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Comparison of seven packages that compute ocean carbonate chemistry

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We thank both referees for their comments, which have resulted in numerous improvements to the manuscript. We also thank the four scientists who provided short comments, which have also helped to improve the comparison. All comments are repeated below in gray, our responses follow in black, and our changes to the manuscript are indicated in blue.

Response to Referee, Prof. Andrew Dickson

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 try to explicitly link discrepancies in computed values to inferred discrepancies in the various data that are enshrined in the various codes; to the extent these discrepancies cannot be directly identified (due to lack of access to the internal code) the reasons for such discrepancies, though plausible, may not be proven.

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.

In section 2.1 of the revised manuscript we further detail our rationale for choosing the CO2SYS-Matlab as our reference. In the same section we added a final sentence emphasing that this arbitrarily chosen reference may of course still have errors. We have also rephrased text where we assign causes, when we don’t have source code. We consider these related conclusions to be very likely, not merely plausible, but of course in science virtually nothing is ever perfectly certain.

I did wonder at the added value of using the GLODAP data as an exercise strategy for comparing the codes over a range of conditions; it certainly makes clear those codes that are slow, but does not seem to have added much more than a carefully structured examination of the S, T, p space might have done.

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.

We have modified the subsection regarding the GLODAP-based comparison (section 3.1) to include more on the comparison of out-dated versions, in particular versions that had significant discrepancies in the the Discussion paper but have been updated. The final paragraph mentions why the GLODAP-based comparison is of interest, namely to "assess how discrepancies among packages vary spatially across the global ocean."

The discussion of difficulties with making "correct" pressure adjustments to the various equilibrium constants is salutary. It points out how much this area depends on a single paper by Frank Millero in 1995, and on Ernie Lewis's interpretation of how to implement them in his version of CO2SYS, as well as his extensive work on tracking down typographic errors (see Appendix in Lewis Wallace, 1998). It is certainly a good thing that the authors include the various coefficients used in these adjustments in their Table 7, so others have them all in one place, however it might be a good time to revisit this and to assess the likely uncertainty resulting from such adjustments. It was interesting to note that the authors choose to present data for a "new" set of K1 and K2 in Table 10, noting that the published values for these coefficients and the values in a spreadsheet of Prof. Millero differ. I would point out that if the authors wish to assess whether or not the values published for the total hydrogen ion scale are equivalent to those for an alternate pH scale, the best approach is to look at the ratio K1/K2 which should remain independent of the choice of pH scale. If this is not true, there is certainly a problem ...

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.

In the revised manuscript, we have added a paragraph at the end of section 2.7 to emphasize that although all packages use the same approach to make pressure adjustments to the equilibrium constants, there are substantial uncertainties on the order of at least several percent for some constants. Secondly, we have closely followed the Referee's advice and now include a plot of K_1/K_2 for the values of those constants (Fig. 16) calculated with the same Millero (2010) formulation but with 4 sets of coefficients (SWS and Total scale as given in the publication and the different sets given in the corresponding spreadsheet). None give the same ratio. Relative differences reach up to 1.5%.

It was interesting to see how the authors used sensitivity analyses to better discriminate between alternate hypotheses as to the likely sources of errors. I would like to point out, however, that the sensitivity coefficients in Table 9 are themselves function 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.

In the revised manuscript, we have added footnotes to Table 9 to indicate the results are sensitive to solution composition. We have also added 3 sentences to Section 4.1 to mention that differences in the two approaches, namely our use of A_T as opposed to the use of A_C by Dickson and Riley (1978), may partly explain the discrepancies.

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 adjustments). 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.

We have modified the Conclusions to bring up, as concisely as possible, some of the critical points mentioned above.

Response to Referee, Dr. Jón Ólafsson

The Referee's comments are repeated below in gray; our response follows in black.

A bit over two decades ago there was no publicly available software for the calculation of sea water carbon chemistry parameters. A few gurus had developed their own programmes. There was also lively debate on the reliability of the different literature sources for the carbonic acid dissociation constants. The choice of analytical methods for sea water carbonate chemistry and best analytical practices were a matter of different groups or schools. The situation is very different now due to efforts generated within the oceanographic community and for individual or team efforts that have provided invaluable service to this community.

In 1998 Lewis and Wallace made publicly available the CO2SYS software for carbonate chemistry. It provided several options for input and output choices of conditions and of thermodynamic parameters. CO2SYS was thoroughly documented. Currently there are six additional publicly available packages for the computation sea water carbonate chemistry. The paper under review here is important for the chemical oceanographic community and anyone who studies the sea water changes that are driven by anthropogenic releases of carbon dioxide. The sea water carbonate computation packages have applications in global models on mainframe computers, on personal computers and who knows, the youth you see busy with an iPhone may be checking on aspects of future ocean acidification.

This is a timely contribution. The comparability of the computation packages has been an open and important question in discussions on different data evaluations. Another application of the software packages is in chemical oceanography education and training. In this paper the basis for the comparison tests is clearly described and the different results of the comparisons are also clearly presented. The authors explain the comparison results and outline where there is safe ground to tread. They also give attention to recently emerging issues, such as that of boron alkalinity and to the long standing questions on the carbonate system in low salinity waters. There the authors have devoted a thorough effort to explain observed differences between the software packages when applied to the low salinity range. Finally the authors provide several recommendations for software developers and users. No doubt, this work will also lead to improved versions of the currently available carbonate computation packages.

