title Manuscript prepared for Biogeosciences Discuss. with version 4.0 of the LATEX class copernicus_discussions.cls. Date: 5 December 2014

Author Response on "Improved routines to model the ocean carbonate system: mocsy 1.0"

James C. Orr¹ and Jean-Marie Epitalon^{1,*}

¹LSCE/IPSL, Laboratoire des Sciences du Climat et de l'Environnement, CEA-CNRS-UVSQ, France *now at: Geoscientific Programming Services, Toulouse, France

Correspondence to:

We thank the three referees for their many thoughtful comments, which have resulted in numerous improvements to the code and the manuscript. Referree comments are repeated below in gray, our responses follow in black, and our changes to the manuscript are indicated in blue.

5

Response to Referee #1, Prof. Andrew Dickson

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 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 pCO_2 or even Ω_{arag} , possibly in the way they have considered the implications of choosing

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 pCO_2 when 5 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 10 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 sensitivities of some computed variables (Orr et al., 2014, Table 9) including pCO_2 to K_0 , CO_3^{-2} to K_B , and the Ω 's to Ksp_A and Ksp_C . The reason is that today there is not a wide choice of up-to-date formulations for these constants. Indeed, community members 15 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.

20

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 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.

25

In the revised manuscript, comparison of the different formulations for K_1 and K_2 , the constants to which computed variables are most sensitive, has been elaborated as described below. Otherwise, we have not added propagation of errors for reasons mentioned above. That critical effort requires refining the scientific approach used until now and thus may not be ideally suited for a publication in GMD. It is left for future work through a project that has just been funded.

Other more specific comments

The discussion throughout refers to the *p*CO₂. Insofar as the Weiss (1974) formulation relates [CO2] to the CO₂ 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 pCO2.

In mocsy, we use K_0 from Weiss (1974) to compute $f CO_2$ from CO_2^* and the fugacity 15 coefficient C_f (Weiss, 1974; Dickson and Goyet, 1994; Dickson et al., 2007) to compute pCO_2 from fCO_2 .

$$[\mathrm{CO}_2^*] = K_0 f \mathrm{CO}_2 = K_0 C_f p \mathrm{CO}_2 \tag{1}$$

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

$$F = K_0 C_f \left(1 - p H_2 O \right)$$
 (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 pCO_2 and xCO_2 . The latter is not yet computed in mocsy (see below).

25

20

5

How is pCO_2 calculated at pressure? Is the Weiss (1974) approach to high-pressure CO_2 solubility used? (I don't think it is mentioned either in Millero (1995) or in Orr et al. 2014,

Discussion Paper

(3)

Table 7.)

We confirm that neither Millero (1995) nor Orr et al. (2014) mention anything about pressure corrections for K_0 , from which $f CO_2$ is computed from $[CO_2^*]$. 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):

 $[CO_2^*] = K_0 fCO_2 \exp[(1-P)\bar{v}_{CO_2}/RT]$

- ¹⁰ 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.
- A new section in the revised manuscript, section 2.1.3, discusses these points in detail as well as the critical pressure correction of C_f , which dramatically affects calculated subsurface pCO_2 .

Finally, does mocsy allow for computation of the more common form used for the atmosphere: x(CO2) in dry air?

20

The mocsy 1.0 package does not currently compute any atmospheric variables, neither xCO_2 , pCO_2 , nor fCO_2 . It only computed oceanic variables. Being designed for ocean models, which do not assume air-sea equilibrium, mocsy 1.0 computed only the ocean side of the air-sea difference in pCO_2 as well as other oceanic carbon system variables. Models compute the air-sea CO₂ flux from the air-sea difference in pCO_2 . Models do not carry oceanic pCO_2 as a tracer but need to compute it from two passive tracers A_T and C_T . For the atmospheric side, the xCO_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

xCO₂, they compute atmospheric pCO₂ 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 pCO₂ and xCO₂ in the next version of mocsy.

Inspired by this comment, we now provide routines in mocsy 2.0 code to convert between pCO_2 , fCO_2 , and xCO_2 , on both the oceanic and atmospheric side of the air-sea interface. Where appropriate, these routines account for humidity and atmospheric pressure, and hydrostatic pressure. We also provide new routines to compute the air-sea CO2 flux, following the OCMIP2 approach but correcting its small iconsistencies. These new routines are mentioned in section 2.1.3 and documented in the mocsy 2.0 manual that is mentioned in final section.

The use of the particular chemical formulae PO₄³⁻ and SiO₂ 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 mannuscript, we will use P_T and Si_T following the guide for best practices (Dickson et al., 2007).

Done, throughout the manuscript.

5

The decision to use an analytical expression for the Revelle Factor, whether that of Frankig noulle (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 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 dervie from numerical issues.

5

We now solve for the Revelle factor with a numerical approach (centered finite difference) to compute the derivative as described in the new section 2.1.4. We also show that this new formulation is at least 6 times more accurate in the deep ocean. That is, our numerical approach accounts for nutrients, whereas the older analytical approach did not (section 3.1).

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^{--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.

Discussion Paper

In the revised manuscript we use only the term "equilibrium constants".

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.

5

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

In the revised manuscript we define $B_{\rm T}$ at total dissolved inorganic boron. We now use that symbol or refer to total boron, and never use "total borate".

10

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.

¹⁵ In the revised manuscript, if we continue to show absolute differences, we will also indicate sizes of the original numbers.

In the revised manuscript, Figs. 4 and 5 (former Figs. 1 and 2) show both relative and absolute differences. Likewise, although Fig. 6 shows absolute differences, it is complemented ²⁰ by a new figure (Fig. 7) that shows the same results as relative differences. Figs. 8, 9, 10, and 11 still show absolute differences but their corresponding relative differences can be estimated by comparing with two new figures (Figs. 1 and 2), which show the baseline. By baseline, we refer to the results computed with mocsy from the GLODAP-WOA2009 data, shown as zonal means and profiles.

25

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 $C_{\rm T}$ decreases. Earlier in the same paragraph, we ⁵ correctly pointed out that $A_{\rm T}$ and $C_{\rm T}$ are unaffected by the boron formulation because both are input variables (in this case). Hence the $A_{\rm T} - C_{\rm T}$ difference remains constant. In the revised manuscript, we will explain the reduction in the Revelle factor in simpler terms after rearranging its equation:

$$R = \frac{\partial p CO_2 / p CO_2}{\partial C_T / C_T}$$

$$= \frac{\partial p CO_2}{\partial C_T} \left(\frac{C_T}{p CO_2} \right)$$
(4)

¹⁰ 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 pCO_2 increases (C_T remains constant).

¹⁵ In the revised manuscript, we refine our explanation above in section 3.3 (second paragraph, last half).

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 alkalinities 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.

In the revised manuscript, we do not use 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):

5 $A_W = [OH^-] - [H^+]_F - [HSO_4^-] - [HF].$

The grouping $([H^+]_F - [HSO_4^-] - [HF])$ 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 $[H^+]$, 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.

15

In the revised manuscript, we have made all these changes (Discussion, paragraph 3).

Fig. 1: The close correspondence between the relative deviation in [H⁺] and in [CO₂^{*}] suggests a slight discrepancy in K₁; the mismatch between the error in [CO₂^{*}] and that in pCO₂ suggests a slight discrepancy in K₀. 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 $[CO_2^*]$ and pCO_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.

⁵ In the revised manuscript, we describe these differences and their causes when we introduce corresponding figures (now Figs. 4 and 5). See section 3.1. Nutrients are now considered in mocsy's new numerical formulation for the Revelle factor (section 2.1.4).

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.

We think that the mean is of interest because by definition it is more typical.

The revised manuscript shows the mean difference. For concision, we limit ourselves to showing the mean vertical profile and the zonal mean distribution of each computed variable (Figs. 4 and 5). The latter shows that relative differences are quite homogeneous across the surface ocean, at least in terms of the zonal mean, which is typically responsible for the majority of the variability. Given these results, showing also the maximum (and minimum) would add little new information while requiring at least another 2 figures and corresponding text. We have opted for simplicity.

Fig. 3: I am not sure that absolute deviations are superior to relative ones here. Certainly I found the scale difference between pCO_2 and the corresponding concentration of unionized CO_2 to be odd.

25

The point is well taken against about the benefit of showing relative differences.

In addition to the figure mentioned (now Fig. 6), which shows absolute differences, the revised manuscript also shows those changes as relative differences in a new figure (Fig. 7).

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

5

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

Done. Response to Referee Comment by Guy Munhoven

10

1 General comments

1.1 Appreciation of the manuscript

In this paper, J. C. Orr and J.-M. Epitalon describe a new Fortran 95 library to model the ocean carbonate system, MOCSY. MOCSY updates and extends the widely used codes from the Ocean Carbon Cycle Model Intercomparison Project, OCMIP (Orr et al., 2000). It extends the choice of stoichiometric constant parameterizations, to comply, as far as possible with the recommendations for best practices (Dickson et al., 2007). Deviations from best practices are clearly stated and entirely justified. MOCSY furthermore provides more complete speciation calculations than the OCMIP codes.

MOCSY also offers its users the possibility to take into account developments that got published after the best practices. These include the new boron-to-salinity ratio from Lee et al. (2010) and more recent parameterizations for the two dissociation constants of carbonic acid. It furthermore goes beyond the recommendations for best practices, by also providing the necessary formulations for pressure correction (Dickson et al. (2007) does not include these since its focus is on the analytical aspects of carbonate system measurements, generally made

Discussion Paper

Discussion Paper

at atmospheric pressure).

Finally, the paper also presents a quantitative assessment of several approximations often made in models: (1) density is constant; (2) the approximation of in-situ temperature by
⁵ potential temperature (the former being, strictly speaking, the temperature actually required for the chemistry calculations, while the latter is what models provide); (3) the equivalence between depths in meters and pressure in dbar; (4) nutrient contributions to alkalinity (i.e., from the silicic and phosphoric acid systems) are negligible.

- ¹⁰ The paper is generally well written. The history and motivations behind the development of MOCSY are informative. In a few instances, the text is not entirely precise—this can, however, be easily fixed. The selection of material to demonstrate the potential of the package is good. Figures are of good quality, but might be improved for a few details (coordinate axes extents).
- The model description is somewhat short. While more or less all of the thermodynamical ingredients are described in full detail, close to nothing is provided regarding the numerical methods applied to actually perform the pH calculations. Above all, the little that is provided is contradictory. Geoscientific Model Development papers are expected to present a complete and detailed description of the models. A minimum of technical details about the methods and
 algorithms used should be given and limitations should also be discussed (see "Manuscript Types" in the "Submission" guidelines). The presentation and discussion of the results contain, unfortunately, a few inaccuracies (see detailed comments below). These do, however, not impinge on the overall conclusions and can be easily corrected.
- In the revised manuscript, we will elaborate on the method used to compute pH and we will do our best to remedy any inaccuracies.

The model description in the revised manuscript has been extended. Former sections have been revised thoroughly. New subsections have been added concerning (1) the new routines

implemented in mocsy 2.0 to solve the total alkalinity pH equation (SolveSAPHE), (2) the new pressure corrections that affect K_0 and C_f (and thus also fCO_2 and pCO_2 , and (3) the new numerical approach to compute the Revelle factor (Sections 2.1.2, 2.1.3, and 2.1.4).

⁵ The "Code availability" section in the paper and the code distribution channel are exemplary. The code is distributed under the MIT license, and can be easily obtained. The included test case compiled and worked out of the box as expected for me.

I am confident that the authors will be able to address all of the shortcomings mentioned. Accordingly, I recommend to publish this paper after a revision of the text.

Much appreciated.

1.2 Discussion

15

25

1.2.1 Constant, variable, or no density correction at all?

Regarding issue (1) above, I expect that applying a constant or even no density correction at all should not make much of a difference in the calculation results! This may seem counterintu-20 itive, but, it is sufficient to notice the following;

- 1. all of the equilibrium constants (except for K_W) carry the units of the proton concentration—for all other concentrations that appear in the equilibrium relationships, any unit conversion factors cancel out;
- 2. in the alkalinity-pH equation, again, only the ratios of the different total concentrations (total dissolved inorganic carbon, C_T , total borate, B_T , sulfate, S_T , etc. ...) to total alkalinity, A_T , are relevant and, as long as all of these are expressed relative to the same reference framework (volume or mass), any density conversion factors will cancel out; the only term in the alkalinity-pH equation that might be affected by an imprecise density will be A_W/A_T , where the water self-ionization alkalinity, A_W , directly depends on the

proton concentration units. That ratio is, however, only of the order of a per mil and an error of the order of a percent in this actual ratio should not make any significant difference in the calculated proton concentration.

- Whatever the units of the total input concentrations, the speciation results will not be affected to any significant extent, since the speciation routine only determines, e.g., what fraction of C_T is CO₂, HCO₃ or CO₃²⁻. Only the calculated proton concentration will always come out in the units of the equilibrium constants (generally mol/kg-soln) and it would be best not to convert it to a volumetric reference at all.
- ¹⁰ Thank you for this clear explanation, which we will consider to improve the revised manuscript.

In the Discussion paper, we stated that the constant density approximation led to no significant errors. However, as a result of the above comments by Dr. Munhoven we ran many tests and discovered that our former statements are wrong. Those conclusions result from a bug in one of our analysis scripts that basically treated the approximation identically to the full rigorous solution (with variable in situ density instead of consant density). Therefore we are now entirely convinced that the constant density approximation does indeed lead to significant errors that grow with depth. Indeed for most variables, it is that approximation that produces the largest contribution to total error of the three approximations. These findings are detailed in the revised manuscript in section 3.2 (Figs. 6 and 7).

Using a different density conversion factor during subsequent model-data comparison than the one that was possibly used for the speciation calculation should not make any significant difference. The model-data comparison must anyway be carried out consistently at the density of the data samples.

Our tests indicate that using a different density conversion factor matters. But we will revisit this issue and detail our findings as to why and how much things differ if we use a different

constant density for concentration conversions before and after the carbonate chemistry calculations.

Our many sensitivity tests confirm our claim. We cannot agree with Dr. Munhoven about 5 the lack of importance of the constant density approximation, as mentioned above. We look forward one day to discussing this in person with Dr. Munhoven and to demonstrate our findings to him directly.

