Biogeosciences

Open Access

Discussions

EG

Interactive comment on "Comparison of seven packages that compute ocean carbonate chemistry" *by* J. C. Orr et al.

J. C. Orr et al.

james.orr@lsce.ipsl.fr

Response to Referee, Prof. Andrew Dickson

We thank Prof. Dickson for his insightful review. His comments are repeated below in gray, and our response follows in black.

As the authors point out, there is a significant interest in correctly performing the various equilibrium calculations that allow one to link the composition of a seawater system (with respect to the concentrations of all the various acid-base species that are present in the seawater) to the more limited number of composition variables that can be measured by some form of chemical analysis. Furthermore, such calculations (and

more particularly the work required to ensure appropriate input data) are of sufficient complexity that many researchers are happy to use a publically available program, rather than develop one for themselves. The question thus arises: are such programs equally "correct"?

For independent implementations of such calculations to be equivalent, a number of aspects need to be identical: first, the set of species that is considered needs to be the same in the two implementations; second the numerical values of every one of the various equilibrium constants required (usually calculated as functions of salinity, temperature, and pressure) need to be identical over the whole range of salinity, temperature, pressure, being considered; and third, the values for each of the remaining analytical parameters that are themselves inferred from salinity (e.g. total sulfate, total fluoride, total boron, . . .) need to be identical over the whole range of salinity being considered. If these are indeed identical, and if the floating-point arithmetic (e.g., IEEE-754) is implemented appropriately, then it is hard to believe that any noticeable discrepancy need exist. Nevertheless, as the authors point out, discrepancies do exist, even to this day.

The reasons for these discrepancies are often not clear; in this manuscript the authors have – perhaps – done their best to identify likely causes. (In many cases as they have not had access to the original computer code, they infer likely errors rather than confirm them.) The principal difficulty seems to derive from the historical complexity of representing acid-base reactions in seawater media, involving as it does 4 alternate "pH scales" that can be inter-related with varying degrees of sophistication; as well as differing approaches that have been used to extrapolate data for equilibrium constants measured at 1 atm total pressure to higher pressures appropriate to the deep ocean. Thus the key reason for most observed discrepancies – put plainly – is probably that the different independent implementations are ultimately using somewhat different

values for the equilibrium constants. The reasons for this vary: on occasion they are a consequence of the proliferation of detectable misprints in the original literature (see e.g., detailed discussions by Lewis Wallace, 1998); on other occasions they probably reflect errors in introducing pressure corrections to the equilibrium constants, possibly confounded by the difficulties in choosing a pressure-dependent approach to convert constants from one pH scale to another.

If we are to avoid this in the future, then the community needs access to a clear statement of the chemical model (i.e., indicating all the various species that are being considered) together with their equilibrium relationships; it also needs to agree on an unambiguous statement of the values of the various equilibrium constants (and any salinity-dependent total concentrations) as straightforward functions of salinity, temperature, and pressure. It would then be practical for separate groups to implement subsets of the calculations in a consistent fashion and that are optimized for their aims. It should also be possible to agree on a formal structure for converting between pH scales that would itself be internally consistent. Of course, at present it should be recognized that any agreement as to the "best" values for any of these equilibrium constants (and salinity-dependent total concentrations) is likely to be far more subjective than objective in its basis and open to future change. This is also, of course, equally true for the "pressure corrections" that are used to adjust 1 atm values to higher pressures.

Nevertheless, such a consistency even if achieved would not be sufficient. It is essential to recognize that such a model has inherent uncertainties. These take two forms: first, the model itself may be incomplete – that is there may be other acid-base systems present in the seawater that have been neglected; second, all the various "data" for equilibrium constants and for salinity-dependent total concentrations are necessarily based on experimental measurements and thus are necessarily uncertain.