Conclusion

This reviewer is a user of sea water carbon chemistry software who finds this work an admirable service to the community and welcomes its publication in Biogeosciences.

We thank Dr. Ólafsson for this review of our manuscript and for providing his view about its value to the community. His historical perspective should be read by young scientists in the field, who may not realize the recent improvements from which they benefit today.

The comments from this Referee have all been complimentary and have not required any changes in the revised manuscript.

Response to Short Comment by Dr. Jean-Pierre Gattuso

Orr et al. (2014) identified bugs in the R package seacarb, which had very little effect on computed results when used with the best practices constants (Dickson et al., 2007), and highlighted very long processing time on big data files. Version 3.0 has just been released and can be downloaded from CRAN. The package has been modified to fix the minor bugs and optimize the code, leading to a dramatic increase in speed (35x to 50x faster). See the change log for more details. Note that there remains an issue with the formulations of the two dissociation constants of carbonic acid, K_1 and K_2, from Millero et al. (2010). This issue should be resolved soon and seacarb updated accordingly. In the meantime, it is suggested to refrain from using this formulation in seacarb.

As always, any bug report and suggestions are welcome (gattuso(at)obs-vlfr.fr).

Change log, version 3.0, 2014-03-06

1. Major update led by Jean-Marie Epitalon, who has become a coauthor of the package.
2. Speed optimisation of the computation of dissociation constants by (1) using vectors rather than loops and (2) passing optional parameters. The increase in speed is up to 35x.

3. Computation of dissociation constants:
   - One or two pHScale conversion factor(s) are passed as optional parameter(s) to speed-up computation: (i) kSWS2scale to convert from the seawater scale (SWS) to the pH scale selected at the hydrostatic pressure value indicated and (ii) ktotal2SWS_P0 to convert from the total scale to the SWS at an hydrostatic pressure of 0. These conversion factors are calculated using function kconv() if they are not given.
   - Computations are vectorized rather than using loops.
   - Warning messages for out-of-validity-domain: only one message per constant (instead of one per data entry).
4. Pressure correction function Pcorrect:
   - Two pHScale conversion factors are passed as optional parameters to speed-up computation: (i) kconv2Scale to convert from the pH scale selected to the SWS (or free for Kf) scale at the hydrostatic pressure value

We thank Dr. Gattuso for this notification of improvemnts to the seacarb package, notably its dramatic acceleration, and hope along with him for resolution of the discrepencies between Millero's (2010) different sets of coefficients for K_1 and K_2. In the revised manuscript, we will update the text and figures with results from the latest version of seacarb.

This short comment is informative, but has not required any changes in the manuscript.

Response to Short Comment by Dr. Ernie Lewis and Dr. Douglas Wallace

We read with interest the manuscript comparing the various packages that calculate parameters of the CO2 system in seawater and would like to commend the authors for their authoritative comparison of these programs. We found the review insightful, balanced, and informative, and were amused to see that conversions among pH scales and pressure corrections remain a source of mystery, error, and ambiguity, as they have for the last 20-odd years. We have one minor comment on the manuscript: that the programming language for the original

CO2SYS be listed as QBasic rather than DOS (which is the operating system under which the program runs); this would make description of the original CO2SYS more parallel to other versions for which languages such as C, Fortran, Excel, etc. are listed.

We will improve the description of CO2SYS in the revised manuscript, mentioning that it is written in QBasic, not DOS. Thank you for this catching this glitch.

Done.

As authors of the original version of CO2SYS, upon which most of the other programs were based, we thought that some historical perspective might be of interest. We also highlight some lesser known features of the project that we consider to be of continued utility. The version of CO2SYS used in the manuscript by Orr et al. as the standard for comparison is the MATLAB version. It is one of the versions that took the original CO2SYS code written and made available by us and translated by others into Excel or MATLAB (the manuscript mentions that there are four versions of CO2SYS). Neither of us were actively involved in translating CO2SYS into other languages, although we worked with others in some instances to fix errors in those versions. It is worth noting that the original CO2SYS, and earlier programs from which it evolved, were based on DOE (1994), Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water, version 2, eds. A. G. Dickson and C. Goyet, ORNL/CDIAC-74, and a later version of this handbook, under Andrew Dickson's oversight, remains the ultimate standard of ”best practices” for this topic.

This comment raises an important point about the lineage of the translations of CO2SYS into Excel and Matlab, which will do our best to relay in the revised manuscript. We will also state that CO2SYS was based on Dickson and Goyet (1994).

Done.

The original CO2SYS is still widely used, and to this day we receive several emails each month with questions or comments on it. It has held up to the test of time very well, and to the best of our knowledge it is error-free (the one item we would change is to allow more spaces for outputs; for instance, a value for fCO2 of 12,345.6 μatm would be written ”%12345.6” with the ”%” denoting that an insufficient number of spaces were allowed to print the output). Although it is perhaps a bit dated at this point—there are more recent sets of constants that are not included, and it is difficult to run on current operating systems (although we are able to run it on the 64-bit version of Windows 7 and on Mac OS-X using DOSBox)—the original version has some useful features that we think should be included in any similar, follow-on program.