1.2.2 Depth-pressure conversion: how significant are the errors that we try to avoid?

10

Regarding issue (3) above, Lewis and Wallace (1998) already noted that depth expressed in meters and pressure expressed in dbar differ by only 3% at 10,000 dbar and less at lower pressures, which is well within the uncertainties of the pressure effects on the equilibrium constants. To my best knowledge, there has not been any progress in reducing the uncertainties of the pressure correction coefficients since the compilation of Millero (1995) and the reviewing efforts of Lewis and Wallace (1998): the currently used coefficients are more than 30 years old; some of them remain are merely expert guesses – the coefficient for the first dissociation constant of silicic acid is estimated from that of boric acid (Millero, 1995).

We agree that there is a dire need for studies devoted to better estimate the pressure adjustments needed for the equilibrium constants. Although this is not something that mocsy or other carbonate chemistry packages can answer, it is also not an excuse to be sloppy in our calculations. We do not think that it is a huge effort to make the pressure corrections as they were intended to be made. We do this in mocsy as do other public packages (CO2SYS, seacarb, etc).

In the revised manuscript, we continue to make the pressure corrections as they were intended to be made, consistent with CO2SYS and other packages.

Accordingly one may ask whether the tiny improvement resulting from the more accurate depth-to-pressure conversion is really worth the effort, since the resulting changes do not have any measurable significance.

Yes the uncertainties in the basic pressure correction are large and the difference between meters and decibars small. However, the latter is a systematic bias that is easy to correct for and requires insignificant additional computational resources. The mocsy package allows the user to choose whether or not to make this correction. It does not impose it. In the Discussion paper we show that it is small error. In the revised manuscript we will emphasize this point further,
 but we will still allow mocsy users to decide on the best approach for them.

In the revised manuscript, we make it clear that the pressure correction is optional.

Furthermore, the common practical application of the pressure correction of the equilibrium constants leaves, in my opinion, an unpleasant aftertaste of inconsistency: for any chosen work 15 pH scale, to adjust the value of an equilibrium constant calculated at atmospheric pressure to any other given pressure, Lewis and Wallace (1998) recommend to first convert it to the seawater (SWS) or the NBS scales, then apply the pressure correction, and finally convert the result back to the selected work pH scale (using the pH scale conversion factor at the final pressure). Since NBS scales are nowadays rarely used in seawater chemistry, the pressure 20 correction is generally made on the SWS scale. Results will nevertheless most probably be different depending on whether the SWS or the NBS pathways are chosen. This protocol must be followed for all equilibrium constants, except for the dissociation of hydrogen sulfate and fluoric acid, which should be pressure-adjusted on the free scale. These are indeed required for the pH scale conversions, and the common reference in pH scale conversions is the free pH 25 scale.

The cited text from Lewis and Wallace (1998) lends itself to misinterpretation. In fact, for a given constant, there is no choice for the pH scale upon which the pressure correction is

made. For K_S and K_F the pressure correction should be made on the free scale. For the other constants (except K_0 , K_A , and K_C , which are independent of pH scale) the pressure correction must be made on the seawater scale. Our two previous responses also address this criticism as does our next response.

5

Given the misinterpretation above, we find no cause to change our approach.

While I see the usefulness of a well-defined protocol for performing these pressure adjustments, we are now in the somewhat surrealist situation where the best practices recommend the use of equilibrium constants on the total pH scale, these constants need to be temporarily converted to the SWS scale for pressure correction, and back to the total scale, except for two of them, that need to stick to the free scale, although the pressure correction coefficients are certainly not precise enough to distinguish between the different scales. Why not carry out the pressure correction on the free scale and gain at least in consistency?

15

20

Today, all seven public packages that compute ocean carbonate chemistry that were compared by Orr et al. (2014) use the same approach to make pressure adjustments to the constants. Our mocsy package is one of those. The only exception is the csys package, which made pressure adjustments on the total scale instead of the seawater scale. But the latest version of csys, recently revised, now offers the option to follow the standard procedure outlined by Lewis and Wallace (1998). We see no good reason to change this approach in mocsy. Moreover, converting constants intended to be on the seawater scale to the free scale before making pressure corrections is a more substantial adjustment that would lead to significant systematic biases in their pressure-corrections.

25

We maintain our approach for pressure corrections of equilibrium constants in mocsy 2.0 and the corresponding revised manuscript.

1.2.3 Nutrient alkalinity: how significant are the differences between the results?

Although, once again, the assessment and the discussion of the importance of nutrient related acid systems in the alkalinity composition is very interesting, I am not convinced ⁵ about the significance of the consequences of including or neglecting them. As far as I can see, the quality of even our most advanced global model results is still far from sufficient to make the observed differences relevant. Locally in the deep-sea, inter-model differences in the calculated carbonate ion profiles remain far larger than the quoted 1.6 μ mol/kg. A polynomial pH-solver based upon practical alkalinity may easily be an order of magnitude faster (even if safe-guarded) than a full solver required with the complete representation of AT.

As pointed out in our Discussion paper, the neglect of nutrient alkalinity leads to a systematic bias of up to -6 μ atm in *p*CO₂ for the Southern Ocean zonal mean. We think that is substantial, even if it comes from a model. A bias of -6 μ atm might seem small, but a shift of that magnitude is enough in many models to incorrectly assign the Southern Ocean as a sink rather than a source. We recall also that a global air-sea CO₂ flux of 2 Pg C yr⁻¹ (roughly the ocean's current uptake of anthropogenic CO₂) results from only a 4 μ atm difference between atmospheric and oceanic *p*CO₂. In the late 1990s there was a discussion about whether or not to include phosphoric and silicic acid systems in the alkalinity equation for the protocols of the model simulations made as part of the Ocean Carbon Cycle Model Intercomparison Project (OCMIP, Phase 2). It was agreed then to include both to avoid the systematic biases mentioned above.

Hence, we think it is inappropriate to neglect nutrient alkalinity in model simulations even if it costs more. And we suspect that the extra cost must remain a very small fraction of the total time needed to run most large-scale ocean biogeochemical models.

We stand by our choice to include nutrient alkalinity in the total alkalinity equation of mocsy, and to recommend that models try do the same (as stipulated by OCMIP2). The revised manuscript emphasizes this concern in the Discussion and Conclusion.

Finally, using observed present-day nutrient climatologies for studies of the past and future evolution of the ocean carbon cycle, where production-remineralization-burial patterns differ from the present ones, may possibly lead to even larger errors than those that we are trying to address here.

5

10

We agree that it would be inappropriate to use present-day nutrient climatologies when studying the distant past. For the future though, e.g., year 2100, we would expect that overall, larger errors would be introduced by assuming that nutrient concentrations are always zero. A better solution for carbonate chemistry calculations in models that carry dissolved inorganic nitrogen but not dissolved inorganic phosphorus would be to compute the latter from the former assuming a constant Redfield ratio (as suggested by Referee 3). We will bring up these points in the revised manuscript.

Done.

15

2 Specific comments

In the following, when reference is made to CO2SYS, it should be understood that it is the MATLAB version that is meant (van Heuven et al., 2011), the only version for which that I was able to inspect the source code.

Page 2880, lines 18–19: this is rather cryptic. Does this mean that the errors listed by Lewis and Wallace (1998) for Millero (1995) have been taken into account? If so, it would be helpful to make the text more precise.

25

Yes, errors listed by Lewis and Wallace (1998) have been taken into account in mocsy. We use the same pressure adjustment coefficients as given in our companion paper (Orr et al., 2014, Table 7). We will emphasize these details in the revised manuscript.

Discussion Paper

Done.

Page 2881, line 6: PO_4^{3-} is ambiguous (is it the species or the total dissolved phosphate that is meant?). I guess it should read "total phosphate".

5

In the revised manuscript, we will systematically replace PO_4^{3-} and SiO₂ with total dissolved inorganic phosphorus P_T and total dissolved inorganic silicon Si_T , respectively.

Page 2881, lines 14-16: it was previously said (p. 2880, ll. 18-19), that the pressurecorrection coefficients came from Lewis and Wallace (1998). Here we find other references. 10 Are those the same coefficients? If so, the original reference should be cited; if not, how do they differ? Please clarify.

Thanks for signaling the potential for reader confusion between these 2 passages. There are differences between the two, because they do not refer to the same code. In the cited passage 15 on p. 2880, we are discussing the mocsy code; in the subsequent passage on p. 2881 we are referring to its precursor code that was never published. Some of the pressure adjustment coefficients in the precursor code were erroneous which lead to minor differences in computed variables as shown in our companion manuscript. We will make things clearer in the revised manuscript. (Orr et al., 2014). 20

The revised manuscript emphasizes that these are two different codes.

Page 2881, lines 10–12: The description of the method used to solve the alkalinity-pH equation is insufficient and does not appear to be correct: 25

1. Maier-Reimer (1993) uses the practical alkalinity approximation and specifies that a Newton iteration is used to solve the alkalinity-pH equation, expressed as a variant of the rational function form (see, e.g., Munhoven (2013) for the different forms of the equation);

- 2. Aumont and Bopp (2006) describe the PISCES model, which, although it derives from HAMOCC5 (Aumont et al., 2003), claims to use the OCMIP protocol (i.e., Newton + bisection) for its carbonate chemistry, with practical alkalinity as an approximation to total alkalinity;
- inspection of the MOCSY code shows that the adopted method is actually not a Newton method, as the cited literature might suggest, but, in the classification of Munhoven (2013), a fixed-point iterative carbonate alkalinity correction (ICAC) method, combined with a pH = 8 initialization scheme.

To the best of our recollection, when O. Aumont was first developing PISCES he tried using the OCMIP code as is, but to solve the alkalinity-pH equation he switched to a faster iterative scheme coded by E. Maier-Reimer. We looked at the PISCES code back in 2004 and adopted its iterative scheme when developing the precursor to mocsy. The same iterative scheme is used in mocsy 1.0. However that will change with mocsy 2.0, for reasons we describe below. In the revised manuscript, we will do our best to clear up any confusion.

15

After checking and recent discussions with Olivier Aumont, we stand by our statements made in the Discussion paper about this historical perspective.

It would be worth noting that among the six different solution algorithms studied by Munhoven (2013), icacfp, which is equivalent to the ICAC algorithm adopted here, was the second-least efficient one, two to three times slower than the best (if we only consider the SW1 and SW2 benchmarks that it passed and disregard the SW3 benchmark that it failed). Unless the cubic initialization scheme of Munhoven (2013) was used, it also failed the RTC1 stress-test in about 40–90% of the cases, and the RTC2 stress-test in 77–100% of the cases (Munhoven, 2013, suppl.). The safe-guarded algorithms presented by Munhoven (2013), on the other hand, passed both stress-tests in 100% of the cases, and were at worst 15% slower than the fastest methods in the SW1, SW2, and SW3 benchmarks. As further shown by Munhoven (2013), ICAC methods present inherent convergence problems at high $AT \div C_T$ ratios and at low C_T values. These convergence problems are unavoidable and can be alleviated only to a very limited extent. There is no way to efficiently safeguard them, as it is the underlying recurrence that becomes divergent. f

5

10

ICAC methods are fine for typical present-day conditions, although comparatively slowly converging. It is, however, risky to rely on them for conditions that deviate from present-day. They are, e.g., not the best choice in 3D models that are intended to be used to assess the effects of alkalinization, a geoengineering technique to mitigate ocean acidification and that may locally lead to extremely high A_T concentrations, or the impact of melt water pulses, which might locally lead to too dilute C_T for ICAC methods.

Many of these aspects and possible alternatives are covered in detail by Munhoven (2013).

Dr. Munhoven's arguments are most convincing. As a result, we have now replaced the mocsy 1.0 iterative scheme (ICAC) with the his new algorithm (SolveSAPHE, solve_at_general) and included his cubic initialization scheme. Our first tests yield results that are identical to at least the 6th digit after the decimal in terms of pH, but the the new approach is about 5 times faster than our old scheme. Although mocsy is used by its authors for open-ocean conditions
(SW1 and SW2), some users may eventually wish to apply it to more extreme cases (such as SW3), so we welcome SolveSAPHE's other benefits. This improvement will be described in the revised manuscript, which will be accompanied by the release of mocsy 2.0. We thank the Referee for emphasizing the features of SolveSAPHE relative to the iterative scheme used in mocsy. His routines provide a major step forward.

25

In mocsy 2.0 we have indeed adopted the SolveSAPHE routines from Munhoven in place of mocsy's former ICAC routines. We describe this choice in a new section 2.1.2 dedicated entirely to that pH solver, and we emphasize its importance in the Conclusions.

The model description needs to be corrected, completed and possible limitations discussed. It could also be better streamlined: e.g., in the current manuscript, the pressure-correction of the equilibrium constants is mentioned in four different places (p. 2880, ll. 18–19; p. 2881, ll. 14–15; p. 2882, ll. 13–15; p. 2884, ll. 2–5), and still, only insiders are likely understand the implications.

We will correct the problems mentioned in the model description. We will also streamline the text regarding pressure corrections. Note that the 1st passage (p. 2881) is a synopsis in the Introduction and the 2nd passage (in the Methods) does not refer to mocsy but its precursor, which was different.

The model description has been expanded, for instance with new subsections on the pH solver, the new formulation for the Revelle factor, and the new pressure corrections to K_0 and C_f , which dramatically affect $f CO_2$ and $p CO_2$. Other aspects of the model description have 15 also been improved.

Page 2881, lines 24–28: There are a few more exceptions than these three. Similarly to K_S , K_F must also be referenced on the free scale (and that is actually how it is implemented in the code). K_0 is also independent on pH scale.

20

5

10

In the revised manuscript, we will also mention that that K_0 is independent of the pH scale.

We clarify these points in the revised manuscript. Note that K_F is not necessarily on the free scale, as we also explain in the revised manuscript.

25

Page 2882, line 17: please notice that, if the calcium content is calculated following Riley and Tongudai (1967), as stated, then the correct Ca-to-chlorinity ratio is 0.02128 and not 0.02127, as reported by Dickson et al. (2007, chap. 5, tab. 2). The 0.02127 value has been around in the literature for a while without an adequate reference: it can at least be traced back

to Millero (1982), where the cited original references do not allow an unequivocal attribution. I speculate that it was obtained by averaging the 0.02126 from Culkin and Cox (1966) and the 0.02128 from Riley and Tongudai (1967).

