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Comparison of seven packages that compute ocean carbonate chemistry

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Abstract

To study ocean acidification and the carbon cycle, marine scientists often use two measured or modeled carbonate system variables to compute others. These carbonate chemistry calculations, based on well-known thermodynamic equilibria, are now available from seven public packages: CO2SYS, csys, seacarb, swco2, CO2calc, ODV, and mocsy. We compared results from these packages using common input data and the set of equilibrium constants recommended for best practices. All packages agree within ± 0.00025 units for pH and $\pm 0.5 \mu\text{mol kg}^{-1}$ for CO_3^{2-} , and six packages agree within $\pm 0.2 \mu\text{atm}$ for $p\text{CO}_2$ in terms of zonal-mean surface values. In the remaining package (csys), the surface $p\text{CO}_2$ variable is up to $1.4 \mu\text{atm}$ lower than in other packages, but that is because it is mislabeled. When compared to surface $f\text{CO}_2$, it differs by less than $0.2 \mu\text{atm}$. The csys deviations in $f\text{CO}_2$, pH, and CO_3^{2-} grow with depth but remain small. Another package (swco2) also diverges significantly but only in warm deep waters as found in the Mediterranean Sea. Discrepancies between packages derive largely from their code for the equilibrium constants. Analysis of the sensitivity of each computed variable to changes in each constant showed the expected dominance of K_1 and K_2 , while also revealing comparable sensitivity to K_B , e.g., with the A_T - C_T input pair. Best-practice formulations for K_1 and K_2 are implemented consistently among packages, except those in csys deviate slightly at depth (e.g., 0.5% larger values at 4000 db) due to its pressure corrections made on the total instead of the seawater pH scale. With more recent formulations for K_1 and K_2 designed to cover a wider range of salinities, packages disagree more, e.g., by $8 \mu\text{atm}$ in $p\text{CO}_2$, $1 \mu\text{mol kg}^{-1}$ in CO_3^{2-} , and 0.006 units in pH under typical surface conditions. These discrepancies stem from packages using different sets of coefficients for the corresponding salinity dependence of the new formulations. Although each set should be equally viable after simple conversions, we show they are fundamentally inconsistent. Despite general agreement between current packages, agreement was much worse with outdated versions, e.g.,

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differences reached up to $2.5 \mu\text{atm}$ in $p\text{CO}_2$, $1.4 \mu\text{mol kg}^{-1}$ in CO_3^{2-} , and 0.007 units in pH for surface zonal means when using the best-practice constants.

1 Introduction

Our ability to assess ocean carbon uptake and associated impacts from ocean acidification relies on an accurate representation of marine carbonate system. Fortunately, the seawater carbonate system is well constrained, allowing any two of its variables to be used to calculate all others, given associated temperature T , salinity S , pressure P , and nutrient concentrations. For example, it is common to measure or simulate two conservative variables, dissolved inorganic carbon C_T and total alkalinity A_T , and then compute from associated thermodynamics the corresponding pH, partial pressure of carbon dioxide $p\text{CO}_2$, and concentrations of carbonate CO_3^{2-} and bicarbonate HCO_3^- ions as well as related buffer factors and saturation states of aragonite Ω_A and calcite Ω_C . It is the CO_2 -driven changes in these variables that drive the largest reductions in the ocean carbon sink (Sarmiento et al., 1995; Orr, 2011) and the biological impacts from ocean acidification (Gattuso and Hansson, 2011; Kroeker et al., 2013; Wittmann and Pörtner, 2013).