The online help feature in the original CO2SYS, albeit perhaps a bit crude by today’s standards, explains the program, describes the various options, and lists references for the constants used in the program. There is also an accompanying report (available at http://cdiac.ornl.gov/oceans/co2rprt.html) that describes the program and provides a list of typographic errors in the relevant literatures (this will be discussed further below). The list of options in CO2SYS is comprehensive and covers most if not all of what would have been of any utility at the time the program was written: the choice of any two of the four CO2 system parameters (total alkalinity, total dissolved inorganic carbon, pH, and either fCO2 or pCO2); the choice of fCO2 or pCO2; the choice of either of two definitions of total alkalinity; the choice of four pH scales; the choice of eight sets of CO2 dissociation constants (including a freshwater choice and the GEOSECS choice, which would now be of historical interest only); the choice of two constants for dissociation of sulfate; and the choice of both input and output temperature and pressure (which readily allows for conversion between in situ and standard reporting conditions). The original CO2SYS also runs in single-input mode or batch mode (with either tab-separated or comma-separated inputs).

The CO2SYS report (Lewis and Wallace, 1998) proved valuable for our comparison and was cited heavily in the Discussion paper. We used CO2SYS’s batch mode for our comparison of

CO2SYS with its translations into Excel and Matlab.

Other features of CO2SYS that would (in our opinion) be useful for any similar program today involve the quantities calculated. The following quantities are reported in CO2SYS at both input and output conditions (i.e., temperature and pressure): the other two CO2 system parameters; contributions to the alkalinity from various species; speciation of CO2 (i.e., dissolved CO2, carbonate, and bicarbonate); fCO2, pCO2, and xCO2 (the latter in dry air at 1 atm); saturation of both calcite and aragonite; the Revelle factor; the value of pH on all four pH scales; and the values of the first and second dissociation constants of CO2 (K1 and K2), and of the dissociation constants for borate and the hydroxyl ion (KB and KW) on all four pH scales. Additionally, the program in single input mode calculates and lists the sensitivities of the two calculated CO2 system parameters to uncertainties in the two input parameters; salinity; both input and output conditions (i.e., temperature and pressure); and K1, K2, and the solubility of CO2 in seawater (K0). We feel that this last feature, what we call ”partials,” is one of the most useful attributes of the program for teaching purposes and is especially important, as it readily illustrates how accurately the calculated quantities can be determined.

It is a valuable feature to be able to compute calculated variables both at input and output temperatures, and it remains a feature that is only offered by CO2SYS and its derivatives. The partials feature offered by the original CO2SYS program has unfortunately been lost in the CO2SYS derivatives. Those calculations will be critical to recover for those who wish to do error propagation or compute a range of buffer factors.

The original CO2SYS is a combination of earlier programs CO2SYSTM.EXE, FCO2TCO2.EXE, PHTCO2.EXE, and CO2BTCH.EXE that were released in May, 1995 (this was back in the days when program names were limited to eight characters, with a limit of three characters for the extension). To the best of our knowledge, no serious errors have been found in these programs (the fits listed for the dissociation constants are not valid for extrapolation to salinity 0, but as the programs were designed for the oceanic CO2 system, this wasn't an issue). CO2SYSTM (for which there were versions 1.00, 1.01, and 1.02) calculated any two of the four CO2 system parameters from the other two, allowed for a choice of four sets of CO2 dissociation constants, and included sensitivity of the outputs to the two CO2 input system parameters, temperature and salinity, and K0, K1, and K2; speciation of CO2 (i.e., dissolved, bicarbonate, and carbonate); and contributions to the alkalinity at both input and output conditions. However, all inputs and outputs were on the total pH scale using Dickson's value for the dissociation constant of sulfate. FCO2TCO2.EXE and PHTCO2.EXE were similar, but the former is for fCO2 or pCO2 and the latter is for pH. Both use total dissolved inorganic carbon and either pH or fCO2 (or pCO2) as inputs and allow choice of carbonate constants, fCO2 or pCO2 as the desired variable, and input and output temperatures. The program then calculates the other CO2 system variables at both input and output temperatures and sensitivities of these variables to input temperature.

Thank you for this historical perspective. We may well add some of it to the description of CO2SYS in the revised manuscript.

The revised manuscript does a better job of representing the origins of the original CO2SYS program. Fortunately, all the details above are available to the interested reader on the Interactive Discussion page our our Discussion Paper.

Program CO2SYS.EXE replaced and extended the above four programs. At the time, there were no publicly available programs to perform these types of calculations, and the few in-house programs had no conformity on pH scales, CO2 dissociation constants, etc. Version 0.00 (February, 1997) was preliminary and the pressure corrections to the carbonate solubilities were incorrect. Version 1.02 (March, 1997) contained incorrect pressure corrections to the pH scale conversions (although this has only a minor effect on outputs in most cases). Version 1.03 (May, 1997) is believed to be correct. Version 1.04 (May, 1997) and Version 1.05 (October, 1997) differ from Version 1.03 only cosmetically (typos corrected, more efficient codes, etc.), and no differences exist between calculations performed using these versions and Version 1.03.