⁵ We had noticed these tiny differences previously when comparing the source code of different public packages. We are grateful for this reminder, which will prompt us to mention it in the revised manuscript in the context of our next response (below).

Done (section 2.3).

10

The difference is definitely small, but if confusion can be avoided ...

This small difference may explain why the discrepancy between mocsy and CO2SYS is slightly larger for Ω_A than for CO_3^{2-} (Fig. 2 of the Discussion paper).

15

We explore the discrepancy in section 3.1 of the revised manuscript.

Pages 2884–2885, section 3.1: Where do the diagnosed differences in the species concentrations come from? For identical input, I would expect no differences at all (at least to within an order of magnitude of machine precision or so). The differences are not random, so there must be some intrinsic differences between the ways MOCSY and CO2SYS carry out these calculations.

Yes there are some very small systematic differences between mocsy and CO2SYS. We have already provided a preliminary response to the same question from another Referee (Andrew Dickson). We will report back more fully in the revised manuscript.

We detail the causes for differences in section 3.1 of the revised manuscript.

Discussion Paper

Discussion Paper

The reported discrepancies in the Revelle factor are quite interesting: the largest differences arise where the nutrient contributions to alkalinity are the largest. This points out an important shortcoming in MOCSY's Revelle factor calculation: the implemented analytical buffer factor formulation of Frankignoulle (1994) was derived for the practical alkalinity approximation. CO2SYS, on the other hand, uses a finite difference approach to calculate the Revelle factor, using results derived with the (most) complete alkalinity representation. Despite being based upon a numerical approximation only, the CO2SYS approach might be more reliable, since it is consistent with the adopted A_T approximation.

We concur. We will address this in the revised manuscript. 10

In section 3.1 of the revised manuscript, we discuss the causes of differences in the computed Revelle factor. They are six times smaller with mocsy 2.0 with the new numerical formulation that accounts for effects of nutrient alkalinity.

15

20

25

5

Pages 2885–2886, section 3.2: this section is not totally accurate and partially contradictory.

- 1. The 4% increase of the total borate concentration, B_T , does not translate into a 4% increase of borate alkalinity, A_B , as could be easily verified with, e.g., MOCSY. There is some buffering. Indeed, if total alkalinity, A_T , stays constant, together with all the other total concentrations, pH will adjust (decrease), such as to decrease all of the other alkalinity contributions besides A_B . Calculations with SolveSAPHE 1.0.1 (Munhoven, 2013) indicate that that $4\% B_T$ increase leads to A_B increase of close to 3% (using the practical alkalinity approximation for the sake of simplicity).
- 2. The B_T increase does not affect A_T as stated, nor does it affect C_T (also an input variable). The conclusion that "the C_T must also decline" (p. 2886, l. 12) does therefore not make sense. While it is correct that carbonate alkalinity A_C must decline, as a result of the increased AB, this decline is brought about by a pH decrease, not by a C_T change. The buffer capacity is dependent on the actual levels of all of the total dissolved acid concentrations, and on pH (which of course depends on all the previous). With a different

Discussion Paper

pH, a different buffer capacity is obtained. It is difficult to predict the evolution of the buffer capacity for this change a priori, as its analytical expression involves a complicated product of factors that present counteracting variations.

3. For the same reasons (i.e., A_T and C_T are input variables), and contrary to what is written at ll. 12–13, A_T minus C_T remains constant. Here, the commonly made approximation $[CO_3^{2-}] \simeq A_T C_T$ is terribly misleading. It would be far more ac curate to use $[CO_3^{2-}] \simeq A_C C_T$, which is more compatible with what is observed here.

In the revised manuscript, we will be more precise about the increase in A_B that accompanies a 4% increase in B_T . We slipped when we stated that C_T declines. It contradicts our sentence earlier in that same paragraph that says it cannot change since it is an input variable. We will remedy this confusion in the revised manuscript. We will also offer a simple explanation as detailed in the response to another Referee, Andrew Dickson.

Done (see section 3.3, paragraph 2, first 3 sentences of the revised manuscript).

5

Page 2886, line 16 – page 2886, line 2: issues related to the use of constant density are probably not as important as outlined here (see general comments above).

For the revised manuscript, we will double check our calculations. If they hold up, we will be more quantitative and offer a clearer explanation about the potential errors associated with using a different density to convert back to model concentration units (mol m⁻³) relative to the constant value assumed when converting from mol m⁻³ to mol kg⁻³ before making the calculations.

We do not agree, as mentioned in an earlier response to the same Referee. The constant density approximation does indeed lead to significant errors in the deep ocean, as detailed in section 3.2. Pages 2887–2888: how significant are the calculated differences? Are inter-model differences not far larger than this?

5

Whether or not intermodel differences are larger, we think that a systematic error of +6 μ atm in *p*CO₂ should be fixed, especially when the fix costs so little. In regards to the Southern Ocean, the simulated air-sea CO₂ flux can differ between models by only a tenth of a Pg C yr⁻¹, equivalent to less than 1 μ atm in the air-sea difference in *p*CO₂ (Dufour et al., 2013, Table 1). A systematic shift of -6 μ atm would be enough to switch some models from net CO₂ loss to net CO₂ uptake in some regions such as the Southern Ocean, i.e., for natural CO₂.

10

These points are made in the revised manuscript (Discussion, paragraph 2).

Page 2888, line 20: " PO_4^{3-} " is ambiguous—should probably read "total phosphate"

In the revised paper, we will use total dissolved inorganic phosphorus P_T and total dissolved inorganic silicon Si_T .

Done.

20 3 Technical corrections

Page 2880, line 17: strange sentence "[. . .] recommended by for best practices [. . .]" – please check.

In the revised manuscript, we will change "by for" to "for".

Done.

Page 2897, Fig. 3: the horizontal axes on the top left and on all of the lower panels should be modified to better separate the different curves. Much space is currently wasted.

We designed Fig. 3 to have the same range (max - min) for each variable as used in subsequent figures (Figs. 4, 5, 6, and 7). Because differences shown in Fig. 3 are generally small, we prefer not to zoom in on them excessively to avoid giving the impression that they are large.

In the revised manuscript, we have tried to reduce excessive whitespace for cases when consistency between figures is not an issue.

4 Code

4.1 Availability and distribution

15

Two ways to get the code are indicated, together with a link to a dedicated website of the code, where extensive information is available. The common user who does not have git installed can easily go to the github page and download the zip archive.

I have downloaded, compiled and executed the code on a Linux machine with the gfortran compiler. Everything worked out of the box.

Good to know. Thanks.

- 4.2 Comments on the code
 - 1. Users will appreciate the extensive comments and references in the source code.
 - 2. make test_mocsy produces a libmocsy.a library, which is nevertheless not used (not even linked into the produced test_mocsy).

- 3. The code is a mixture of single and double precision operations. While this is perfectly valid, it leads, in my personal opinion and in my experience as a teacher and instructor in Fortran programming, to unnecessary numerical artifacts. Why not use a uniform real type throughout, the more since the flexible typing mechanism offered by Fortran 90 and later is already used?
- 4. In some of the subroutines one reads in the comments that they are "Needed because xyz is a function (cannot accept arrays)". While this was to some extent true in FORTRAN 77 (arguments could well be arrays, but results not), it is definitely not correct in the Fortran 90 and later standards. Those do also allow array-valued functions. In MOCSY, converting the functions from scalar to array- valued might be interesting for performance reasons, since most (if not all) of the concerned function/subroutine pairs only perform straightforward calculations (no iterations) and might thus take advantage of the efficient whole-array operations.
- 5. The Dickson and Riley K_F is converted from the free to the total pH scale, to be converted back to the free scale right away before being corrected for pressure. The two conversion steps could of course be skipped (and the Perez and Fraga K_F directly converted to the free scale instead).

1. Thanks.

5

10

15

20

25

- 2. We have changed the makefile so that the test program test_mocsy links with libmocsy.a instead of the object files. Done.
- 3. The mixture of single and double precision is intentional. It allows calculations to be performed at double precision but input and output to mocsy to be single precision. To save disk space, most model output such as from CMIP5 is stored as single precision. Individual users who wish to change everything to double precision can do so easily because mocsy exploits the flexible typing system of Fortran 90. Changing the type in the module singledouble.f90 would change the type throughout the code.

- 4. The mocsy code was recently converted from Fortran 77 to Fortran 90. We will consider the possibility of converting some functions so that arguments are passed as arrays not scalars. And we will remove the comment. For backwards compatibility, we have not changed the structure of mocsy 2.0 to accomodate this concern. Some functionalities are available both as subroutines and functions.
- 5. We convert K_F from Dickson and Riley (1979) from the free to the total scale so that it can be treated consistently (later in the code), i.e., just as the alternative case when the user chooses to use K_F from Perez and Fraga (1987), which is on the total scale to start with.

Response to Comments by Referee 3

We thank Referee 3 for his comments, which are repeated below in gray; our responses follow in black.

Summary

15

20

5

The manuscript presents a revised and updated oceanic carbonate chemistry scheme, MOCSY, intended for use by both observational scientists and carbon cycle modellers. Updates include a number of amendments to existing schemes, some new parameterisations and a general effort to permit a range of possible inputs that will suit most researchers (e.g. units, in situ vs. potential temperature). The manuscript also includes instructions to allow readers to download the scheme.

Overall, the manuscript is clear and well-written, though I have a number of minor criticisms described below. The associated Fortran code is easy to access, compile and run, both with the included test case and as part of custom code (essential if it is to be adopted by modellers).

Please note that I am a user of carbonate chemistry calculators like MOCSY rather than a chemical oceanographer. As such, my comments deal more with use of MOCSY than its

fundamentals.

Specific comments

⁵ The following are minor comments relating mostly to edits that may slightly improve the manuscript. They are followed by a few remarks concerning my experience building and running MOCYS.

Pg. 2878, ln. 28: Careless readers (such as this one) may misinterpret "nutrient contributions"
to refer to the consequences for proton concentration (and thus pH) of the use of nitrate and ammonium by phytoplankton; probably later rather than here, a "not-to-be-confused-with" statement might head this off

An excellent point. We will add such a statement in the revised manuscript.

To avoid confusion we explicitly refer to inorganic P and Si in referenced passage, and we define nutrient alkalinity as $A_{\rm P} + A_{\rm Si}$ later in the Discussion when that term is first used.

Pg. 2879, ln. 7: "In many models ..." – it might be helpful if the authors gave a few examples, more so that readers are aware of the diversity of uses to which the OCMIP code has been put;
citing examples of use of the code by OCMIP itself might be useful too

We will add some references to the end of this sentence in the revised manuscript.

We have added 3 references to the end of this sentence.

25

Pg. 2881, ln. 3-4: "... from only one input pair ..." – this is slightly confusing because the code makes use of other inputs (which are mentioned later); perhaps this needs to be qualified with a specific reference to these being carbonate inputs – my reading of this is the authors are hinting at possible (but unstated) alternative inputs that are sometimes used to constrain the

In the revised manuscript, we plan to change this potentially confusing sentence into 3 sentences: "Fortunately the ocean carbonate system is well constrained so that any pair of carbonate system variables can be used to compute all others when also given temperature, salinity, and nutrient concentrations. Yet unlike other public packages, mocsy is designed for models. Thus it offers users only one input pair of carbonate system variables, C_T and A_T , from which to compute all others."

- We have changed the first 3 sentences of section 2.1 to "The ocean carbonate system is well constrained. Any pair of carbonate system variables can be used to compute all others. Because only two carbonate system variables, $C_{\rm T}$ and $A_{\rm T}$, are carried as passive tracers by all ocean carbon models, mocsy offers only that input pair."
- ¹⁵ Pg. 2883, ln. 26: "[HF]" is not defined; please make sure that all chemical terms are defined when first used (or, probably better here, in a table); this work will likely be used by non-specialists involved in carbon and climate research and it is important that they are not waylaid by abbreviated terms that they are unfamiliar with
- ²⁰ In the revised manuscript we will mention that [HF] means hydrogen fluoride.

When it is first used, the [HF] term is now defined as hydrogen fluoride as are the other chemical terms.

Pg. 2884, section 3.1: the authors present this section almost as a "disagreement" between "gentlemen models" and do not make it clear whether one model is better or worse than the other; perhaps this cannot readily be assessed to the required accuracy, but the authors could simply say so if this is the case

In the revised manuscript we will clarify that there is no absolute reference when it comes to computed carbonate system variables. Both packages could in principle be wrong even if both agree. However we compare mocsy to CO2SYS because the latter is the first public package made available to compute these variables, it was developed with great care (Lewis and Wallace, 1998), and it is used widely. Our companion manuscript goes into more detail about why we arbitrarily chose CO2SYS as the reference (Orr et al., 2014).

Most of the explanation above, although slightly modified is now include in section 2.4 of the revised manuscript.

10

15

5

Pg. 2885, section 3.2: this section refers, correctly, to the errors caused by making the assumptions mentioned, but associated figure 3 instead presents these errors in the context of "corrections"; the implication being that one could keep using the approximations and just adjust the answers appropriately – surely we don't want people to do this?; it would be better if the paper was consistent in its branding of these differences as errors to be avoided (by, for example, using mocys-1.0!)

For the revised manuscript, we are considering remaking these plots, showing the errors directly, not the corrections.

20

25

The figure mentioned has been replaced by 2 figures (nos Figs. 6 and 7). We no longer speak of "corrections" but of "absolute changes that would result by avoiding each of the three ocean-model approximations". We consider it more didactical to orient the reader with a reference that refers to where models stand now so that the changes described represent where they will be if it is done right.

Pg. 2885, ln. 25: as the authors present the magnitude of errors or differences elsewhere I would expect them to give some notional (quantitative) idea of why the differences caused by

the Kf option can be neglected

Because K_F is used only to convert between the seawater and total pH scales, and the difference between the two is small (~0.01 units of pH), for all intents and purposes the computed carbonate system variables are insensitive to changes in K_F . We will mention these details in the revised manuscript. We will also refer the reader to the sensitivities of computed variables to each constant that are shown in our companion paper (Orr et al., 2014, Table 9).

We now explain the lack of sensistivity to the formulation for $K_{\rm F}$ in 4 sentences at the beginning of section 3.3.