These equilibrium computations are made with a number of software packages, either those developed and used by individual scientists or, more commonly, those that have already been made available publicly. The latter have become indispensable for many ocean scientists, whether they study marine chemistry or impacts of ocean acidification on marine biota. Yet how packages differ is seldom addressed. Lewis and Wallace (1998) documented differences in basic variables among three existing packages at a time when no such package was available publicly. Provided with the same input, computed output from the three packages differed by $21 \mu\text{atm}$ for $p\text{CO}_2$, 0.16 units for pH, and $15 \mu\text{mol kg}^{-1}$ for CO_3^{2-} as well as HCO_3^- . Packages used different pH scales, different formulations for some of the constants (K_1 , K_2 , K_B , and K_S), and different definitions of total alkalinity, all apparently hard-coded. These differences prompted

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Lewis and Wallace (1998) to develop a publicly available package, CO2SYS, which provides many options to select from the available pH scales and constants. Since that time, other packages have also been developed and released publicly, yet to this day no study has been published that compares their results. One may assume, given continued efforts to establish and refine procedures for best practices (Dickson and Goyet, 1994; Dickson et al., 2007; Dickson, 2010), that differences among currently available packages are less than what was found 15 years ago. But even that poor level of agreement has not been established. Without a quantitative understanding of the accuracy and precision of these packages, we cannot rigorously compare studies that aim to assess, e.g., air–sea CO₂ fluxes and thresholds associated with ocean acidification.

At this writing, there exist seven publicly available software packages. The first among them is the previously mentioned CO2SYS, but that now exists in four different versions: the original program for DOS (Lewis and Wallace, 1998), two versions as Excel spreadsheets (Pierrot et al., 2006; Pelletier et al., 2007), and most recently a version as MATLAB scripts (van Heuven et al., 2011). Another package, csys, was also written in MATLAB but it was released a decade earlier, already in 2001 as a supplement to the book by Zeebe and Wolf-Gladrow (2001). The development of csys inspired seacarb, an R library (R Development Core Team, 2012) released two years later (Proye and Gattuso, 2003) and since improved with frequent revisions (Lavigne and Gattuso, 2011). About the same time as the release of the two Excel interfaces to CO2SYS, the swco2 package was also released with a similar spreadsheet interface but a distinct library of core routines written in Visual Basic (Hunter, 2007). Three years later, oceanographers saw the release of two new carbonate chemistry packages, CO2calc and ODV, both of which also exploit the core CO2SYS code. While CO2calc provided completely new interfaces for Mac, PC, and iPhone (Robbins et al., 2010), ODV provided carbonate chemistry calculations as an add on to an already widely used visualization and analysis tool (Schlitzer, 2002). Parallel to those developments for the observational community, the Ocean Carbon-Cycle Model Intercomparison Project (OCMIP) provided routines to compute surface $p\text{CO}_2$ and air–sea CO₂

fluxes from simulated A_T and C_T (Orr et al., 1999). Those were adapted to include the full suite of other carbonate system variables (Orr et al., 2005), then later improved and released publicly as the mocsy package (Orr and Epitalon, 2014). With a goal here to assess the consistency of these seven packages, we compared results generated by running them with common sets of constants, pH scales, and input data.

We limit this study to package comparison. For brevity, we avoid redocumenting the associated approaches and algorithms, which are now commonly used and for which abundant literature already exists (e.g., Dickson et al., 2007; Munhoven, 2013). Likewise, we do not address the debate raised by Hoppe et al. (2012) concerning poor agreement between measured $p\text{CO}_2$ and that computed from A_T and C_T , a disaccord found to be worse than in previous studies by marine chemists (e.g., Lueker et al., 2000). Nonetheless, we go beyond simply identifying differences between packages; we also seek to identify their causes. It is hoped that this effort will inspire subsequent package developments and facilitate their validation, while tightening agreement. The ultimate goal is to reach a point where users will no longer need to merely assume that packages provide the same results. Packages can then be legitimately chosen based on convenience, efficiency, functionality, and the level of programming experience of the user. For instance, users without any programming experience may well prefer spreadsheet based programs (CO2SYS, CO2calc, swco2). Users who use ODV for general oceanographic data analysis and visualization can easily compute carbonate system variables using its predefined derived-variable facility. Users with some programming experience may prefer packages that are available in languages that they are already familiar with: MATLAB users will prefer CO2SYS or csys, R users can use seacarb, Visual Basic users may opt for swco2, and users of python or Fortran can use mocsy.