The original CO2SYS was written in QBasic, which we chose because it ran on any 80x86 computer with the DOS operating system by typing the program name on the command line. We intended that the program could be used for decades: in our infinite wisdom, despite the advent of early versions of Windows, we felt that DOS would be the operating system of the future and we placed our bets on this. In our defense, it was probably the best choice at the time: an executable file could be created and distributed and it would run on any DOS-based computer without the necessity to install anything else (the same cannot be said for MATLAB or other programs, which require more than merely an executable to run). The program did not run on Macs, although they were not as common back then. Computers were very different back then, in ways that are probably difficult for younger programmers to understand. CO2SYS had to be broken into two parts and compiled separately, then combined. Lest this give the impression that it was a large program, consider the following text from the program: "PROGRAMMER'S NOTE: This program is DANGEROUSLY close to the DOS-imposed 64K limit : : : Don't make any unnecessary changes or the limit will be exceeded."

Predicting the future is dangerous, especially when its about computers. The fact that CO2SYS still runs today is an accomplishment.

As stated above, there was a large section in the CO2SYS report on typographic errors in the literature. One common feature in oceanographic papers not seen in other fields is the use of check values for expressions for dissociation constants and other quantities; i.e., the value of the expression at a specified set of conditions (salinity, temperature, pressure). These check values are of immense help in determining if coefficients are listed correctly in the manuscript and if they are incorporated correctly in computer codes. Errors in listed coefficients on if their transcription can cost hours of time, in addition to leading to incorrect values. Thus, a compilation of such errors would be very useful for the community. We had compiled such a list while writing CO2SYS, which we were originally hesitant about presenting publicly, for several obvious reasons. However, Rik Wanninkhof convinced us that making this list available would be a service to the community, and we think that it has been. Considering how often such typographic errors continue to appear in the literature, we recommend that the outdated version on the CDIAC website (http://cdiac.ornl.gov/oceans/co2rprt.htmltypos) be updated and made available. Perhaps this manuscript will prompt those who have updated CO2SYS or similar programs by including more recent constants will make those available and someone will come forward to collate and publish them.

The list of typographical errors provided in Lewis and Wallace (1998) has been a great service to the community. We used that for this comparison and when developing individual packages (seacarb and mocsy). Updating that list should be a high priority for the field.

We thank Drs. Lewis and Wallace for this historical perspective, which we hope package developers can take advantage of to make improvements in the future.

The revised manuscript has been improved because of these comments.

Response to Short Comment by Dr. Lisa Robbins

Orr et al. have done an admirable and thorough job comparing calculation packages for carbon, which is a real service for the community of users. They have set forward useful recommendations for developers that should provide enhanced reproducibility for users.

We thank Dr. Robbins for sharing her view on the utility of this study.

With respect to CO2calc, we have a few comments and edits for the manuscript: At line 24-25, the authors note that: “Our early findings led developers to update two of those packages, seacarb and CO2calc” it is unclear to the reader whether the analysis presented here reflects those updates, which for CO2calc, does not. The particular problems that were revealed relate to a coding error specific to the Lueker calculation. This error was immediately corrected and the updated version of CO2calc (1.2.9 and later) can be found at http://pubs.usgs.gov/of/2010/1280/. This is the primary link for CO2calc and should be reflected in the manuscript.

In the revised manuscript, we will make it clearer that the text and figures reflect the most recent results from CO2calc as well as the other packages. The only exception will be the figure where we show results from older versions, some of which deviate significantly. The revised manuscript will also provide the URL mentioned above as the reference for CO2calc.

The revised manuscript is crystal clear mentioning that the old version of CO2calc is only shown in one figure. Elsewhere we only discuss results from the current (updated) version.

In Table 11, the pK1, pK2 and pKB values are incorrect for CO2calc. The actual pK1 and pK2 values for the Table 11 should be: 5.84715289, 8.96595149, and 8.59697, respectively. We believe these discrepancies stem from the fact that the authors calculated the various equilibrium constants based on output data rather than with the source code (although the source code has always been available on request). Because the output values do not have enough significant figures to back calculate the K values, the resulting values provided in Table 11 erroneously produced an artifact of high variability for pH (the increased variability about the mean noted by the authors in section 3.2.3) and many of the other parameters, as illustrated in the figures. The precision for pH output in CO2calc is limited to 3 decimal places for pH, and does not reflect the internal calculations that use pH in the CO2calc calculations. However, this finding does suggest that, for users that are likely to use CO2calc pH output in future calculations, CO2calc output for pH should be increased to 6 decimal places. We also found that a short-hand description of the Mojica Prieto and Millero (2002) constants in CO2calc lacked information, and therefore, will be adding the correct reference for these constants.

In the submitted manuscript, we did point out the same probable cause of the variability for CO2calc's pK_1 and pK_2. It is nice to have that confirmed by the CO2calc developers. We are still considering how to change Table 11. For consistency, we wish to provide only the results from our analysis, not from what any of the developers has come up with on the side. This problem could be resolved though if the CO2calc developers would provide a new public version with more significant figures in some of their output variables, including pH. Even better would be a new version where values of the equilibrium constants were also made available to the user. Of course, any other improvements, such as that mentioned concerning documentation would be welcomed, even if not critical to our analysis.