Pg. 2886, ln. 2: "substantial differences" caused by 1. total boron and 2. K1 and K2 are both mentioned here, but while numbers are presented in the following paragraph for boron, K1 and K2 go unmentioned; is Figure 4 doing all of the talking?; a clarifying remark might help

15

In the revised manuscript, we will add discussion on the differences in K_1 and K_2 shown in Fig. 4.

A new paragraph has been added at the end of section 3.3 in order to fully respond to this request to describe results for K_1 and K_2 in addition to the description of the results concerning the new formulation of total boron.

Pg. 2886, ln. 3-4: is this tantamount to saying that models using the GLODAP climatology of alkalinity are effectively setting the oceanic inventory of this property wrongly?; I'm surethat I'm misreading that, but it may give readers this idea

No, this interpretation by Referee 3 is not what we meant to say. We appreciate the question though, because it does raise a flag for potential misinterpretation. The total alkalinity A_T in the GLODAP climatology is based on measurements of total alkalinity. If on the side we decide

to calculate the individual contributions to alkalinity (A_C , A_B , A_W etc) using equilibrium constants and total concentrations (other measurements) that does not affect the total measured alkalinity. In the revised manuscript we will elaborate to avoid this potential confusion.

⁵ In the revised manuscript, we say "Yet modeled total alkalinity $A_{\rm T}$ is unaffected, being an input variable (along with $C_{\rm T}$)." The same paragraph has also been further modified in an attempt to remedy any potential misconceptions along these lines.

Pg. 2888, ln. 19-22: given the strong linear correlation between dissolved inorganic nitrogen
and dissolved inorganic phosphorus, models that include N but not P could use a Redfield-scaled N as a substitute for P; this is likely to be a temptation for a number of models and this may be something that the authors could comment on here

This is a fine idea. It would allow a modeler to approximate the alkalinity from total dissolved
 inorganic phosphorus from the modeled total dissolved inorganic nitrogen. Unfortunately, we cannot use the same approach to approximate the alkalinity from total dissolved inorganic silicon. We will mention this potential partial solution in the revised manuscript.

We have brought up this suggestion in the Discussion of the revised manuscript.

20

Pg. 2890, Code availability: I would imagine that mocsy performs – in a computational sense – similarly to previous iterations (or rival packages), but it would be useful if the authors reported on any comparisons that they have made on it; for instance, does it typically converge in the same number of iterations?; I would expect so, but the additions to the complexity of
the modelled chemistry may impact on this; one of the main groups of scientists who will be interested in this are ocean biogeochemical modellers, and reassuring them that the code performs comparably to what they currently use would doubtless help with its uptake by the community
Discussion Paper

Discussion Paper

The complexity of the chemistry in mocsy is identical to that agreed upon for the Ocean Carbon Cycle Model Intercomparison Project (OCMIP, Phase 2). In addition, it also computes the full suite of carbonate system variables, but that is not costly. We expect that the computational time of mocsy 1.0 is similar to that for the OCMIP2 code, but we have not tested it. ⁵ On the other hand, for the costliest part of the code we have recently implemented a much improved approach, a new cubic initialization scheme combined with a more robust solver of the Alkalinity-pH equation, both from Munhoven (2013). With these improvements, mocsy 2.0 is up to 5 times faster. More details are provided in our response to another Referee of the manuscript, Guy Munhoven. The revised manuscript will present this new version of the code and discuss its improvements.

We discuss these improvements in the last paragraph of the Discussion and compare mocsy with the old standard iterative solver (ICAC) to the the same code with the new solver that is five times faster and more stable, converging in all conditions (unlike ICAC).

15

Pg. 2897, figure 3: the legend is ambiguous about the identity of the black dotted line; panel 1 labels it up, but it wouldn't hurt if the legend did too

In the legend to Fig. 3 in the revised manuscript, we will add: "Also shown is the sum of the three effects (black)."

Done.

Experience with code:

25

- Code successfully downloaded via OCMIP5 website (git has passed me by)
- Code initially failed to compile using ifort ...

sw_adtg.f90:11.19: USE msingledouble

1 Fatal Error: File msingledouble.mod opened at (1) is not a $_{\rm 5}$ GFORTRAN module file

- However, switching to gfortran in the makefile fixed this and was successfully able to build test_mocsy; the above error is most likely caused by local environment configuration
- test_mocsy successfully runs producing sample output for "model" and "observational" test datasets; I was also able to easily incorporate it within an existing Fortran subprogram ready for adoption within our local BGC model

Thank you for this feedback about your experience with the code. We have had no problem compiling and running it with either the ifort or gfortran compilers, nor have others that we have been in contact with. We are happy to hear that it could be included easily in your ocean biogeochemical model.

The final section has not been criticized. It remains as pertinent now as when written for the Disucussion paper and has not changed.

20 **References**

references

Dickson, A. G. and Goyet, C.: Handbook of methods for the analysis of the various parameters of the carbon dioxide system in seawater; version 2, CDIAC-74, ORNL, 187 pp., 1994.
Dickson, A. G. and Millero, F.: A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media, Deep-Sea Res., 34, 1733–1743, 1987.

25

10

15

38

- Dickson, A. G. and Riley, J. P.: The estimation of acid dissociation constants in seawater media from potentiometric titrations with strong base. I. The ionic product of water K_W , Mar. Chem., 7, 89–99, 1979.
- Dickson, A. G., Sabine, C. L., and Christian, J. R.: Guide to best practices for ocean CO₂ measurements, , PICES Special Publication 3, 191 pp., http://aquaticcommons.org/1443/, 2007.
- Dufour, C. O., Sommer, J. L., Gehlen, M., Orr, J. C., Molines, J.-M., Simeon, J., and Barnier, B.: Eddy compensation and controls of the enhanced sea-to-air CO2 flux during positive phases of the Southern Annular Mode, Global Biogeochem. Cycles, 27, 950–961, doi:10.1002/gbc.20090, 2013.

Egleston, E., Sabine, C. L., and Morel, F. M. M.: Revelle revisited: Buffer factors that quantify the re-

- ¹⁰ sponse of ocean chemistry to changes in DIC and alkalinity, Global Biogeochem. Cycles, 24, GB1002, doi:10.1029/2008GB00 340, 2010.
 - Frankignoulle, M.: A complete set of buffer factors for acid/base CO₂ system in seawater, J. Mar. Sys., 5, 111–118, 1994.

- boron to chlorinity for the North Pacific and North Atlantic oceans, Geochim. Cosmochim. Ac., 74, 1801–1811, doi:http://dx.doi.org/10.1016/j.gca.2009.12.02710.1016/j.gca.2009.12.027, 2010.
 - Lewis, E. and Wallace, D. W. R.: Program Developed for CO₂ System Calculations, ORNL/CDIAC-105, Carbon Dioxide Inf. Anal. Cent., Oak Ridge Natl. Lab., Oak Ridge, Tenn., 38 pp., 1998.

Lueker, T. J., Dickson, A. G., and Keeling, C. D.: Ocean pCO₂ calculated from dissolved inorganic

- carbon, alkalinity, and equations for K_1 and K_2 : validation based on laboratory measurements of CO_2 in gas and seawater at equilibrium, Mar. Chem., 70, 105–119, 2000.
 - Millero, F. J.: Thermodynamics of the carbon dioxide system in the oceans, Geochim. Cosmochim. Ac., 59, 661–677, 1995.

doi:http://dx.doi.org/10.1071/MF0925410.1071/MF09254, 2010.

5

25

30

- Munhoven, G.: The mathematics of the total alkalinity—pH equation—pathway to robust and universal solution algorithms: the SolveSAPHE package v1.0.1, Geosci. Model Dev., 6, 1367–1388, doi:10.5194/gmd–6–1367–2013, 2013.
- Orr, J. C., Gattuso, J.-P., and Epitalon, J.-M.: Comparison of seven packages that compute ocean carbonate chemistry, Biogeosciences Disc., 11, 5327–5397, doi:10.5194/bgd-11-5327-2014, 2014.
- Perez, F. F. and Fraga, F.: Association constant of fluoride and hydrogen ions in seawater, Mar. Chem., 21, 161–168, 1987.

Lee, K., Kim, T.-W., Byrne, R. H., Millero, F. J., Feely, R. a., and Liu, Y.-M.: The universal ratio of

Millero, F. J.: Carbonate constants for estuarine waters, Mar. Freshwater Res., 61, 139–142,

- Uppström, L. R.: The boron/chlorinity ratio of deep-sea water from the Pacific Ocean, in: Deep-Sea Research and Oceanographic Abstracts, vol. 21, pp. 161–162, Elsevier, 1974.
- Weiss, R. F.: Carbon dioxide in water and seawater: the solubility of a non-ideal gas, Mar. Chem., 2, 203–215, 1974.
- 5 Weiss, R. F. and Price, B. A.: Nitrous oxide solubility in water and seawater, Mar. Chem., 8, 347–359, 1980.

Manuscript prepared for Geosci. Model Dev. Discuss. with version 2014/09/16 7.15 Copernicus papers of the LATEX class copernicus.cls. Date: 5 December 2014

Improved routines to model the ocean carbonate system: mocsy 1.02.0

J. C. Orr¹ and J.-M. Epitalon^{1,*}

¹LSCE/IPSL, Laboratoire des Sciences du Climat et de l'Environnement, CEA-CNRS-UVSQ, France ^{*}now at: Geoscientific Programming Services, Toulouse, France

Correspondence to: J. C. Orr (james.orr@lsce.ipsl.fr)

Discussion Paper

Discussion Paper

Abstract

Modelers compute ocean carbonate chemistry is often based on often with code from the Ocean Carbon Cycle Model Intercomparison Project (OCMIP), last revised in 2005. As an update, we offer here new Here we offer improved publicly available Fortran 95 routines to model the ocean carbonate system (mocsy 2.0). Both codes take as input dissolved inorganic carbon $C_{\rm T}$ and total alkalinity $A_{\rm T}$, the only two tracers of the ocean carbonate system that are unaffected by changes in temperature and salinity and tracers that are conservative with respect to mixing , properties that make them ideally suited for ocean carbon models. With the same basic thermodynamic equilibria, both codes and changes in temperature and salinity. Both packages use the same thermodynamic equilibria to compute surface-ocean pCO_2 in order to and simulate air-sea CO₂ fluxes. The mocsy package goes beyond the OCMIP code by computing, but mocsy 2.0 solves the alkalinity-pH equation with the fastest and safest algorithm available (SolveSAPHE), applicable even under extreme conditions. The OCMIP code computes only surface pCO_2 , while mocsy computes all other carbonate system variables (e.g., pH, , and saturation states) and by doing so throughout the water column. Moreover, it It also avoids three common model approximations: that density is constant, that modeled potential temperature is equivalent equal to in situ temperature, and that depth is equivalent equal to pressure. These approximations work well at the surface, but total errors in computed variables Errors from these approximations grow with depth, e.g., reaching $-\frac{8in}{3\%}$ or more for pCO_2 , +0.010 in pH, and +0.01in-H⁺, and Ω_A at 5000 m. Besides-The mocsy package uses the equilibrium constants recommended for best practices, mocsy also offers users three new options: (1) a recent formulation for total boron that increases its ocean content by. It also offers an option to use the recently reassessed total boron concentration $B_{\rm T}$ that is a 4, (2) an older formulation for K_F common to all other such software, and (3) recent formulations for % larger and a second option to use new K_1 and K_2 designed to also formulations designed to include low-salinity waters. More total boron increases borate alkalinity and reduces carbonate alkalinity, which is calculated as a difference from total alkalinity. As a result, the computed Each of these options matters, e.g., enhancing surface pCO_2 increases by 4 to 68 µatm, while the computed aragonite saturation horizon (ASH) shallows by 60in the North Atlantic and by up to 90in the Southern Ocean. Changes due to the new formulation. Yet they should not be used before (1) best-practice equations for K_1 and K_2 enhance p by up to 8 in the deep ocean and in high-latitude surface waters. These changes are comparable in magnitude to errors in the same regions associated with neglecting nutrient contributions are reevaluated with the new B_T and (2) the low-salinity formulations of K_1 and K_2 are tuned to be consistent among pH scales. Substantial errors are found when neglecting contributions from inorganic P and Si to total alkalinity, a common practice in ocean biogeochemical modeling that should be abandoned. The mocsy code with the standard options for best practices and none of the 3 approximations agrees with results from the CO2SYS package generally within 0.005.

% for the three inorganic carbon species (concentrations differ by less than 0.01 μ mol kg⁻¹); conversely mocsy's subsurface $f CO_2$ and $p CO_2$ can be many times larger than those from CO2SYS, because mocsy includes pressure corrections for K_0 and the fugacity coefficient, unlike other packages which calculate only potential $f CO_2$ and $p CO_2$.

1 Introduction

To compute air–sea CO_2 fluxes, ocean carbon cycle models compute the partial pressure of carbon dioxide (pCO_2) from two passive, tracers, namely dissolved inorganic carbon C_T and total alkalinity A_T . In many models, that thermodynamic calculation is based on documented code from the Ocean Carbon Cycle Model Intercomparison Project (OCMIP), which is publicly available at http://ocmip5.ipsl.jussieu.fr/OCMIP/. Although modified versions of that code are used widely (e.g., Müller et al., 2008; **?**; Aumont and Bopp, 2006), it has not been updated since 2005. Meanwhile, there have been developments in recommended community standards for equilibrium constants (Dickson et al., 2007; Dickson, 2010). Models require computationally efficient routines that are compatible with other model components, typically written in Fortran. Hence, model simulations are not made with widespread widely used publicly available software packages that are designed to compute other carbonate system variables from any pair, given corresponding in situ temperature, salinity, pressure, as well as phosphate and silicate concentrations concentrations of total dissolved inorganic phosphorus P_T and total dissolved inorganic silicon Si_T (Dickson et al., 2007). Models also differ because they typically carry potential temperature θ , use concentration units of mol m⁻³, and are referenced to depth (m); conversely, equations for carbonate system thermodynamics require in situ temperature T, concentrations in mol kg⁻³, and in situ pressure. Unit conversion is straightforward, but for simplicity modelers often make three approximations: (1) that θ is equivalent to T, (2) that ocean density is constant (e.g., 1028 kg m⁻³), and (3) that depth (m) is equivalent to in situ pressure (dbar).