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2 Methods

To compare all publicly available packages, our approach was to install them in a one location, define common input data and constants, and use those with each package to generate a data archive for centralized analysis.

2.1 Packages and reference

All seven publicly available software packages for the ocean carbonate system (Table 1) take two of those system variables as input and compute the others from basic thermodynamics. All packages were first downloaded in November 2012. Our early findings led developers to update two of those packages, seacarb and CO2calc. Results from an older version of each package are included in one of the earlier figures to illustrate the discrepancies associated with running software that is out of date. Subsequent comparison refers only to the latest version of each package.

To compare packages, it was necessary to define a common reference. Although check values exist for most of the equilibrium constants (Dickson et al., 2007), none are available for computed variables. Hence we chose one of the packages as a relative reference, namely CO2SYS, for three reasons: (1) it was the first publicly available package; (2) its core routines already serve as the base code for two other packages (CO2calc and ODV); and (3) its documentation and code reveal the intense effort that its developers have put into ferreting out the right coefficients from the literature and the most appropriate version of formulations for the constants.

However, selecting CO2SYS as the reference requires further specification, because it comes in at least 4 variants: the original for DOS (Lewis and Wallace, 1998), two others both interfaced to Excel (Pelletier et al., 2007; Pierrot et al., 2006), and another for MATLAB (van Heuven et al., 2011). The first two variants may be considered legacy codes because they do not provide options to use formulations for K_1 and K_2 from Lueker et al. (2000), as recommended for best practices (Dickson et al., 2007). Thus, we reduced our choices for the reference to the latter two versions of CO2SYS (MAT-

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LAB code and Pierrot et al.'s Excel version), both of which provide options to use all constants recommended for best practices (with one minor exception). Both versions give essentially identical results (Fig. 1). But they differ significantly from the legacy versions run with the closest substitutes for Lueker et al.'s K_1 and K_2 , namely earlier refits by Dickson and Millero (1987) of the same measured constants from Mehrbach et al. (1973). Finally, the CO2SYS reference also had to be efficient, since all packages needed to be compared with an input data set of nearly 1 million records (Table 2). Thus we chose the MATLAB version of CO2SYS as the reference.

2.2 Features

The seven packages compute results from the same thermodynamic equilibria, but software features differ, including available input pairs, pH scales, and constants. Package diversity covers all commonly used operating systems: seven packages run on Windows, six packages on Mac OSX, and four packages on Linux (Table 3). Source code is available in four packages in standard programming languages (MATLAB, R, and Fortran 95), thereby allowing code validation and improvements by users on all three operating systems mentioned above. The number of possible input pairs of carbonate system variables varies widely between packages, from 1 to 22 (Table 4). The mocsy package, treats only one input pair A_T-C_T , the two carbonate system variables carried by models. The CO2SYS package and its derivatives (CO2calc and ODV) allow the user to select from six commonly measured pairs (A_T-C_T , A_T-pH , A_T-pCO_2 , C_T-pCO_2 , C_T-pH , and $pH-pCO_2$); in addition, they allow equivalent pairs where fCO_2 replaces pCO_2 . The csys package provides 10 more input pairs by allowing pair members to include one or more of the 3 inorganic carbon species: CO_2^* , HCO_3^- , and CO_3^{2-} . Although the two former species can only be calculated, promising new techniques are being developed to measure the latter (Byrne and Yao, 2008; Martz et al., 2009; Easley et al., 2013). Yet despite csys's enhanced number of input pairs, it limits pCO_2 to be used as input only when combined with pH. The two remaining packages, seacarb and swco2, include the same 16 pairs as csys but also add 4 others, all including pCO_2 .