Although we have included in the revised manuscript the latest version of CO2calc (1.3.0) made available after our Discussion mansuscript was published, its output comes with the same number of significant figures as the former version. Hence we were unable to provide more precision for the constants that we computed from the CO2calc computed variables. This is mentioned clearly in the revised manuscript.

We will stand by our usage of the Millero (2010) calculations using the K2 as provided by Millero until a resolution is determined.

Given the discrepancies identified by our Discussion paper, it seems that if a user would choose to employ the Millero (2010) K_1 and K_2 constants, the best bet would be to calculate them with the unpublished set of coefficients that Millero provided personally to CO2calc developers. However, the discrepancies between the results when using different sets of coefficients are large. Until Dr. Millero himself addresses this issue, we consider it premature to use the Millero (2010) constants with any set of coefficients. We think that even some of the unpublished sets may lack sufficient precision, as pointed out in the manuscript.

We recommend even more clearly in the revised manuscript that it is not yet time to use the Millero (2010) constants as they give inconsistent results with the different sets of coefficients.

We suggest that editing the plots will make the paper more “readable”, using unique colors and/ or symbols to represent the programs. Also use consistent symbols representing the programs between the figures. Without zooming into the plots, the symbol and color for some programs were easily mistaken for another. One small typo is noted at the top of the Figure 5: “Salinity” is misspelled. Otherwise the manuscript is very well written.

In the revised manuscript, we will strive to make the plots clearer. The above-mentioned spelling error will be corrected. Many thanks for these comments and the advice.

In the revised manuscript we have tried to make the plots as clear as possible, given the necessarily small size of many subplots with multiple packages on each that must be compared. Perhaps the complaint about readability derives from potential confusion of casual readers between line signatures for swco2 and CO2calc, the latter being the package developed by the author of this short comment. In our defense, we do use different line signatures and different colors for each, and we find that it is not difficult to distinguish them. The colors we use were carefully chosen as a set that is supposed to be distinguishable even by color-blind readers. We think that the only problem might be for a casual reader who only glances at some figures and does not read the text. But even there, one only needs to zoom in on one of the plots to get the story straight. The online nature of Biogeosciences seems well suited for this trivial operation. We have also corrected the spelling error.

Response to Short Comment by Dr. Richard Zeebe

Errors and typos in numerical routines that lead to differences in CO2 system calculations should of course be rigorously eliminated. Ideally, numerical routines using the same equations should agree within round-off error. Actual fundamental / systematic differences between packages may be eliminated in the future by agreeing on a common approach.

For the most part, the packages that we compared in the Discussion paper did follow the same approach, as outlined in the guide for best practices (Dickson et al., 2007). Although that guide did not specify how to perform pressure adjustments of equilibrium constants, packages still followed the same basic approach. They usually differed due to slight variations or errors in implementations.

In the revised manuscript, all packages follow the same approach. As a result of our Discussion paper, the csys package (of which Dr. Zeebe is an author) was revised largely to give more comparable results to the reference (CO2SYS).

However, the practical user may be more interested in evaluating the package comparison in light of realistic measurement uncertainties. For example, Dickson (2010) provides the following estimated uncertainties for a single measurement on a sample of surface seawater:
TA: 2-3 umol/kg
DIC: 2-3 umol/kg
pH: 0.005
pCO2: 2 uatm

This applies to state-of-the-art methods using reference materials and: “... performed by an experienced laboratory with well-trained analysts, and with a good quality assurance program in place.” In fact, all differences between relevant surface variables from the various packages shown in Orr’s Figs. 2, 3, 5, 6*, 7, 8, 9, 10, and 11 are smaller than the measurement uncertainties cited above. This even includes ”pCO2” from csys (which is actually fCO2 and agrees with CO2SYS’ fCO2 to within $\sim$0.1 uatm, see below). *One exception is Fig. 6 for salinities $<$ 10, where K1 and K2 from Lueker et al. (2000) cannot be applied. Note that Dickson’s (2010) Table 1.5 referred to in Orr’s manuscript gives uncertainties for *Reference Materials* distributed by Dickson’s laboratory. These are *not* uncertainties for typical measurements performed in the user’s laboratory.

We agree. In regard to Dickson’s Table 1.5, our Discussion paper referred to the “best measurement uncertainty”, not the uncertainty for typical measurement. For numerical packages not to add substantially to total uncertainty, they should agree to within much less than the measurement uncertainty (as detailed in our section 2.3). Since we arbitrarily divided the measurement uncertainty by ten to obtain a threshold for numerical uncertainty, changing the best measurement uncertainty to the typical measurement uncertainty values given by Drs. Zeebe and Wolf-Gladrow would not substantially alter our evaluation of when differences between packages should be considered significant.

Furthermore, the errors listed above are typically considered as random errors. Those are fundamentally different than systematic errors (biases) such as those due to errors in calculation programs.

We consider that our approach is sound and have not changed it in the revised manuscript.

In summary, the presented package comparison may be put into perspective as follows. For the vast majority of users dealing with measurement uncertainties in surface samples equal to or larger than those given above, there is virtually no difference as to which carbonate chemistry package they prefer to use. The reason is that in most cases the measurement uncertainties vastly exceed differences between numerical routines.

The comment above is a fair statement for the findings of our comparison when packages used the set of constants recommended for best practices (Dickson et al., 2007). However, with K_1 and K_2 from Millero (2010), packages disagreed by much more than the numbers given above. Furthermore, we are not convinced that all users would be happy to use a package that was known to give a biased answer even if that bias was less than the random errors listed above.