The errors Errors associated with these simplifications are considered to be negligible, while the reasons behind them are largely historical. Most studies with ocean carbon cycle models have focused on large-scale patterns of air–sea CO_2 fluxes and related near-surface changes in the open ocean. More recently, with growing concern for ocean acidification (Caldeira and Wickett, 2003; Orr et al., 2005), attention has also turned to the deep ocean, the high latitudes, and local impacts in the coastal zone. Errors associated with the three approximations may will be larger at depth, where θ diverges from T, where densities are greater than average surface values, and where there are larger absolute differences between pressure and depth. One may also question use of the constant density approximation in waters affected by excess evaporation (e.g., in the equatorial Pacific, Arabian Sea, and Mediterranean Sea) or large freshwater input (e.g., in the Arctic and coastal zones with heavy river influence).

To fill these gaps, we provide here an improved set of routines to model the ocean carbonate system (mocsy 2.0). This new package uses the classic approach, taking simulated A_{T} and C_{T} and computing all other carbonate system variables, while adding refinements. Relative to its precursor (OCMIP model code), mocsy offers several ameliorations: (1) it no longer makes the three approximations mentioned above, (2) it computes all carbonate system variables, not only pCO_2 and pH, (3) it provides these variables at all model levels, not only at the surface, and (4) it uses, as a default, the constants and the pH scale recommended by for best practices (Dickson et al., 2007). The latter All constants except K_0 (the CO_2 solubility) are corrected for pressure effects (Millero, 1995) with modified coefficients adopted from CO2SYS (Lewis and Wallace, 1998); both K_0 and the fugacity coefficient are corrected for pressure effects following Weiss (1974). Options are also provided to replace formulations for K_1 and K_2 and for total boron that are recommended for best practices (Dickson et al., 2007) with more recent formulations, choices that substantially alter computed results will be shown to affect results significantly.

After describing the mocsy code and its use (Sect. 2), we compare its results to CO2SYS, a standard software package used widely by observationalists, and evaluate how mocsy's refinements alter computed carbonate system variables (Sect. 3).

2 Methods

2.1 Basic code Code description

The mocsy package allows users to compute

2.1.1 Basics

The ocean carbonate system is well constrained. Any pair of carbonate system variables can be used to compute all others. Because only two carbonate system variables from only one input pair, $C_{\rm T}$ and $A_{\rm T}$. Those are the only two carbonate system variables that are, are carried as passive tracers by all ocean carbon models. Other required input variables for these calculations include, mocsy offers only that input pair. Thus it is unlike other public packages designed largely for observationalists. To calculate the remaining carbonate system variables, one only needs to provide additional input for temperature, salinity, , and $P_{\rm T}$, and $Si_{\rm T}$ as well as pressure or depth. A precursor to mocsy was developed in 2004 and used to project future ocean acidification from simulated $C_{\rm T}$ and $A_{\rm T}$ in the OCMIP2

models (Orr et al., 2005). That precursor code was never released publicly and should not be confused with the preexisting OCMIP2 or OCMIP3 code, which only computes surface pCO_2 . Its development began by combining the Fortran code for equilibrium constants from OCMIP2 and the efficient an iterative algorithm to solve for pH (Maier-Reimer, 1993; Aumont and Bopp, 2006). The precursor code was already then modified to compute all carbonate system variables throughout the water column. Thus it included pressure corrections for equilibrium constants (Millero, 1995) with pressure-correction coefficients (some now known to be erroneous) taken from version 0.95 of seacarb (Proye and Gattuso, 2003; Lavigne and Gattuso, 2011), which itself adopted code from csys (Zeebe and Wolf-Gladrow, 2001). From the seacarb code, we the precursor code also included the analytical formula for the Revelle factor from Frankignoulle (1994). Our feedback from this early development led to bug corrections that were later implemented in seacarb.

Since 2005, this precursor code has continued to be improved. The current release, the first public version , is was denoted as mocsy 1.0 (?). Here along with a revised version of that Discussion paper, we provide an improved version of the code, mocsy 2.0. The equilibrium constants and the pH scale pH scale adopted in mocsy are those recommended by the Guide to Best Practices for Ocean CO₂ Measurements (Dickson et al., 2007). All but three of the The equilibrium constants are generally on the total pH scale. The firstThere are four exceptions: the CO₂ solubility K_0 , K_5 , must be referenced on the free pH scale the solubility product for aragonite K_A , and the analogous solubility product for calcite K_C (Mucci, 1983). By definition, K_0 , because it is used K_A , and K_C are independent of the pH scale: they do not involve [H⁺]. Although K_5 includes [H⁺], it is maintained on the the free scale, as needed to convert between the free and total scales. The other two exceptions are the apparent solubility products for aragonite K_A and calcite K_C (Mucci, 1983), which by definition are independent of the pH scale Conversely, the equilibrium constant that is used to convert between total and seawater scales, K_F , is maintained on the total scale along with all other constants.

The other basic features of mocsy also adopt For its basic calculations, mocsy adopts the recommendations of Dickson et al. (2007). These include (1) the Weiss (1974) formulation

describing the solubility of CO₂ in seawater (K_0); (2) the Lueker et al. (2000) formulations for first and second dissociation constants of carbonic acid (K_1 and K_2), refits of measurements from Mehrbach et al. (1973) on the NBS scale to the total pH scale; (3) the Millero (1995) formulations for equilibrium constants of boric acid ($K_{\rm B}$), phosphoric acid (K_{1P}, K_{2P}, K_{3P}) , silicic acid (K_{Si}) , and water (K_W) , converted which mocsy converts from the seawater scale to the total scale (Dickson et al., 2007); (4) the Dickson (1990) formulation for the equilibrium constant for the dissociation of bisulfate (K_{S}) on the free scale (see above); (5) the Perez and Fraga (1987) formulation for the equilibirum constant for hydrogen fluoride HF (K_F) on the total scale; and (6) the Mucci (1983) formulations for the CaCO₃ solubility products for an agonite and calcite (K_A and K_C). Because these equilibria use concentrationsinstead of activities, they are apparent equilibrium constants. They These equilibrium constants use concentrations, not activities. All of them except for K_0 are further adjusted for pressure using the approach of Millero (1995), with corrected coefficients from Lewis and Wallace (1998) (see Orr et al., 2014, Table 7). Constant ratios relative to salinity are used to compute concentrations of total inorganic boron (Uppström, 1974), fluoride (Riley, 1965), sulfur (Morris and Riley, 1966), and calcium (Riley and Tongudai, 1967). The product of the Ca^{2+} and CO_3^{2-} concentrations divided by the apparent solubility product (either K_A or K_C) yields the saturation state (i.e., for aragonite Ω_A or for calcite Ω_C , respectively).

2.1.2 Solver of the total alkalinity-pH equation

In mocsy 2.0, to solve the total alkalinity-pH equation, we have replaced the classic fixed-point iterative carbonate alkalinity scheme (ICAC) in mocsy 1.0 with a new, universally convergent algorithm from Munhoven (2013). We now call the cubic initialization routine followed by the standard safe-guarded solver routine solve_at_general, both from Munhoven's SolveSAPHE package v1.0.1. Our tests using typical open-ocean conditions indicate that results from both are identical to at least the sixth digit after the decimal in terms of pH, but that SolveSAPHE is about 5 times faster than our former ICAC routine.

Discussion Paper

Discussion Paper

Discussion Paper

(1)

(2)

Moreover, the SolveSAPHE routines allow mocsy 2.0 to avoid any convergence problem under extreme conditions. The ICAC methods do not always converge, for example under low $C_{\rm T}$ when $A_{\rm T}/C_{\rm T} > 1$ (Munhoven, 2013, Figure 3c). Our experience is that non-convergence may occur in high-resolution, global biogeochemical models under present-day conditions, because local effects from freshwater river input are heightened. An example comes from recent test simulations with the ICAC scheme imbedded in 2°, 0.5°, and 0.25° versions of the NEMO-PISCES model at our laboratory. At the highest resolution, the ICAC scheme generates negative [H⁺] in the model's Ob estuary where simulated $A_{\rm T}$ and $C_{\rm T}$ are both very low as are salinities. We expect that these negative [H⁺] will disappear once the SolveSAPHE algorithms are implemented in the model.

For use with mocsy 2.0, we made minor modification to the SolveSAPHE routines (1) to use mocsy's equilibrium constants and (2) to remove arguments and equations for NH_4^+ and H_2S acid systems.

2.1.3 From aqueous CO_2 to pCO_2

In mocsy, we use K_0 from Weiss (1974) to compute fCO_2 from CO_2^* and the fugacity coefficient C_f (Weiss, 1974; Dickson and Goyet, 1994; Dickson et al., 2007) to compute pCO_2 from fCO_2 :

 $[\mathsf{CO}_2^*] = K_0 f \mathsf{CO}_2 = K_0 C_f p \mathsf{CO}_2.$

For this calculation of oceanic pCO_2 , mocsy does not use the combined coefficient F from Weiss and Price (1980), where

 $F = K_0 C_f \left(1 - p \mathsf{H}_2 \mathsf{O}\right),$

because it includes a wet-to-dry air conversion (term in parentheses), which is inappropriate for the conversions in Eq. 1. Rather, that combined term is commonly used when converting between atmospheric pCO_2 and xCO_2 . Although those atmospheric conversions are now

(3)

Discussion Paper

also offered with new functions in mocsy 2.0, we still do not use F in order to make calculations in a stepwise fashion and to avoid potential confusion.

The mocsy 2.0 package also differs substantially from other packages because it adjusts for effects of subsurface pressure on K_0 as well as C_f . All packages compared by Orr et al. (2014) compute K_0 with the same standard equation (Weiss, 1974, Eq. 12), but none of them make the exponential pressure correction (Weiss, 1974, Eq. 5):

 $[\operatorname{CO}_2^*] = K_0 \ f \operatorname{CO}_2 \exp\left[(1-P) \overline{v}_{\operatorname{CO}_2} / RT\right],$

where *P* is the total pressure (atmospheric + hydrostatic, both in units of atm), \bar{v}_{CO_2} is the partial molal volume of CO₂ (32.3 cm³ mol⁻¹), R is the gas constant (82.05736 cm³ atm mol⁻¹ K⁻¹), and T is the absolute temperature (K). Thus the computed fCO_2 refers only to potential values considering the total pressure as that at the surface. Weiss (1974) indicated that that simplification is adequate down to about 100 m, below which the pressure correction is not negligible and should be included. In mocsy 2.0, we account for the pressure correction term.

Likewise the effects of subsurface pressure on the fugacity coefficient C_f were not considered in the public packages compared by Orr et al. (2014), including mocsy 1.0 (?). All packages considered that total pressure was the same as atmospheric pressure, always equal to 1 atmosphere. Conversely, mocsy 2.0 also accounts for subsurface pressure effects on C_f (Weiss, 1974, Eq. 9):

$$f \mathsf{CO}_2 = p \mathsf{CO}_2 C_f = p \mathsf{CO}_2 \exp \left[\left(B + 2 x_2^2 \delta_{12} \right) P / B \mathcal{I} \right]$$

where *B* is the virial coefficient of CO₂ (Weiss, 1974, Eq. 6), x_2 is the sum of the mole fractions of all remaining gases $(1 - xCO_2$, when $xCO_2 << 1$), and $\delta_{12} = 57.7 - 0.118T$. Once again, P is the total pressure (atmospheric + hydrostatic) in atm and R and T are as described for Eq. 3.

(4)

Other public packages have used only atmospheric pressure for P, tpically fixed at 1 atm, in Eqs. 3 and 4. In that case, computed subsurface fCO_2 and pCO_2 may be considered as potential values that a water parcel would have if brought back to the surface. Yet that second approach misses the correction of the effect of pressure on temperature. Hence we propose a third approach to compute the true potential fCO_2 and pCO_2 by also using θ in place of T in Eqs. 3 and 4. This true potential fCO_2 and pCO_2 consider that subsurface water is brought adiabatically back to the surface. In mocsy 2.0, all three approach, at in situ temperature and total pressure.

The effects of these pressure corrections on K_0 and C_f are shown in terms of their multiplicative effect on fCO_2 and pCO_2 . For K_0 , the effect is shown as components of the exponential term in Eq. 3 (Fig. 1, left). For C_f , it is shown as the ratio between the exponential term in Eq. 4 where P is total pressure over the same term with P equal to atmospheric pressure (Fig. 1, right). At 100 m, factors already reach 1.014 for fCO_2 and 1.05 for pCO_2 . At 5000 m, the total multiplicative effect reaches more than a factor of 2 for fCO_2 and 20 for pCO_2 . The effect of pressure on temperature (T) is a small effect compared with the total correction (T + P). Hence the second and third approaches above provide similar results. Because mocsy 2.0's default is to include these large subsurface pressure corrections, its subsurface fCO_2 and pCO_2 will be much larger than those from other packages (Orr et al., 2014). Conversely, calculations of other variables will not be affected by pressure adjustments of K_0 and C_f .

2.1.4 Revelle factor

Another new feature in mocsy 2.0 is that it accounts for the effects of P_T and Si_T on the Revelle factor R_f .

 $= \frac{\partial p \mathsf{CO}_2 / p \mathsf{CO}_2}{\partial C_{\mathsf{T}} / C_{\mathsf{T}}} = \frac{\partial p \mathsf{CO}_2}{\partial C_{\mathsf{T}}} \left(\frac{C_{\mathsf{T}}}{p \mathsf{CO}_2}\right)$

(5)

To do so, mocsy 2.0 replaces the analytical formula for R_f from Frankignoulle (1994) that was used in mocsy 1.0 with a numerical centered-finite-difference solution to compute the derivative. This second-order accurate numerical approach is like that used in CO2SYS, with two differences. The most significant is that CO2SYS uses fCO_2 in place of pCO_2 . Secondly, in CO2SYS the step size h for the numerical approximation of the derivative $(df/dx = (f(x_0 + h) - f(x_0 - h))/2h$, where x is C_T and f(x) is pCO_2) is ten times larger than ours $(h = 0.1 \mu \text{mol kg}^{-1})$, an optimal value that produced the minimum difference between the numerical and analytical solutions, when nutrient concentrations are set to zero. However, both step sizes yield identical computed R values up to the fourth decimal place.