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5 Computed variables are affected by the choice of the pH scale and the constants. All packages allow users to work on the total pH scale as recommended for best practices (Table 5) and as used for this comparison. The mocsy package provides only the total scale, while the six others allow for conversion to the free scale. Out of those six, only
10 csys does not allow users to work on the seawater scale. Three packages (CO2SYS, CO2calc, and swco2) also offer the NBS scale. The choice of the pH scale affects the values of the constants for which H^+ is part of the equilibrium equation. For K_1 and K_2 , CO2SYS and its derivatives (CO2calc, ODV) offer a large range of choices (Table 6). Yet most of those may now be considered out of date, having been replaced by more
15 recent assessments, often made with the same data. All packages offer the K_1 and K_2 formulations from Lueker et al. (2000), as recommended for best practices. Four packages also offer the most recent formulations for K_1 and K_2 that have been proposed as more appropriate for low-salinity waters (Millero, 2010). The formulations for K_1 and K_2 from the two latter studies are used individually in this comparison to assess associated differences between packages. For the other constants, all packages provide the formulations recommended for best practices, except for K_F , a difference shown later to have no consequence.

20 Some packages also offer additional features. For example, CO2SYS and CO2calc allow users to compute variables at a temperature that differs from that at which the input pair was measured. They also distinguish different components of total alkalinity, including those from total B, P, and Si. The seacarb package provides explicit functions to the user to allow conversion of pH and constants between the free, total, and seawater scales; other packages make such conversions internally, but do not provide user-callable functions. The seacarb package also offers functions to help design
25 perturbation experiments to investigate effects of ocean acidification (Gattuso and Lavigne, 2009).

2.3 Input data

To compare packages, we used two different kinds of input data. A first analysis compared variables computed in each package as a function of latitude and depth using as input the 3-D gridded data products for A_T and C_T from GLODAP (Key et al., 2004) combined with comparable products from the 2009 World Ocean Atlas (WOA2009) for temperature T (Locarnini et al., 2010), salinity S (Antonov et al., 2010), and concentrations of phosphate PO_4^{3-} and silica SiO_2 (Garcia et al., 2010). A second analysis focused on comparing packages while separating the effects of physical input variables (T , S , and P) on computed variables. For that, we started with five commonly used input pairs: A_T - C_T , A_T -pH, A_T - $p\text{CO}_2$, C_T - $p\text{CO}_2$, and C_T -pH. Then for each pair, we computed the other carbonate system variables over ranges of T , S , and P , assuming zero nutrient concentrations. More precisely, all other carbonate system variables were first calculated with one package (seacarb) from $A_T = 2300 \mu\text{mol kg}^{-1}$ and $p\text{CO}_2 = 400 \mu\text{atm}$ at global average surface conditions ($T = 18^\circ\text{C}$, $S = 35$, and $P = 0$ db). Then two surface data sets were produced for each pair (and each package) by varying T and S , individually, and recalculating all other carbonate system variables from the fixed input pair. For the first, T was varied from -2 to 50°C , while for the second S was varied from 0 to 50. In both cases, pressure was held at 0 db. To assess how packages differ below the surface, we used the same approach, varying pressure between 0 and 10 000 db and maintaining $S = 35$. But pressure corrections are highly sensitive to temperature (Sect. 2.7), so for each package we made two data sets: (1) holding $T = 2^\circ\text{C}$ (typical of the deep open ocean) and (2) holding $T = 13^\circ\text{C}$ (typical of deep waters of the Mediterranean Sea).

2.4 Best-practices comparison

Comparisons were made using the total pH scale and constants recommended for best practices by Dickson et al. (2007). The equilibrium constant for the solubility of CO_2 in seawater K_0 is from Weiss (1974). The equilibrium constants K_1 and K_2 are from

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Lueker et al. (2000), who refit the constants determined by Mehrbach et al. (1973) to the total pH scale. The formulation for K_B is from Dickson (1990b) and is also on the total pH scale. Formulations for K_W , K_{1P} , K_{2P} , K_{3P} , and K_{Si} are from Millero (1995), who provides equations for the seawater scale, and those are converted to the total scale. The formulation for K_S is from Dickson (1990b) on the free scale (see above). The solubility products for aragonite K_A and for calcite K_C are from Mucci (1983). All are apparent equilibrium constants, given in terms of concentrations, not activities. The only constant for which the formulation was not that recommended by Dickson et al. (2007) is K_F , because that best-practices formulation (Perez and Fraga, 1987) is not offered by CO2SYS, CO2calc, and ODV. Instead, we used the K_F formulation by Dickson and Riley (1979) on the total scale, which is offered by all the packages. Dickson et al. (2007) recommend the former but also state that results from the two formulations are in reasonable agreement.

