

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

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(1) A perspective on the package comparison based on measurement uncertainties

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.

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

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of surface seawater:

TA: 2-3 $\mu\text{mol}/\text{kg}$

DIC: 2-3 $\mu\text{mol}/\text{kg}$

pH: 0.005

pCO₂: 2 μatm

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 $\sim 0.1 \mu\text{atm}$, 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.

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.

(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

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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.

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 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

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).

(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 μmol/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:

$$DpCO_2 = \sqrt{(4.4^2 + 5.5^2 + 5.2^2 + 6.6^2)} = 11 \text{ uatm}$$

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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 $\mu\text{mol/kg}$ and DIC = 2080 $\mu\text{mol/kg}$. This uncertainty is about 100 times larger than the difference between numerical packages (order 0.1 μatm) as discussed by Orr.

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.

(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%.

In the manuscript, Orr suggests that constants should be first converted to the sea-

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water 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%.

In summary, this would mean one should apply a correction of $\sim 0.4\%$ 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.

(5) Equilibrium constant for water (KW)

Dickson (2007) converts K_w 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 pressure coefficients a_0 , a_1 , and a_2 for KW given in Millero (1995, Table 9) appear to be for water rather than seawater (Millero, 1983). They have been changed in csys.

(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

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invited, the discussion of KF in csys and the comparison of KF with other packages (Fig. 17) should be deleted.

(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.

(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.

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.

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.

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

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