2.2 Options

Since the publication of the last best practices guide (Dickson et al., 2007), there have been developments that merit close attention given their potential impacts on computed carbonate chemistry variables. First, Lee et al. (2010) estimate that the total borate boron concentration in the ocean, i.e., its linear relationship with salinity, is 4 % greater than estimated previously (Uppström, 1974). Lee et al. (2010) used a more precise measurement technique on more samples (n = 139) collected from a wider geographic distribution than did Uppström (1974) whose total boron : salinity ratio is based on 20 samples from the deep Pacific.

Second for K_1 and K_2 , Millero (2010) combined the same set of measurements used by Lueker et al. (2000) from Mehrbach et al. (1973) along with his own (Millero et al., 2006) to fit new formulations that are applicable over larger ranges of salinity (1 to 50) and temperature (0 to 50 °C) than are the recommended formulations of K_1 and K_2 those recommended for best practices (Lueker et al., 2000). The latter are intended to be used only when 19 < S < 43 and $2 < T < 35^{\circ}$ C. Salinities and temperatures below these thresholds do occur even in coarse-resolution global models in areas such as the Arctic, which routinely experiences subzero temperatures and intense freshwater input from rivers -as well as land- and sea-ice melt. Generally low salinities near rivers are also common in regional models and will become more prevalent in global models as resolution increases. To model such conditions properly, we may need to go beyond the best-practices recommendation (Dickson et al., 2007). Thus in mocsy, we have implemented options for the user to choose to replace the formulations use the newer formulations mentioned above for K_1, K_2 , and total boron recommended by the best practices guide with the more recent formulations mentioned above. Likewise, in place of those recommended for best practices. Likewise for $K_{\rm F}$, we allow the user to choose either the Dickson and Riley (1979) formulation recommended by Dickson and Goyet (1994) or the Perez and Fraga (1987) formulation recommended by Dickson et al. (2007), but which is intended to be limited to waters where 10 < S < 40 (practical salinity scale) and $9 < T < 33 \,^{\circ}$ C.

Discussion Paper

2.3 Exceptions to best practices

The best-practice formulations for K_W , K_{1P} , K_{2P} , and K_{3P} proposed by Dickson et al. (2007) are those from Millero (1995) with 0.015 subtracted from the constant term as a simple means to convert from the seawater to the total hydrogen ion scale (Dickson and Goyet, 1994; Dickson et al., 2007, Chap. 5, footnote 5). In mocsy, we do not impose this constant correction, preferring instead to use the classic approach to convert equilibrium constants between the two pH scales (e.g., Millero, 2010, Eq. 6), resulting. That results in a pH-scale correction that varies with [HF]. The same variable correction is used in CO2SYS.

Dickson et al. (2007) do not discuss pressure corrections of equilibrium constants. For thatUnlike in other public packages, mocsy 2.0 makes pressure adjustments for K_0 and the related C_f (Eqs. 3 and4), thus affecting computed fCO_2 and pCO_2 (see Sect. 2.1.3). For the remaining equilibrium constants, mocsy follows the lead of CO2SYS using Millero's equations, quadratic functions of pressure and temperature (Millero, 1995, Eqs. 90–92) with corrections to associated coefficients from Lewis and Wallace (1998) as detailed in a recent comparison elsewhere (Orr et al., 2014, Table 7).

To compute the Ca^{2+} concentration from salinity, mocsy 2.0 uses a Ca-to-chlorinity ratio of 0.02128 from Riley and Tongudai (1967) instead of the slightly different value of 0.02127 that appears in the best-practices guide (Dickson et al., 2007, chap.5, Table 2). The latter states it uses the ratio from the former reference.

2.4 Evaluation

There is no absolute reference for computed carbonate system variables. To validate mocsy, its computed variables were compared to those from CO2SYS-MATLAB (van Heuven et al.,

2011) run with identical input data. Input data for Although both packages could in principle be wrong even if both agree, we compare mocsy to CO2SYS because the latter is the first public package made available to compute these variables, it is used widely, and it was developed with great care (Lewis and Wallace, 1998). Moreover, it has served as a base for other public packages to build on. A companion manuscript further details the reasons for our arbitrarily choice of CO2SYS as the reference (Orr et al., 2014). The input data with which we compared the two packages includes A_{T} and C_{T} are from the three-dimensional, global gridded data product on a $1^{\circ} \times 1^{\circ}$ grid known as GLODAP (Key et al., 2004). The other input data are Other necessary input data on the same grid were taken from the 2009 World Ocean Atlas (WOA2009) gridded data product, which includes in situ temperature (Locarnini et al., 2010) and salinity (Antonov et al., 2010) as well as phosphate and silicate concentrations (Garcia et al., 2010). The CO2SYS code was chosen as the reference because it was the first publicly available software package (Lewis and Wallace, 1998) and it may still be the most widely used by the community. Furthermore, it has been updated regularly, and a close inspection of the code and documentation reveals the extreme care that has gone into its development and the process of rooting out potential errors. concentrations of P_T and Si_T (Garcia et al., 2010).

3 Results

As a baseline reference for later evaluation and sensitivity tests, we present carbonate system variables computed with mocsy 2.0 from the gridded GLODAP-WOA2009 data. Magnitudes and patterns of the surface zonal-mean distributions (Fig. 2) are as expected based on previous studies Orr et al. (2005); Orr (2011). Corresponding global mean

vertical profiles (Fig. 3) have not been detailed previously. Both fCO_2 and pCO_2 continue to increase with depth, particularly the latter, because of pressure corrections to K_0 and C_f , respectively. Conversely, the CO_2^* concentration increases from the surface to about 1000 m, where it reaches three times the surface level. Below, it declines slowly to values at 5000 m that are just over twice those at the surface. The CO_3^{2-} profile mirrors that for CO_2^* , as expected from the zonal mean distributions. Vertical distributions of the saturation states Ω_A and Ω_C generally follow the CO_3^{2-} profile but are influenced by pressure effects on K_A and K_C . The shape of the H⁺ concentration profile is similar to that for CO_2^* but shows two maxima at 1000 and 5000 m, both at about twice the surface concentration. The Revelle factor also reaches a maximum at 1000 m, but it declines only slightly below, with values remaining at nearly double the surface level.

3.1 Evaluation

Our evaluation reveals that the extent to which mocsy's computed variables variables computed from the GLODAP-WOA2009 data differ from those computed when the same data is used with the CO2SYS-MATLAB package, but generally by less than. Relative differences remain within ± 0.005 . Consistently small differences are found for area-weighted, % for computed concentrations of CO₂^{*}, HCO₃⁻, CO₃²⁻, and H⁺, both for surface zonal means (Fig. 4) and global average vertical profiles (Fig. 5)as well as for surface zonal means (Fig. . Corresponding absolute differences are within 0.01 µmol kg⁻¹ for each of the three inorganic carbon species, and within 0.0002 4) of computed *p*nmolkg⁻¹ for H⁺. The latter translates into pH differences of less than 0.00002 between the two packages. Tighter agreement cannot be expected because CO2SYS computes pH with a Newton method that stops iterating once the change in pH from the previous iteration is

less than 0.0001. The slight difference in H⁺ between packages explains the slight offsets in the three inorganic carbon species, because both packages yield identical results for the computed K_1 and K_2 equilibrium constants (Orr et al., 2014).

Relative differences between packages are slightly larger for Ω_A and Ω_C , with a constant offset of 0.018% throughout the water column. Comparison of the source code of the two packages revealed that the offset is due to differences in the atomic weight of calcium: CO2SYS's uses 40.087, whereas mocsy uses 40.078, the recommended value (Dickson et al., 2007, chap. 5, Table 1). Nonetheless, these relative differences remain small. They correspond with differences in computed saturation states of less than 0.001 unit between the two packages. Of similar magnitude are the relative differences for the Revelle factor R_f of about 0.02% at the surface. Relative differences in R_f grow to 0.2% at 5000 m, but the corresponding absolute differences remains less than 0.03 units. With the new numerical solution of R_f in mocsy, differences relative to CO2sys are six times smaller than with the analytical formula used in mocsy 1.0.

Concerning the two remaining computed variables, at the surface fCO_2 and concentrations of , , pCO_2 both track CO_2^* , and . Disagreement is larger yet remains small for computed Ω_C (up to 0.07) and Ω_A (up to 0.13) The largest disagreement is found for mocsy's computed Revelle factor, which reaches up to 0.7greater in Southern Ocean surface waters and up to 1.5larger at in both packages. Hence differences between packages for both variables are similarly small (0.005%) at the surface. Yet discrepances grow to extraordinary levels at greater depths. At 5000 m, on average. mocsy's fCO_2 is twice as large as that in CO2SYS, while its pCO_2 reaches more than twenty times more. The cause of these large differences are the pressure corrections to K_F and C_f in mocsy 2.0 (Eqs. 3 and 4) as shown in Fig. 1, which are not accounted for in CO2SYS.

Discussion Paper

3.2 Model approximations

The three approximations that have been widely used in models lead to significant errors in some computed variables in the deep ocean (Fig. 7). For Errors from all three model approximations increase with depth (Figs. 6). Maximum total errors reach 3% or more for p, the total error is -1CO₂, H⁺, and Ω_A at 1000m and -8at 5000 m, almost entirely from the temperature approximation. There is only a slight compensation by the error. Yet the causes differ. For pCO_2 , the largest error comes from the pressure approximation(e.g., reaching + 0.5), while errors from the other two approximations are smaller and nearly compensate one another. For Ω_A there is little compensation, while the error from the constant density approximation dominates; it alone reaches 3% at 5000 m). The constant density approximation produces no significant error neither for pnor for any of the other computed tracers. For pH, the total error also grows with depth reaching up to +0.010 at 5000. Most of that derives m. For H⁺, there is no compensation and errors from the temperature approximation, but the pressure approximation also contributes in the same direction. For, the total error remains negligible, with small dominate. The total relative error for computed fCO_2 in the deep ocean is about half that for pCO_2 because the error associated with the pressure approximation is more than four times smaller while errors from the temperature approximation (e.g., -0.2at 5000) being compensated by nearly equal and opposite other two approximations are similar. Total errors from the pressure approximation, three approximations remain less than 1% even in the deep ocean for the three inorganic carbon species as well as for the Revelle factor.

Errors in Ω_A have a similar pattern but the error from the pressure approximation weighs more heavily leading to a slight total error of +0.01 units somewhat similar patterns to those of CO_3^{2-} . Yet at 5000 m. The difference in relative errors between m, the magnitude of the total relative error of Ω_A and reaches 4%, more than five times greater than for CO_3^{2-} is thus. That relative enhancement of the former over the latter is partly due to the sharp decline in Ω_A , e.g., below 1000 m, whereas CO_3^{2-} concentrations remain relatively stable (Fig. 3). The dominance of the error from the pressure induced variability in the pressure induced increase in K_A outweighing the largely outweighs its sensitivity to temperature. For computed and the Revelle factor, the errors are similarly dominated by the temperature approximation and grow with depth but, unlike for CO_3^{2-} .

None of the three approximations is without error, but it is the constant density approximation which leads to the largest errors in most computed variables (except for pCO_2 , H⁺, and fCO_2). Yet total absolute errors generally remain small, even at 5000mthey reach only -0.005 and -0.01 units, respectively m, e.g., less than 0.6 µmol kg⁻¹ for the three inorganic carbon species, less than 0.02 for Ω_A , and less than 0.07 for R_f (Figs. 7). Conversely, at the same depth the absolute error in pH reaches 0.015 while for pCO_2 it reaches 350 µatm.

3.3 Options

The effects of the three options on computed variables differ by region and depth. The choice for the K_F option has little virtually no effect on computed quantities and can be neglected. Conversely, there are substantial differences that depend on That is, K_F appears in the total alkalinity equation as detailed later, but its relative importance may be thought of simply in terms of pH, as it is used to convert between the seawater and total pH scales. The difference between the two scales is small (~0.01 units of pH), and the two formulations alter that very slightly. Practically then, computed carbonate system variables are insensitive

to different formulations of K_F . More details about the sensitivity of computed variables to each of the constants can be found elsewhere (Orr et al., 2014, Table 9). Larger differences result from the choice of the two other new options:, for total boron and the for formulations for K_1 and K_2 .

The new formulation for total boron (Lee et al., 2010) 4% increase in total boron with the new formulation from Lee et al. (2010) increases borate alkalinity $A_{\rm B}$ by about 4., e.g., by about 3% in typical surface waters. The latter increases less because $A_{\rm B} = B_{\rm T}/(1 + [{\rm H}^+]/K_{\rm B})$ and $[{\rm H}^+]$ also increases by 1%. Yet modeled total alkalinity $A_{\rm T}$ is unaffected, being an input variable (along with $C_{\rm T}$). Since Because $A_{\rm T}$ is unchanged and $A_{\rm B}$ is higher, then modeled carbonate alkalinity $A_{\rm C}$ must be lower. This decline in $A_{\rm C}$ reduces surface $\rm CO_3^{2-}$ everywhere, from $-1.5\,\mu\rm{mol}\,\rm{kg}^{-1}$ in the Southern Ocean to $-3 \,\mu$ mol kg⁻¹ in the tropics (Fig. 8). The corresponding decline in surface Ω_A is between 0.02 to 0.04. Simultaneously, computed surface pCO_2 increases by 4 to 6 µatm and surface pH declines by 0.006 units. Nonetheless Yet the Revelle factor declines by 0.04, i.e., the buffer capacity increases. That is, despite the reduced and increased decline can be understood by studying Eq. (??). The partial derivative on the right hand side 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_f decreases because pCO_2 , by maintaining the same total alkalinity while reducing carbonate alkalinity, the increases ($C_{\rm T}$ must also decline. Hence the $A_{\rm T}$ minus $C_{\rm T}$ increases, as must then the buffer capacity. remains constant). In the deep ocean, the new total boron formulation leads to nearly uniform changes in ppH of $+5 \pm 1$, in pH of $-0.005 \pm 0.001 - 0.005 \pm 0.001$ units, and in CO_3^{2-} of $-1\pm0.1\pm0.1\mu$ mol kg⁻¹. There is also an exponential increase in pCO₂ up to 110 μ atm at 5000 m (Fig. 9). The latter represents a 1% increase in the baseline pCO₂ (Fig. 3).