Additionally, all packages used consistent formulations for total concentrations of boron (Uppström, 1974), sulfur (Morris and Riley, 1966), and Ca^{2+} (Riley and Tongu-dai, 1967), each proportional to salinity. Six packages compute saturation states for aragonite Ω_A and calcite Ω_C from the product of the concentrations of Ca^{2+} and CO_3^{2-} divided by the corresponding apparent solubility product, either for aragonite K_A or calcite K_C (Mucci, 1983), respectively. Only the csys package does not provide output for Ω_A and Ω_C . To simplify comparison, all figures plot results as an absolute differences, i.e., computed values are shown after subtracting off corresponding results from the reference.

2.5 Sensitivity tests

The most extensive comparison was made with the A_T-C_T input pair, the only one that is available in all packages. With that pair, packages were also compared in terms of how their computed variables were affected by nutrient concentrations, varying phosphate PO_4^{3-} and silica SiO_2 concentrations across the observed range. Additionally, the same pair was used to quantify effects of two important developments since the

best practices were published in 2007. For the first, we quantified effects on computed variables of Lee et al. (2010)'s assessment that the total boron in the ocean may be 4 % larger than considered previously (Uppström, 1974). For the second, we assessed impacts of using Millero (2010)'s new K_1 and K_2 formulations, which are designed to cover a wider range of input S and T relative to recommended constants (Lueker et al., 2000).

2.6 Constants

To better assess the most probable causes of the differences in computed carbonate system variables, we also compared associated constants. For the packages where source code was available (CO2SYS-MATLAB, csys, seacarb, mocsy), we used existing routines or slightly modified versions to output all the constants for the same physical input data (T , S , and P) that we used for computing variables. For swco2, we retrieved its constants using its documented parameter numbers and its routine to extract anything with a parameter number. For other packages where source code was not available, we were able to compute some of the constants from available output variables. Thus with output from CO2calc, we computed its K_0 , K_1 , K_2 , K_B , K_W , K_A , and K_C ; from ODV output, we computed its K_0 , K_1 , K_2 , K_A , and K_C .

2.7 Pressure correction

Following Millero (1995), all packages correct for the effect of pressure P on each equilibrium constant K_i with the equation

$$\ln \left(K_i^P / K_i^0 \right) = - (\Delta V_i / RT_k) P + (0.5 \Delta \kappa_i / RT_k) P^2, \quad (1)$$

where the left hand side is the ratio between K_i at depth (P in bars) and at the surface (P at 0 bars), R is the gas constant, T_k is temperature in K, ΔV_i is the partial molal volume, and $\Delta \kappa_i$ is the change in compressibility. For each constant, Millero (1995)

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provided empirical fits, quadratic in temperature:

$$\Delta V_i = a_0 + a_1 T_c + a_2 T_c^2, \quad (2)$$

$$\Delta \kappa_i = b_0 + b_1 T_c + b_2 T_c^2, \quad (3)$$

5 where T_c is temperature in °C. Some of these original coefficients (Millero, 1995, Table 9) contained typographical errors as identified in the code and documentation of CO2SYS (Lewis and Wallace, 1998, Appendix). Nonetheless, they have persisted in some of the packages as well as in the literature (e.g., Millero, 2007). To help amend this situation, Table 7 lists these coefficients for each constant where known errors
10 have been corrected. To determine the fidelity of packages to this array of coefficients, we studied available source code and evaluated patterns of discrepancies in results, making sensitivity tests to decipher fingerprints characteristic of previous errors.