In any case, the purpose of this comparison was to compare packages quantitatively and to report the results. Because of our Discussion paper, the community now knows that the packages, when used with the best-practice constants, do agree closely enough to be used interchangeably for most studies. Yet even small differences among packages (e.g., when all of them use K_1 and K_2 from Lueker et al., 2000) seem to be of interest to some marine chemists as well as to package developers, three of which have responded with updated versions.

In the revised manuscript, the five packages were updated as a result of differences that we identified in the Discussion paper are compared. Differences among packages have been reduced even more. They are now entirely negligible at the surface and even for low-temperature deep waters.

(2) pCO2 from csys

The reader should note that the ”pCO2” from csys as plotted in Orr’s manuscript (Figs 2, 3, 5, 6, 8) is actually fCO2 (fugacity), rather than pCO2. At the time when we (Wolf-Gladrow and Zeebe) started csys (prior to 1993) and later provided csys as a supplement to our book (Zeebe and Wolf-Gladrow, 2001), we never imagined that csys would be used for the purpose of sub-uatm calculations/inter-comparisons. In that case (which applies to Orr’s comparison), one needs to take into account the difference between fCO2 and pCO2, which is about 1 uatm at typical surface ocean conditions (Zeebe and Wolf-Gladrow, 2001, Chapter 1.4). In fact, csys’ surface fCO2 agrees with CO2SYS within 0.1 uatm or so.

We state clearly in the Discussion paper that the $p\mathrm{CO}_2$ variable in csys was actually $f\mathrm{CO}_2$, a statement for which we are later criticized for by Dr. Zeebe. That finding was never published previously as far as we are aware. We presume that the mislabeling of $f\mathrm{CO}_2$ as $p\mathrm{CO}_2$ in csys was unintentional. The documentation of csys did not contain any warning about when not to use the mislabeled $p\mathrm{CO}_2$ variable.

The authors were well aware of the fact that csys’ “pCO2” is actually fCO2 (see their Abstract and Conclusion section), so it remains unclear why they compare this variable to pCO2 from other programs on a sub-uatm scale. If a revised version of the ms will be invited, this should be corrected.

For the comparison in the Discussion paper, we simply compared all variables that were labeled $p\mathrm{CO}_2$ in all packages. Because that variable from csys differed slightly, we thought it might actually be $f\mathrm{CO}_2$, and we confirmed that by studying the source code and comparing it with $f\mathrm{CO}_2$ from the other packages. So yes of course, we were aware of it, as clearly stated in the Discussion paper. Should we have hidden it?

By being open about this difference, the community now knows that calculated $p\mathrm{CO}_2$ made with csys and published previously contains the same error. We are happy that the csys developers took this finding into account and have now provided a new version of csys that rectifies this confusion between $p\mathrm{CO}_2$ and $f\mathrm{CO}_2$, while providing not one but both variables as output. In the revised manuscript, we will not hide this finding, but it will be be much less apparent. It will be confined to only 1 figure that discusses how old versions of packages diverge from the reference. Elsewhere, we will show the $p\mathrm{CO}_2$ from the most recent version of csys, which has been corrected.

We thank Dr. Zeebe for remedying this confusion between $f\mathrm{CO}_2$ and $p\mathrm{CO}_2$ in the latest version of csys that we compare in the revised manuscript.

or users dealing with high-quality data/applications, csys has been updated to compute and output both fCO2 and pCO2. We have also added a user option to csys if one wishes to compare csys output to that of CO2SYS:

http://www.soest.hawaii.edu/oceanography/faculty/zeebe_files/CO2_System_in_Seawater/csys.html

Thank you for this correction and the useful addition of the option to facilitate comparison with CO2SYS.

The revised version of our manuscript uses this new csys option in all comparisons. It now compares very well with csys and the other packages.

However, note that in order to resolve measurement differences of order 1 uatm, high laboratory standards and reference materials are required (see above and below).

We think there is no reason not to correct a systematic bias in calculations if it is known, even if it is relatively small. Our Discussion paper made it known, and the cys developers corrected it.

Our revised manuscript as well as the Discussion paper focuses on the calculations, not the measurements. As pointed out there, we wish to have errors in the calculations that are much better than measurement precision and accuracy so that they do not affect errors of computed variables.

(3) The more daunting issues

A realistic error assessment of CO2 system calculations needs to consider the uncertainties associated with input variables and the fundamental constants used in the calculations. For example, pCO2 may be calculated from measured TA and DIC (a ”good” combination as opposed to e.g. calculating DIC from pH and pCO2). To estimate the error in calculated pCO2, one needs to consider (at least) errors in TA, DIC, pK1, and pK2. Assuming realistic uncertainties of +-3 umol/kg in TA and DIC and +- 0.006/+-0.011 in pK1 and pK2 (e.g. Millero et al., 2006), the uncertainty in calculated pCO2 (DpCO2) may be estimated as:

DpCO2 = sqrt(4.42 + 5.52 + 5.22 + 6.62) = 11 uatm

where the four terms of the sum are the individual squared uncertainties owing to uncertainties in TA, DIC, pK1, and pK2 at T = 25C, S = 35, P = 0, TA = 2400 umol/kg and DIC = 2080 umol/kg. This uncertainty is about 100 times larger than the difference between numerical packages (order 0.1 uatm) as discussed by Orr.