4 Discussion

The constant density approximation imposes that the same density, typically 1028, be used to convert input (A_TThe new option where the formulations of K_1 and K_2 from Millero (2010) are used instead of those from Lueker et al. (2000) yields changes that are less uniform and in some places larger than those from using the new option for B_{T} . Changes from the new option for K_1 and K_2 are larger in the Southern Ocean, i.e., C_{T_1} and nutrients) from model concentration units (mol) to data units (molpCO₂ increases by up to +7) as needed for μ atm, corresponding to a 2% increase in CO₂, while pH declines by up to 0.006. In contrast, in the lowest latitudes corresponding changes in pCO_2 and CO_2^* are negligible. In the Southern Ocean, changes in pCO_2 , CO_2^* , and pH from using the new K_1 and K_2 option reinforce those from the equilibrium calculations. Resulting concentrations of computed variables (e.g., new B_T option. But in the same region, changes from the two options partly compensate one another for CO_3^{2-}) are then reconverted back to model units with the same density. When the same constant density is used in all subsequent analysis that compares computed variable concentrations to data (converting from moland Ω_A , while they reinforce one another in the lower latitudes. Due to these regional differences in compensation, total absolute changes are largest in the Southern Ocean for pCO_2 (+12 to or vice-versauatm), errors are always negligible. Conversely, if a different constant density or a variable density is used in subsequent model-data comparison, associated errors can surpass those from the other two approximations. Hence mocsy avoids the constant density

(6)

approximation, while also providing the model's in situ density as output. CO₂^{*} (+4%), pH (-0.012), and R_f (-0.30), whereas they are largest in the lower latitudes for CO_3^{2-} $(-3.5 \,\mu\text{mol kg}^{-1})$ and Ω_A (-0.06). With depth, mean absolute changes due to both options grow for pCO_2 and CO_2^* , change little for pH and R_f , and decline for CO_3^{2-} and Ω_A . These differences appear greatly affected by the structure of the baseline profiles (Fig. 3). So far, we have focused

Discussion

4

Our focus has been on quantifying errors in computed variables from the three model approximations and in assessing how variables are affected by the three user options. A more general concern is how computed variables are affected by the frequent practice of neglecting nutrient concentrations in carbonate system calculations. In high-nutrient regions, the changes in computed variables due to phosphate and silicate alkalinity (Figs. 10 and 11) are similar in magnitude and have the same sign as do those due to the change to the from changing to the new formulation for borate alkalinity total boron (Figs. 8 and 9). All three contribute to non-carbonate alkalinity and hence total alkalinity,

$$A_{\mathsf{T}} = A_{\mathsf{C}} + A_{\mathsf{B}} + A_{\mathsf{W}} + A_{\mathsf{P}} + A_{\mathsf{Si}} + A_{\mathsf{O}}$$

where

In brief, contributions on the right side of Eq. (6) come from components of carbonic acid, boric acid, water, phosphoric acid, silicic acid, and other species, respectively. The latter include bisulfate (also used to convert between free and total pH scales) and hydrogen fluoride (used to convert between total and seawater scales). sum of last three terms in Eq. (??) are often represented simply as $[H^+]$, namely the hydrogen ion concentration on the seawater scale. Hence, water alkalinity A_W provides an indicator of how a given seawater sample differs from acid-base neutrality.

As an input variable, $A_{\rm T}$ is not affected by the choices such as using a more simplified alkalinity equation, by neglecting nutrient concentrations, or by choosing a different formulation for total boron. Indeed, measured $A_{\rm T}$ is unaffected by any of our calculations. Yet $A_{\rm C}$ is affected, being computed by difference. As any of $A_{\rm B}$, $A_{\rm P}$, or $A_{\rm Si}$ increase, computed A_{C} must decrease. In the surface ocean, nutrient alkalinity $(A_{P} + A_{Si})$ substantially alters computed carbonate system variables where nutrient concentrations are largest, e.g., in the equatorial Pacific and in the high latitudes (poleward of 40°). The largest surface effects occur in the Southern Ocean where computed pCO_2 changes by $+6 \mu atm$, once nutrients are accounted for, which is six times more than estimated by Follows et al. (2006). At the same time, CO_3^{2-} changes by $-1.6 \,\mu$ mol kg⁻¹ and pH by -0.007 (Fig. 10). Sometimes differences between some models may be larger in some regions, but this is far from a general rule. In the Southern Ocean, simulated air-sea fluxes of natural CO₂ often differ between models by only a tenth of a Pg C yr⁻¹, equivalent to less than 1 μ atm in the air-sea difference in pCO₂ (Dufour et al., 2013, Table 1). The shift mentioned above would be more than enough to switch some of them from net sinks to net sources of natural CO_2 .

These biases concern models that carry only practical alkalinity $(A_{C} + A_{B} + A_{W})$, i.e., which neglect alkalinity from neglect contributions of phosphoric and silicic acids - to alkalinity (by assuming $A_{T} = A_{C} + A_{B} + A_{W}$). Equivalent biases occur when nutrient concentrations are assumed to be zero in offline calculations with output from models that include these nutrients in the alkalinity equation. Without other compensating biases, this simplification would lead to a simulated aragonite saturation horizon that is too deep (Fig. 12), a simulated onset of aragonite undersaturation in polar surface waters ($\Omega_A < 1$) that is too late, and a simulated interhemispheric north-to-south oceanic transport of carbon (Sarmiento et al., 2000) that is too weak. Our results illustrate where and by how much models err when they neglect nutrient alkalinity, either because of a simplified alkalinity equation or equivalently by assuming null nutrient concentrations (e.g., in offline calculations). Remedying these errors requires little extra coding and does not add significantly to a model's computation time. For models that do not carry and P_T and S_{i_T} as tracers, the bias in computed carbonate system variables would be reduced by imposing that calculating the alkalinity from those absent tracers follow as that from observed nutrient climatologies (Garcia et al., 2010). (e.g., Garcia et al., 2010). Alternatively, models that carry inorganic N but not inorganic P as a tracer could approximate the latter by mutiplying the former by a fixed Redfield ratio. Yet alkalinity associated with Si_T would still be missing.

When combined with the new formulation for total boron (Lee et al., 2010), the magnitude of the total change in the deep ocean is nearly double that from nutrients alone (sum from Figs The combined effect from nutrient alkalinity and the new $B_{\rm T}$ formulation are often greater than the individual effects in the surface ocean (Fig. 8 and + Fig. 10). On average, the combined effect in the deep ocean In the deep ocean, the average combined effect shifts CO_3^{2-} by -3μ mol kg⁻¹, pH by -0.018, and pCO_2 by 18 μ atm (sum from FigsFig. 9 and + Fig. 11). The combined effect also shallows the computed modern ASH by about 100 m in the North Atlantic and up to 300 m in the Southern Ocean (Fig. 12).

Unfortunately, neither the new option for B_T nor that for K_1 and K_2 can be recommended at present. The new boron option leads to substantial changes in computed variables, but those results rely on best-practice formulations of K_1 and K_2 that predate the

Lee et al. (2010) study and depend themselves on $B_{\rm T}$ (Mehrbach et al., 1973, Eq. 8). Likewise, the option to use new formulations of K_1 and K_2 from Millero (2010) leads to large differences in computed variables, but those constants are not consistent when calculated from sets of coefficients made available on different pH scales (Orr et al., 2014).

5 Conclusions

Although fCO₂ and pCO₂ typically calculated are measured or at the surface. e.q., to estimate air-sea CO₂ fluxes. а limited number of with studies also concerned those quantities below the surface are (e.g., Brewer and Peltzer, 2009; Cocco et al., 2013; Bates et al., 2013). Here we recommend that future studies concerned with subsurface values should choose one of two options: (1) compute in situ $f CO_2$ and $p CO_2$ after making pressure corrections to K_0 and the fugacity coefficient following Weiss (1974) using total in situ pressure and in situ temperature or (2) calculate potential fCO_2 and pCO_2 at 1 atm pressure while using potential instead of in situ temperature. Results should then be clearly labeled as either in situ or potential fCO_2 and pCO_2 . We make this recommendation to avoid ambiguiity, especially because pressure effects are large, e.g., multiplying $f CO_2$ by 2 and $p CO_2$ by 20 when at 5000 m. The mocsy 2.0 package offers the first choice as a default and the second as an option. Other public packages currently offer neither option, computing fCO_2 and pCO_2 at 1 atm total pressure with in situ temperature.

For simplicity, modelers typically make ocean carbonate chemistry calculations with the following three assumptions: assuming (1) that model density is constant, (2) that simulated potential temperature is an adequate proxy for equivalent to in situ temperature,

and (3) that model depth is equivalent to pressure. None of the three approximations produces significant errors at the surface. Below the surface, errors in some Yet errors in computed variables grow with depthdue to combined effects from the temperature and pressure approximations; the constant density approximation does not contribute unless a different density is used to convert computed concentrations, e. g., to. At 5000 m, total the sum of the relative errors from the temperature and pressure approximations reach 8in three approximations reach more than 3% for pCO_2 , +0.010 in pH, $+0.1\Omega_A$, and H⁺ (pH shift of up to 0.015). Yet they remain at less than 1% for the three inorganic carbon species (≤ 1 in , and +0.005 in Ω_A . µmol kg⁻¹). The mocsy modeling routines avoid these errors with little additional coding and trivial increases in computational time.

The same code also offers two new options to provide for survey effects of developments since the publication of the best practices guide (Dickson et al., 2007). Those options concern an assessment that seawater contains 4% more total boron than thought previously (Lee et al., 2010) and new formulations for K_1 and K_2 designed to include low salinity waters (Millero, 2010). The new boron option leads to substantial shifts in computed surface variables, e.g., +4 to +6 µatm in pCO_2 , -1.2 to -2.5 µmol kg⁻¹ in CO_3^{2-} , and -0.006 in pH. Comparable shifts at depth lead to a shallower computed ASH by 50 m in the North Atlantic and by up to 90 m in the Southern Ocean. The new option for K_1 and K_2 leads to an even larger a shift of +7 µatm in surface pCO_2 in the Southern Ocean. When both options are combined, the Southern Ocean's surface pCO_2 becomes 3 µatm higher than in the high northern latitudes and 6 µatm higher than in the tropics. A third option, specifying use of the Dickson and Riley (1979) formulation for K_F instead of that recommended for best practices (Perez and Fraga, 1987) produces no significant differences.

Of additional concern is the common modeling practice of neglecting nutrients, either in the model's equation for alkalinity (practical alkalinity) or the equivalent assumption that nutrient concentrations are zero. Resulting errors in computed surface *p*have similar magnitudes and patterns as do the shifts associated with the change in the Yet despite their large effects, we cannot yet recommend either new option. Before using the new $B_{\rm T}$ formulation, the community needs an assessment of how K_1 and K_2 will change because those measurements depend on $B_{\rm T}$. And before the community uses the new formulations for K_1 and K_2 . They too lead to similar meridional differences in surface *p*. Accounting for nutrient alkalinityfurther shallows the computed ASH(for low-salinity waters), the provided sets of coefficients from which users calculate them must be refined to give consistent results.

For simplicity, models often neglect contributions of total phosphorus and silicon to total alkalinity. Doing so biases computed variables, e.g., by about 50 shifting Southern Ocean surface pCO_2 by +6 m in the North Atlantic and by 100 to µatm and the ASH below by up to ± 200 min the Southern Ocean.

Therefore, modelers would do well to avoid the three common approximations, to use the new boron option, and to . Because biases are not uniform, they also affect lateral and vertical gradients. For greater consistency, we invite all modelers to account for nutrient alkalinity in model equations and offline calculations. Although, the new formulations for K_1 and K_2 also lead to large differences in computed variables, we consider their use premature, because the published sets of coefficients have an inadequate number of significant figures and are inconsistent among the different pH scales (Orr et al., 2014) .As open software, modelers are free to use mocsy directly or borrow from it to refine their simulated carbonate chemistry and air-sea fluxes carbonate system calculations and to avoid the three common model approximations for subsurface calculations. The mocsy 2.0 is package removes these limitations while following best practices. It also adopts the fastest and safest method to solve the total alkalinity-pH equation (Munhoven, 2013). That solver always converges, even under extreme conditions, e.g., in estuaries subject to intense freshwater fluxes where other solvers may fail.

Code availability

The mocsy package is distributed under the MIT license and is available from github. It can be retrieved in the conventional manner with git, namely by issuing the following command

git clone git://github.com/jamesorr/mocsy.git

in an X terminal on Linux, Mac or PC operating systems. If that fails, install git and try again, or go to the main web page on github https://github.com/jamesorr/mocsy and click on the link "Download ZIP". Once downloaded, mocsy can be compiled by typing

make

More details on the code, its compilation, and examples of its use in Fortran and when called from python can be found in the mocsy manual at http://ocmip5.ipsl.jussieu.fr/mocsy/.

Acknowledgements. We thank the original OCMIP code developers (C. L. Sabine, R. M. Key, and R. G. Najjar) and those who provided subsequent corrections or comments (A. Mouchetand, K. Lindsay, J. Christian, and G. McKinley). We are indebted to E. Maier Reimer for providing the code for the iterative loop for pH, grateful to J.-P. Gattuso, E. Lewis and D. Wallace, as well as S. van Heuven, D. Pierrot, and J. Rae for coding and making public their packages (seacarb, CO2SYS, and

CO2SYS-MATLAB), which have been no small inspiration for mocsy. We also thank P. Brockmann and Y. Meurdesoif for professional advice on coding and distribution strategies. The original manuscript and code have been improved because of three dedicated referees: G. Munhoven shared scientific and technical savvy while making his stable, efficient, and well-documented pH solver (SolveSAPHE) publicly available, allowing us to easily integrate it in mocsy; A. Dickson offered much critical expertise on carbonate chemistry, for instance inspiring us to include pressure corrections that dramatically alter computed subsurface fCO_2 and we thank O. Aumont for passing that along to us. pCO_2 ; and an anonymous referee provided a wider modeler's perspective. We are grateful to F. Perez for pointing out that formulations of K_1 and K_2 depend upon B_T . The OCMIP code was first modified with support from the EU FP5 project NOCES (grant EVK2-CT-2001-00134) and the FP6 project CARBOOCEAN (grant 511176(GOCE)). More recent efforts to refine, document and make the code publicly available were supported by the French ANR project MACROES (MACRoscope for Oceanic Earth System ANR-09-CEP-003) and two EU FP7 projects, CARBOCHANGE (grant 264879) and MedSeA (grant 265103).

