript, plots for  $p\text{CO}_2$  and  $\text{CO}_2^*$  will be much more similar.

Fig.4: Shouldn't the last line of the legend say . . . (1) Uppström (1974) and . . . ?

Yes it should. We will correct this mistake in the revised manuscript.

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