2.8 What is significant?

If software packages with identical input cannot agree to within much less than the measurement precision of a computed variable (e.g., $p\text{CO}_2$), then their varied use would add substantially to the total uncertainty. To avoid this situation, it is necessary for these
15 tools to have a numerical precision that is far superior to the measurement precision. By numerical precision, we mean their agreement, including all coding differences and errors as well as the usually much smaller numerical round-off error. Therefore, we arbitrarily define that cutoff level for numerical precision to be ten times better than the
20 best measurement uncertainty (Dickson, 2010, Table 1.5). A package that agrees with a given variable from the reference package within the numerical cutoff specified in Table 8 will be referred to here as having negligible discrepancy relative to the reference; conversely, a package with a greater difference for a given variable will be considered
25 to have a significant discrepancy.

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3 Results

Packages were compared in terms of how computed variables differed with latitude and depth, using global gridded data, and how individual physical variables and chemical choices affected results, using simplified data. Packages were also compared in terms of computational efficiency.

3.1 Global gridded data

With gridded data products from GLODAP and WOA2009 as input, 6 out of 7 packages agree well in terms of the global-mean profiles of computed variables (Fig. 2). Five packages agree with CO2SYS within $\pm 0.2 \mu\text{atm}$ for $p\text{CO}_2$, $\pm 0.05 \mu\text{mol kg}^{-1}$ for CO_3^{2-} , and ± 0.00025 units for pH, throughout the water column. The same group of six packages show similar close agreement for surface zonal means at all latitudes (Fig. 3). The remaining package, csys, differs significantly from the others with $p\text{CO}_2$ that is up to $1.4 \mu\text{atm}$ lower at the surface and on average up to $2.6 \mu\text{atm}$ lower in subsurface waters. However, those differences shrink by more than a factor of 6 when the csys $p\text{CO}_2$ variable is compared to $f\text{CO}_2$ in the other packages. Other computed variables in csys agree closely with those from the other 6 packages.

Yet agreement was not always so close. For some perspective, the CO2SYS reference was also compared with older versions of three of the packages: CO2calc (version 1.0.4 revised in 18 June 2013), seacarb (version 2.3.3 revised in 2010), and mocsy, an early precursor developed by Orr et al. (2005) but not released publicly. Discrepancies relative to the same reference used to be larger, e.g., up to twice as much for $p\text{CO}_2$ and ten or more times as much for CO_3^{2-} and pH (Fig. 4). With the mocsy precursor, there are significant discrepancies in $p\text{CO}_2$ reaching up to $1.5 \mu\text{atm}$ at the surface. Those grow with depth, e.g., reaching $4 \mu\text{atm}$ at 5000 m. At the same depth, discrepancies in the other variables reach $0.5 \mu\text{mol kg}^{-1}$ in CO_3^{2-} and up to 0.007 in pH. Subsurface discrepancies are mainly due to two common modeling approximations (Orr and Epitalon, 2014) that are corrected in the first public release of mocsy. With CO2calc v1.0.4, sur-

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face discrepancies reach up to $2 \mu\text{atm}$ in $p\text{CO}_2$, up to $1.3 \mu\text{mol kg}^{-1}$ in CO_3^{2-} , and up to 0.007 in pH. Those discrepancies are associated with coding errors in the K_1 and K_2 formulations from Lueker et al. (2000), errors that were corrected in CO2calc version 1.2.0. As for seacarb v2.3.3, there are no significant discrepancies. However, with an even earlier version of seacarb (v2.0.3 released in 2008, not shown), the only package that maintains public access to all previous versions, discrepancies at depth are much larger (e.g., $-7 \mu\text{mol kg}^{-1}$ in CO_3^{2-} and -0.165 in pH at 4000 m), presumably due to errors in the pressure corrections. Thus previous versions of packages often have larger discrepancies, emphasizing the importance for users to keep their carbonate system software up to date.