References

- Antonov, J. I., Seidov, D., Boyer, T. P., Locarnini, R. A., Mishonov, A. V., Garcia, H. E., Baranova, O. K., Zweng, M. M., and Johnson, D. R.: World Ocean Atlas 2009, vol. 2: Salinity, edited by: Levitus, S., Atlas NESDIS 69, NOAA, US Government Printing Office, Washington DC, 184 pp., 2010.
- Aumont, O. and Bopp, L.: Globalizing results from ocean in situ iron fertilization studies, Global Biogeochem. Cy., 20, GB2017, doi:10.1029/2005GB002591, 2006.
- Bates, N. R., Orchowska, M. I., Garley, R., and Mathis, J. T.: Summertime calcium carbonate undersaturation in shelf waters of the western Arctic Ocean—how biological processes exacerbate the impact of ocean acidification, Biogeosciences, 10, 5281–5309, doi:10.5194/bg-10-5281-2013, http://www.biogeosciences.net/10/5281/2013/, 2013.
- Brewer, P. and Peltzer, E.: Limits to marine life, Science, 324, 347–348, doi:10.1126/science.1170756, 2009.

Caldeira, K. and Wickett, M. E.: Anthropogenic carbon and ocean pH, Science, 425, p. 365, 2003.

- Cocco, V., Joos, F., Steinacher, M., Frölicher, T. L., Bopp, L., Dunne, J., Gehlen, M., Heinze, C., Orr, J., Oschlies, A., Schneider, B., Segschneider, J., and Tjiputra, J.: Oxygen and indicators of stress for marine life in multi-model global warming projections, Biogeosciences, 10, 1849–1868, doi:10.5194/bg-10-1849-2013, http://www.biogeosciences.net/10/1849/2013/, 2013.
- Dickson, A. G.: Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K, Deep-Sea Res., 37, 755–766, 1990.
- Dickson, A. G.: The carbon dioxide system in seawater: equilibrium chemistry and measurements, in: Guide to Best Practices for Ocean Acidification Research and Data Reporting, edited by: Riebesell, U., Fabry, V. J., Hansson, L., and Gattuso, J.-P., Publications Office of the European Union, 17–40, 2010.
- Dickson, A. G. and Goyet, C.: Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Seawater, version 2, CDIAC-74, ORNL, 187 pp., 1994.
- Dickson, A. G. and Riley, J. P.: The estimation of acid dissociation constants in seawater media from potentiometric titrations with strong base. I. The ionic product of water $-K_W$, Mar. Chem., 7, 89–99, 1979.
- Dickson, A. G., Sabine, C. L., and Christian, J. R.: Guide to best practices for ocean CO₂ measurements, PICES Special Publication 3, 191 pp., 2007.
- Dufour, C. O., Sommer, J. L., Gehlen, M., Orr, J. C., Molines, J.-M., Simeon, J., and Barnier, B.: Eddy compensation and controls of the enhanced sea-to-air CO2 flux during positive phases of the Southern Annular Mode, Global Biogeochem. Cycles, 27, 950–961, doi:10.1002/gbc.20090, 2013.
- Follows, M. J., Ito, T., and Dutkiewicz, S.: On the solution of the carbonate chemistry system in ocean biogeochemistry models, Ocean Model., 12, 290–301, doi:10.1016/j.ocemod.2005.05.004, 2006.
- Frankignoulle, M.: A complete set of buffer factors for acid/base CO₂ system in seawater, J. Marine Syst., 5, 111–118, 1994.
- Garcia, H. E., Locarnini, R. A., Boyer, T. P., Antonov, J. I., Zweng, M. M., Baranova, O. K., and Johnson, D. R.: World Ocean Atlas 2009, vol. 4: Nutrients (phosphate, nitrate, silicate), edited by: Levitus, S., Atlas NESDIS 71, NOAA, US Government Printing Office, Washington DC, 398 pp., 2010.

Discussion Paper

- Lavigne, H. and Gattuso, J.-P.: seacarb: seawater carbonate chemistry with R. R package version 2.4.2, in: The Comprehensive R Archive Network, available at: http://www.obs-vlfr.fr/~gattuso/files/Lavigne_Gattuso_2011_seacarb_2.4.2.pdf (last access: 24 April 2014), 2011.
- Lee, K., Kim, T.-W., Byrne, R. H., Millero, F. J., Feely, R. A., and Liu, Y.-M.: The universal ratio of boron to chlorinity for the North Pacific and North Atlantic oceans, Geochim. Cosmochim. Ac., 74, 1801–1811, doi:10.1016/j.gca.2009.12.027, 2010.
- Lewis, E. and Wallace, D. W. R.: Program Developed for CO₂ System Calculations, ORNL/CDIAC-105, Carbon Dioxide Inf. Anal. Cent., Oak Ridge Natl. Lab., Oak Ridge, Tenn., 38 pp., 1998.
- Locarnini, R., Mishonov, A., Antonov, J., Boyer, T., Garcia, H., Baranova, O., Zweng, M., and Johnson, D.: World Ocean Atlas 2009, vol. 1: Temperature, edited by: Levitus, S., Atlas NESDIS 68, NOAA, US Government Printing Office, Washington DC, 184 pp., 2010.
- Lueker, T. J., Dickson, A. G., and Keeling, C. D.: Ocean pCO_2 calculated from dissolved inorganic carbon, alkalinity, and equations for K_1 and K_2 : validation based on laboratory measurements of CO_2 in gas and seawater at equilibrium, Mar. Chem., 70, 105–119, 2000.
- Maier-Reimer, E.: Geochemical cycles in an ocean general circulation model: preindustrial tracer distributions, Global Biogeochem. Cy., 7, 645–677, 1993.
- Mehrbach, C., Culberson, C. H., Hawley, J. E., and Pytkowicz, R. M.: Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, Limnol. Oceanogr., 18, 897–907, 1973.
- Millero, F. J.: Thermodynamics of the carbon dioxide system in the oceans, Geochim. Cosmochim. Ac., 59, 661–677, 1995.
- Millero, F. J.: Carbonate constants for estuarine waters, Mar. Freshwater Res., 61, 139–142, doi:10.1071/MF09254, 2010.
- Millero, F. J., Graham, T. B., Huang, F., Bustos-Serrano, H., and Pierrot, D.: Dissociation constants of carbonic acid in seawater, Mar. Chem., 100, 80–94, doi:10.1016/j.marchem.2005.12.001, 2006.
- Morris, A. and Riley, J.: The bromide/chlorinity and sulphate/chlorinity ratio in sea water, in: Deep-Sea Research and Oceanographic Abstracts, 13, 699–705, 1966.
- Mucci, A.: The solubility of calcite and aragonite in seawater at various salinities, temperatures, and one atmosphere total pressure, Am. J. Sci., 283, 780–799, 1983.

Discussion Paper

- Munhoven, G.: The mathematics of the total alkalinity—pH equation—pathway to robust and universal solution algorithms: the SolveSAPHE package v1.0.1, Geosci. Model Dev., 6, 1367–1388, doi:10.5194/gmd-6-1367-2013, 2013.
- Orr, J. C.: Recent and future changes in ocean carbonate chemistry, in: Ocean Acidification, edited by Gattuso, J.-P. and Hansson, L., chap. 3, pp. 41–66, Oxford Univ. Press, 2011.
- Orr, J. C., Fabry, V. J., Aumont, O., Bopp, L., Doney, S. C., Feely, R. A., Gnanadesikan, A., Gruber, N., Ishida, A., Joos, F., Key, R. M., Lindsay, K., Maier-Reimer, E., Matear, R., Monfray, P., Mouchet, A., Najjar, R. G., Plattner, G.-K., Rodgers, K. B., Sabine, C. L., Sarmiento, J. L., Schlitzer, R., Slater, R. D., Totterdell, I. J., Weirig, M.-F., Yamanaka, Y., and Yool, A.: Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms, Nature, 437, 681–686, doi:10.1038/nature04095, 2005.
- Orr, J. C., Epitalon, J.-M., and Gattuso, J.-P.: Comparison of seven packages that compute ocean carbonate chemistry, Biogeosciences Discuss., 11, 5327–5397, doi:10.5194/bgd-11-5327-2014, 2014.
- Perez, F. F. and Fraga, F.: Association constant of fluoride and hydrogen ions in seawater, Mar. Chem., 21, 161–168, 1987.
- Proye, A. and Gattuso, J.-P.: Seacarb, an R package to calculate parameters of the seawater carbonate system, available at: http://www.obs-vlfr.fr/~gattuso/files/Proye_Gattuso_2003_seacarb_0.93. pdf (last access: 24 April 2014), 2003.
- Riley, J. P.: The occurence of anomalously high fluoride concentrations in the North Atlantic, Deep-Sea Res., 12, 219–220, 1965.
- Riley, J. and Tongudai, M.: The major cation/chlorinity ratios in sea water, Chem. Geol., 2, 263–269, 1967.
- Sarmiento, J. L., Monfray, P., Maier-Reimer, E., Aumont, O., Murnane, R., and Orr, J. C.: Sea–air CO₂ fluxes and carbon transport: a comparison of three ocean general circulation models, Global Biogeochem. Cy., 14, 1267–1281, 2000.

- Uppström, L. R.: The boron/chlorinity ratio of deep-sea water from the Pacific Ocean, in: Deep-Sea Research and Oceanographic Abstracts, vol. 21, Elsevier, 161–162, 1974.
- van Heuven, S., Pierrot, D., Rae, J. W. B., Lewis, E., and Wallace, D. W. R.: MATLAB Program Developed for CO₂ System Calculations, ORNL/CDIAC-105b, Carbon Dioxide Inf. Anal. Cent., Oak Ridge Natl. Lab., Oak Ridge, Tenn., 2011.
- Weiss, R. F.: Carbon dioxide in water and seawater: the solubility of a non-ideal gas, Mar. Chem., 2, 203–215, 1974.
- Weiss, R. F. and Price, B. A.: Nitrous oxide solubility in water and seawater, Mar. Chem., 8, 347–359, 1980.




Figure 1. Global-mean Effect of pressure on K_0 and C_f given as factors that would need to be multiplied by (left) $f CO_2$ and (right) $p CO_2$ computed without pressure corrections. These global-mean vertical profiles for the relative difference between were computed with mocsy 2.0 and CO2SYS for each computed variable $100(V_{mocsy} - V_{co2sys})/V_{co2sys}$ the GLODAP-WOA2009 gridded input data.



Figure 2. Surface zonal mean means of the relative difference for computed carbonate system variables , computed as with mocsy 2.0 from the gridded GLODAP data for $A_{\rm T}$ and $C_{\rm T}$ combined with corresponding data from the 2009 World Ocean Atlas for in Figsitu temperature, salinity, P_T, and Si_T.5.



Figure 3. Global-mean vertical profiles of carbonate system variables computed with mocsy 2.0 from the data described in Fig. 2.



Figure 4. Differences in surface zonal means between mocsy and CO2SYS for computed variables shown as (top) percent relative differences $(100(V_{mocsy} - V_{co2sys})/V_{co2sys})$ and as (bottom) absolute differences $(V_{mocsy} - V_{co2sys})$. The absolute differences are given in µmol kg⁻¹ for the 3 inorganic carbon species, in nmol kg⁻¹ for H⁺, and in µatm for fCO_2 and pCO_2 ; other computed variables are unitless.



Figure 5. Global-mean vertical Differences in global-mean profiles of corrections that need to be applied between mocsy and CO2SYS for each of the three ocean-model approximations: (1) that density is constant (blue ρ)computed variable, (2) that potential temperature is equivalent to as in situ temperature (red *T*), Fig. 4. The large differences in *f*CO₂ and *p*CO₂ are shown as ratios (3mocsy/CO2SYS) that depth (mtop right) is equivalent to pressure (dbar) (green *Z*). Associated errors are equal but opposite in sign to each correction.



Figure 6. Relative changes in global-mean profiles that would result by avoiding each of the three ocean-model approximations: (1) that density is constant (blue ρ), (2) that potential temperature is equivalent to in situ temperature (red *T*), and (3) that depth (m) is equivalent to pressure (dbar) (green *Z*). Also shown is the sum of all three effects (black). Associated errors are equal but opposite in sign to the changes shown.



Figure 7. Absolute changes in global-mean profiles of computed variables when each of the three ocean-model approximations is avoided, with line colors and patterns as in in Fig. 6.



Figure 8. Zonal mean of changes Changes in zonal means of computed variables after due to replacing best-practice recommendations with two newer other options: (1) the Lee et al. (2010) formulation for the total boron-to-salinity ratio (blue B), (2) the Millero (2010) formulations for K_1 and K_2 (red, K_1K_2), and (3) the Dickson and Riley (1979) formulation for K_E (green K_E). Differences Absolute differences are shown relative to (1) Lee et al. (2010) and Uppström (1974), (2) Lueker et al. (2000), and (3) Perez and Fraga (1987). Also indicated is the sum of the first two changes (black).



Figure 9. <u>Changes Absolute changes in global-mean vertical profiles of computed variables after</u> <u>due to replacing best-practice recommendations with the same two three</u> options <u>as detailed</u> <u>mentioned</u> in Fig. 8.



Figure 10. Zonal mean Absolute changes in zonal means of computed variables due to alkalinity contributions from phosphate (blue solid), silicate (red dashed), and their sum (black dotted) relative to the case where nutrient alkalinity from phosphoric and silicic acids is neglected (practical alkalinity).

Discussion Paper



Figure 11. <u>Global-mean profiles of the Absolute</u> changes in <u>global-mean profiles of</u> computed variables attributable to nutrient alkalinity, i.e., for the same components shown in Fig. 10.



Figure 12. Changes in the aragonite saturation horizon (ASH) due to (top) using the new formulation of total boron (Lee et al. minus Uppström), (middle) accounting for nutrient alkalinity (total minus practical alkalinity relative to the common simplification where it is neglected), and (bottom) summing both corrections. Changes in ASH (m) are smoothed over 5° bands of latitude and shown for as zonal means over the Atlantic, Pacific, and Indian Oceans. The peaks at 30° S and 12° S in the Atlantic are caused by subtle shifts in horizontal gradients of Ω_A .