There is a clear need for these various uncertainties to be estimated appropriately and then to be propagated into future such calculations. Indeed, ultimately once such uncertainties are well established, it should provide a clearer rationale for the choice of "recommended" equilibrium constants (those with well-understood, and ideally small, uncertainties).

COMMENTS ON THIS MANUSCRIPT

So, though this manuscript certainly does not solve the current problems in a clear way, it does do a good job of outlining the present state of the art in the various computer codes that are widely available. In particular it makes clear that the various codes are not equivalent, and that none of them is complete – offering all likely calculations for all likely input data combinations.

While this is true, we think that on a practical level most of packages satisfy most of the users needs. One important feature, error propagation, is not offered by any package, but we hope that is remedied soon.

The ad hoc approach they have taken: comparing results to those obtained using the MATLAB version of CO2SYS, is reasonable and justified in section 2.1. However, it does leave open the possibility that that code is itself imperfect, and that its imperfections have been adopted (possibly unknowingly) by other codes with which it agrees. Another difficulty they have is in distinguishing between the existence of small (but real) errors, and problems with comparing floating point answers, particularly when the number of significant figures is limited (e.g., CO2calc). They are fairly honest about this (though perhaps do not recognize all the places it could have happened) and have, I believe, addressed the difficulty conscientiously. In a number of cases, they

Our ad hoc choice of CO2SYS-Matlab as the reference does certainly leave open the possibility that it may still have errors. We will emphasize that more in the revised manuscript. We will also be more thorough in addressing places where lack of significant figures in package output limits the comparison. In addition, when assigning causes in cases where we do not have the source code, we will rephrase text to emphasize that our assigned causes for differences are those that appear to us as the most plausible. Our sensitivity tests in another package for which we have source code do indicate that our invoked causes are highly likely, although one can never be certain in such cases.

The reason for comparing packages with the GLODAP data was to provide a global, three-dimensional reference for readers. We think most readers would have a difficult time trying to estimate differences in a particular region, say the Southern Ocean, merely by looking at the other plots where S, T, and p are varied individually. In any case, we would agree that the text on the GLODAP based comparison was probably too brief. We will revamp this section in the revised manuscript, and may include surface maps and zonal-mean sections (latitude vs. depth) to better orient readers in Latitude-Longitude-Depth space.

C4414

As pointed out in the Discussion paper and in this comment, all packages use the same approach to make pressure adjustments to the equilibrium constants. When they differ, it is often attributable to errors in implementing the associated coefficients. For the revised manuscript, we plan to discuss the uncertainty in the basic approach, as also brought up by others in a short comment on this manuscript. The Referee's fine idea to compare K_1/K_2 on the different pH scales for the Millero constants will be adopted in the revised manuscript.

C4415

of the composition of the solution, and thus it would be clearer to indicate that in the Table legend. (I shall reconsider my earliest work in the light of the comments here – may need to pull my PhD back out) – but wonder if the apparent differences are not (at least in part) due to my decision in 1978 to use carbonate alkalinity directly, rather than total alkalinity. The sensitivity factors with respect to calculations involving AT are bound to be different, and also to change with the exact conditions being considered – as noted above.)

Just to avoid confusion, our sensitivity analyses (e.g., tests using slightly modified formulations of the constants) are not linked to the sensitivities (partial derivatives) in Table 9. It is an important point that sensitivities are a function of the solution composition, which we failed to mention in the Discussion paper but which will be rectified in the revised manuscript (Table 9). In the revised manuscript, we will also mention that Dickson and Riley (1978) used A_C whereas we used A_T. Furthermore, we will test how results differ when switching between the two.

CONCLUSIONS

The authors should be encouraged to submit a revised version of this manuscript for publication in Biogeosciences; it is a valuable statement of the current state-of-the art for these calculations. Nevertheless, I feel the authors should be encouraged to elaborate further on my key points from my introduction. That is to try to answer the question: "How do we move forward from here?" (I repeat my opinions below.)