Although the previous analysis let us assess how discrepancies vary spatially across the global ocean, the realistic gridded input data sets that were exploited did not allow us to isolate how discrepancies vary with individual physical variables and chemical input options. We will now focus on those factors, individually, by exploiting simple artificial input data.

3.2 Physical factors

Packages were compared with 5 common input pairs with the same simple data sets where T , S , and P were varied individually. All packages were compared with the A_T – C_T pair. Comparison with 4 other pairs excluded the mocsy package, which is designed to use only A_T – C_T . Comparison with two of the remaining pairs, A_T – $p\text{CO}_2$ and C_T – $p\text{CO}_2$, also excluded the csys package, which does not offer $p\text{CO}_2$ as an input variable.

3.2.1 A_T – C_T

With the A_T – C_T pair, most packages agree closely at the surface and below. Computed variables from 6 out of 7 packages match tightly across ranges of T and S at surface pressure (Fig. 5). As for the gridded data comparison, the exception is the mislabeled csys $p\text{CO}_2$ variable. Although about $1 \mu\text{atm}$ lower than surface $p\text{CO}_2$ in other pack-

ages, it is just $0.1 \mu\text{atm}$ higher when compared to $f\text{CO}_2$ in the same packages. Other surface variables in csys exhibit negligible discrepancies (e.g., $0.06 \mu\text{mol kg}^{-1}$ in CO_3^{2-} , and 0.0002 in pH). Away from the surface, the story is slightly more complicated. In the open ocean with its cold deep waters at around 2°C , pressure corrections in most packages do not add significantly to the discrepancies seen at the surface. At that low temperature, only csys exhibits significant subsurface discrepancies. Those start to become significant when pressures exceed about 2000 db, (excluding the mislabeled $p\text{CO}_2$ comparison). In some isolated regions, deep waters are warmer (e.g., 13°C for the Mediterranean Sea). Discrepancies there would be larger if due to errors in some coefficients of the pressure-correction, a quadratic function of temperature (Eqs. 2 and 3). Indeed, one of the packages, swco2, exhibits substantial discrepancies with a pressure correction at 13°C although only negligible discrepancies at 2°C . For example at 4000 db, its discrepancies at 13°C reach $-1.5 \mu\text{atm}$ for $p\text{CO}_2$, $+0.6 \mu\text{mol kg}^{-1}$ for CO_3^{2-} , and $+0.002$ for pH. At the same temperature and pressure, discrepancies in csys are typically two to four times smaller, e.g., $0.8 \mu\text{atm}$ in $p\text{CO}_2$, $-0.15 \mu\text{mol kg}^{-1}$ in CO_3^{2-} , and 0.0003 in pH. Discrepancies in other packages are much smaller still and always negligible.

3.2.2 A_T -pH

With the A_T -pH pair (Fig. 6), discrepancies at the surface are similar in magnitude to those found with the A_T - C_T pair (Fig. 5). The csys package's surface discrepancies for its mislabeled $p\text{CO}_2$ reach up to $-2 \mu\text{atm}$, while they remain negligible for computed CO_3^{2-} and C_T except at the highest temperatures and salinities. Surface discrepancies for other packages remain negligible. Below the surface, the largest discrepancies come from csys and swco2. For csys, pressure-correction discrepancies for computed $p\text{CO}_2$ and CO_3^{2-} are similar in shape and magnitude to those with the A_T - C_T pair (Fig. 5). The pressure correction at 13°C in swco2 generally leads to discrepancies in $p\text{CO}_2$ and CO_3^{2-} that are barely significant at 4000 db, whereas discrepancies in C_T

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reach $+1 \mu\text{mol kg}^{-1}$ at the same depth. With the pressure correction at 2°C , the swco2 discrepancies are negligible, while the csys discrepancies are not, as already seen for the A_T - C_T pair. For the other packages, the same low-temperature pressure correction results in negligible discrepancies for all variables.