Does this propagation of uncertainty, which is intended for random errors, mean that as long as systematic errors in calculated $p\mathrm{CO}_2$ are less than 11 μatm, then packages can be used interchangeably? Does it mean that we should have never mentioned the systematic difference in $p\mathrm{CO}_2$ of more than 1 μatm from csys in the Discussion paper?

Other fundamental issues for CO2 system calculations include an apparent large effect on pK2 at rising pCO2/DIC (Millero et al., 2002) and possible inconsistencies between parameters when over-determining the system (Hoppe et al., 2010). Regrettably, no suggestions for solutions of these more daunting issues are offered by Orr. Neither are the implications of the numerical package comparison discussed on the background of the fundamental uncertainties listed here.

The focus of our Discussion paper is on discerning systematic differences between packages that compute carbonate chemistry. But that comparison did not put us in a position to resolve all other open issues. Actually, we did mention the work by Hoppe et al. (2012) in our Discussion paper (see p. 5331, lines 8–12). We pointed out that we could not contribute to resolve their dilemma of large inconsistencies between calculated and measured $p\mathrm{CO}_2$, differences that are much worse than found by studies from marine chemists.

Nor does the revised manuscript attempt to resolve these open issues for the reasons mentioned above.

(4) Pressure corrections

The significance of the discussion and the recommendations made regarding pressure corrections and scale conversions as described at length in the manuscript is difficult to comprehend (see Secs. 2.7, 3.2.1-3.2.5, 4.2.1, 4.2.3, 4.2.4, 4.2.6, and 5). The key issue here is to recall that measurements of pressure effects on acid-base equilibria in seawater are sparse and/or uncertain and that estimated values from molal volume and compressibility have substantial uncertainties. For example, the estimated P-correction for KS involves steps using HCO3- (!) as a model for HSO4-; the measured and calculated value for KS in water seem to differ by some 10% at 1000 bar (Millero, 1983). For K1 and K2, the P-corrections from Millero (1983) are based on Culberson and Pytkowicz's (1968) data (short CP68), which were obtained in artificial seawater. CP68 found a difference in the K2 P-correction of 6% relative to previous work and also found significant differences relative to a few measurements made in natural seawater. Millero's (1983) calculated P-corrections for K1 and K2 differ by up to 3% and 8% from CP68's data at 1000 bar and 2 degC. Overall, the uncertainties for the P-corrections for K1 and K2 could also be well of order 10%.

These are all good points. In the Discussion paper, our focus was on comparing results from the seven packages that all used the same approach from Millero (1995) to make pressure adjustments. None of the packages offers another approach. In the revised manuscript, although our focus will remain the same (package precision), we will also mention the accuracy issue raised above about uncertainties in making pressure adjustments to the equilibrium constants.

In section 2.7 of the revised manuscript, we have added a paragraph about the accuracy issue also emphasizing that the focus of this package comparison is on precision.

In the manuscript, Orr suggests that constants should be first converted to the seawater scale (SWS), then P-corrections be applied on the SWS, and finally constants be convert back to say, the total scale. Now the scale conversion depends on KS and KF, which are themselves P-dependent, including large uncertainties (e.g. probably more than 10% for KS). Note that as a result of pressure change, the ratio of the scale conversion at P = 0 and 1000 bar may differ by perhaps 0.4%.

Our discussion paper already states that making pressure corrections without converting to the seawater scale, as done by csys, caused only small differences, e.g., 0.5% for K_1 and K_2 at 4000 db. We wish to clarify though that it is not us who first suggested that the pressure corrections should be made on the seawater scale. Rather it was Lewis and Wallace (1998), who based that assertion on an extensive study of the literature associated with the pressure adjustment proposed by Millero (1995). The same approach is used in all packages except csys.

This does not mean that csys is necessarily less accurate, but it is inconsistent with the others. Once again, our focus is on precision among packages.

In summary, this would mean one should apply a correction of ∼0.4% to a value that is uncertain by perhaps 10%. To make it worse, the 0.4% correction itself is uncertain because the P-correction for the scale conversion is uncertain, owing to its pressure-dependence through KS (order 10%?) and KF. The bottom line is that attempts to gain apparent accuracy by applying scale conversions to pressure corrections are completely lost in a sea of uncertainty that traces back to the original data and theoretical estimates of the pressure coefficients.

It is a small correction and uncertainties are larger. However, in terms of our goal to quantify precision among packages, it is the main reason why at depth calculated variables in csys differ from those in other packages. We thank the csys developers for recently adding the option to allow users to choose to do the pressure correction as in the other packages or to stay with the original csys approach.

In the revised manuscript, the comparison uses csys with the new their new option to do the pressure correction in the same was as the other packages. That along with other improvements to csys allow us to show that its discrepancies relative to the reference are negligible. Of course if the other option is used, they will not be, as shown in our Discussion paper.

(5) Equilibrium constant for water (KW)

Dickson (2007) converts Kw approximately from the SWS to the total scale by subtracting 0.015 from the constant term, which appears well-justified given the much larger fundamental uncertainties described above. We have followed this approach. Some may believe one could strive for more precision than the very laboratory that currently supplies the reference materials for the quality control of ocean CO2 measurements. I do not.