1. First, the marine CO_2 community is in dire need of a clear and unambiguous statement of what might comprise a correct calculation model; ideally this would be based on a particular numerical implementation of an agreed set of constants including appropriate pressure corrections (and perhaps even pH scale adjust-

ments). Ideally this statement would also include estimates of the standard uncertainty for each of the parameters contained in the model. Of course, if "better" constants were to come along in the future, they could be slotted in relatively straightforwardly.

2. There is also an urgent need for a computational tool that takes such a model and implements error propagation appropriately, i.e. including the uncertainties in all of the parameters that contribute to the calculation of a particular value. A variety of other more focused computational tools could also be based on such a model statement.

3. These separate computational tools could, of course, be optimized individually for particular purposes but must be shown to be correct. It would be valuable if the authors were to provide their opinions on how this might be done reliably.

We consider that the best-practice guides already provide a starting point for a working conceptual model, including a recommended set of equilibrium constants. Despite recommendations though, marine chemists tend to use various sets of constants, particularly for the critical K_1 and K_2. It is this more formidable diversity in constants rather than diversity in packages that is responsible for the largest differences in computed carbonate system variables One reason for the diversity may be lack of communication. For instance, why are the K_1 and K_2 from Dickson and Millero (1987) still used widely when the first author recommends to use another set. Is it that the reasons are not known widely, having never been published? Another reason may be that no set of K_1 and K_2 appears clearly superior to the others while at the same time applicable at all input conditions. Although Millero (2010) uses more recent measurements of K_1 and K_2 than any other study and fits those across the widest range of temperature and salinity to date, there remain issues about the lack of data available for low salinities and about the fits themselves.

In any case, there are still too few measurements of K_1 and K_2 at low salinities, low temperatures, and high pressures. And the critical laboratory data from which these constants are computed as well as the resulting constants themselves need to be made available publicly before they are lost, e.g., as senior marine chemists retire. If made available, those data will continue to be useful to verify and perhaps improve previous fits, to provide robust error estimates, and to combine with newer data.

Despite these gaps, it seems that by stipulating the constants recommended for best practices one could already put forward a tentative calculation model, applicable over most of the open ocean. The best-practices guide already also makes recommendations for the salinity-dependent total concentrations. It only leaves out pressure adjustments and error propagation. For the pressure adjustments, all public packages use the same approach (Millero, 1995). Minor inconsistencies and likely fixes were identified in our Discussion paper and could be eliminated with little effort. Although other approaches could be used to make pressure adjustments, few would probably subscribe to using them unless they were shown to be better. Furthermore they would require new coding in every package, opening the door to more sources of disagreement that would take time to track down and resolve. The calculation model should thus go with the Millero (1995) formulation.

As for error propagation, no public package currently offers such a feature. However, there are high hopes that the Ocean Acidification International Coordination Centre (OA-ICC) will launch a recently proposed effort to include error propagation in the different packages, assuming developers are interested. Numerically, all parts of this calculation model except error propagation are already implemented in the different public packages. Having already studied the available source codes, implementations appear generally similar. With little additional effort, we think that minor modifications to some of the packages would allow agreement within numerical round-off error

using a best-practices' calculation model. A streamlined code of the calculation model could also be provided with guidelines and check values to assure that other implementations would produce the same results. We are now considering adding a discussion on these points in the revised manuscript.

Assessment of the robustness of numerical approaches and the consistency of packages is tentatively planned as part of a new OA-ICC effort to develop and share a common code for error propagation. Likewise, the OA-ICC may also launch a parallel effort to help compute a common suite of buffer factors in multiple packages. In the revised manuscript we plan to mention these efforts in a brief statement about future work.

References

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.

Dickson, A. G. and Riley, J. P.: The effect of analytical error on the evaluation of the components of the aquatic carbon-dioxide system, Mar. Chem., 6, 77–85, 1978.

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.

Interactive comment on Biogeosciences Discuss., 11, 5327, 2014.