The simplified approach used in cys is certainly legitimate; it follows the approach recommended by Dickson et al. (2007). In our Discussion paper, we only say that the other packages use a variable offset approach, which is more sophisticated, but we do not say it is better. We thank the csys developers for recently introducing an option to allow the user to choose either approach.

In the revised manuscript, we have used the new option in our comparison as well as the same package's other fixes (including to the K_W pressure-correction coefficients mentioned below). The discrepancies in csys's computed K_W are now negligible.

The pressure coefficients a0, a1, and a2 for KW given in Millero (1995, Table 9) appear to be for water rather than seawater (Millero, 1983). They have been changed in csys.

We appreciate that the csys developers have now fixed these 3 pressure-adjustment coefficients for K_W, errors which we identified in our Discussion paper.

Discrepancies in K_W from the updated version of csys are negligible. The Discussion manuscript's text describing larger discrepancies in the former version of csys has been removed in our revised manuscript.

(6) Equilibrium constant for hydrogen fluoride (KF)

Orr devotes the better part of an entire section (4.2.4) discussing and analyzing KF in our code. However, KF was never used to calculate output because csys works on the total scale (the code lines for KF had been kept from a different version). Thus, KF has zero effect on csys output on the total scale. If a revised version of the ms will be invited, the discussion of KF in csys and the comparison of KF with other packages (Fig. 17) should be deleted.

Subsection 4.2.4 in the Discussion paper contained only 2 paragraphs on K_F. The first of those points out a common error in both seacarb and csys, an erroneous formulation for ionic strength. The second paragraph further details discrepancies in K_F from csys. Since the ionic strength error was corrected in both packages and other discrepancies have also been remedied, our revised manuscript will be naturally much more concise in regards to K_F.

The second sentence in the above comment was true for the version of csys that was compared in the Discussion paper. But K_F is now used in the latest version of csys, released afterwards. With csys's new option to improve comparison with CO2SYS, K_F is used to convert from the total scale to the seawater scale before pressure corrections of some equilibrium constants and then back again afterwards. We will modify discussion in the revised manuscript in order to account for these changes.

In the revised manuscript, we show that the K_F discrepancies in the updated version of csys have become negligible. Thus we no longer discuss them. Here and for other matters where non-negligible discrepancies in csys have been fixed, we have removed or greatly reduced associated text.

(7) Equilibrium constants for phosphoric acid

Also, constants for phosphoric acid (discussed in ms Sec. 4.2.6) are never used in csys to calculate any output (the code lines had been kept from a different version). Thus, constants for phosphoric acid also have zero effect on csys output. If a revised version of the ms will be invited, the discussion of phosphoric acid constants in csys and the comparison with other packages (Fig. 18) needs to be deleted.

We already pointed out in the Discussion paper that the phosphoric acid constants that were computed by csys were not used. Since csys does compute K_{1P}, K_{2P}, and K_{3P}, and its source code is available and can be modified, we felt it appropriate to notify users of these differences. The latest version of csys still computes these 3 constants, but discrepancies have been reduced.

Hence the revised manuscript will say less about the subject.

(8) Comments on csys description

Section 3.2 and caption fig 7: "... csys, which does not allow pCO2 as an input variable" is inaccurate. csys allows pCO2 as input variable but only in combination with pH.

In the revised manuscript, we will correct the corresponding text in section 3.2 and in Fig. 7 to be consistent with Table 4, which does show that csys is able to use the pCO$_2$-pH pair. Thanks for pointing out this inconsist description.

As promised, the revised manuscript has corrected this inconsistency.

Section 4.2.1: "... csys exhibits problems that can be traced back to its implementation of the Lueker et al. (2000) formulations for K1 and K2." is inaccurate. Differences may be due to pressure corrections but not due to the implementation of K1 and K2 based on Lueker et al. (2000). K1 and K2 agree within round-off error with CO2SYS at P = 0.

We thank the csys developers for pointing out this imprecision. We do say earlier in the same section that for K_1 and K_2 from Lueker et al. (2000), all packages agree at the surface. In the revised manuscript, we will modify the sentence mentioned above to be consistent with what was said previously.

In the revised manuscript, we no longer discuss discrepancies in csys's K_1 and K_2 because with the updated version they are now negligible. Hence we've shortened this section to just 1 paragraph. The three equations have been removed, and there is no explicit mention of csys. We now say that all packages have negligible discreprencies.

Total boron: this variable is part of the input section in csys and can be readily changed by the user if Lee et al.'s (2010) value is preferred.

Certainly users are free to modify whatever they like given the source code. If the developers offer this new option for total boron in a later release, we would then consider that csys offers it.

The updated version of csys does not offer the new formulation for total boron Lee et al. (2010), only the standard formulation. Thus for csys we only compare the latter in the revised manuscript.

We have added a user option to csys if one wishes to compare csys output to that of CO2SYS:

http://www.soest.hawaii.edu/oceanography/faculty/zeebe_files/CO2_System_in_Seawater/csys.html

This is particularly useful option. Much appreciated.

In the revised manuscript, we us used this option for the comparison (ocdflag=1).

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