3.2.3 A_T - $p\text{CO}_2$

With the A_T - $p\text{CO}_2$ input pair (Fig. 7), computed variables show discrepancies (relative to CO2SYS) that bear some resemblance to those found with the A_T - C_T pair (Fig. 5). At the surface, all five packages differ by less than $0.05 \mu\text{mol kg}^{-1}$ in C_T and $0.015 \mu\text{mol kg}^{-1}$ in CO_3^{2-} . Likewise for pH, packages generally agree within 0.0001 unit, although CO2calc exhibits larger variability (within ± 0.0004). However, those variations are randomly distributed with a mean near zero, a consequence of CO2calc's limited output precision of only 3 decimal places for pH. The pressure correction when performed at 2°C does not add significant discrepancies, unlike that performed at 13°C , for which discrepancies in swco2 grow linearly with pressure, e.g., reaching $+0.7 \mu\text{mol kg}^{-1}$ in C_T , $+0.1 \mu\text{mol kg}^{-1}$ in CO_3^{2-} , and $+0.0002$ in pH at 4000 db.

3.2.4 C_T -pH

With the C_T -pH input pair (Fig. 8), discrepancies generally resemble most those from A_T -pH pair (Fig. 6), while differing more with those from the A_T - C_T and A_T - $p\text{CO}_2$ pairs (Figs. 5 and 7). With C_T -pH, there is similar agreement for 5 out of 6 packages across ranges of surface T and S . Those 5 packages generally agree within $0.05 \mu\text{atm}$ for $p\text{CO}_2$, $0.007 \mu\text{mol kg}^{-1}$ for CO_3^{2-} , and $0.1 \mu\text{mol kg}^{-1}$ in A_T at surface pressure. As before, only csys exhibits significant discrepancies in $p\text{CO}_2$, largely because it is mislabeled. Surface discrepancies of other variables are negligible in all packages, except for computed A_T in csys. Those discrepancies, relative to CO2SYS, grow exponentially with T and S but become significant only after reaching $T = 25^\circ\text{C}$ and $S = 35$. The pressure correction worsens the csys discrepancy in CO_3^{2-} until it becomes significant

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below 2000 db with the 2 °C pressure correction. Another dissimilarity, relative to previously analyzed pairs, is that with C_T -pH, the swco2 package's pressure corrections do not induce substantial discrepancies in computed subsurface $p\text{CO}_2$ and CO_3^{2-} , even at 18 °C. At that temperature, they do cause significant discrepancies in computed subsurface A_T (e.g., $1 \mu\text{mol kg}^{-1}$ at 4000 db), but those become negligible with the pressure correction at $T = 2^\circ\text{C}$, as with other input pairs. The same contrast in the temperature sensitivity between the same two packages was apparent with the A_T - C_T and A_T -pH input pairs (Figs. 5 and 6).

3.2.5 C_T - $p\text{CO}_2$

With the C_T - $p\text{CO}_2$ pair (Fig. 9), all five packages have negligible surface discrepancies for computed A_T ($\leq \pm 0.1 \mu\text{mol kg}^{-1}$), CO_3^{2-} ($\leq \pm 0.01 \mu\text{mol kg}^{-1}$), and pH ($\leq \pm 0.003$ units). The pressure correction leads to patterns in discrepancies between packages that are qualitatively similar to those seen with a previously discussed input pair, C_T -pH (Fig. 8). Out of the five packages offering both input pairs (excluding csys and mocsy), only swco2 develops significant subsurface discrepancies. Moreover, that exception occurs only for one variable and only with the less realistic pressure correction at 13 °C. At that higher temperature, the swco2 package's discrepancies in computed A_T grow linearly with depth, reaching $1 \mu\text{mol kg}^{-1}$ at 4000 db. Discrepancies in A_T remain negligible with the low-temperature pressure correction. Discrepancies in other variables are always negligible.

Considering results from the 5 input pairs together, we can now make several general comments. Only one package (csys) produces significant surface discrepancies, and for the most part only for its computed $p\text{CO}_2$, largely because that variable is mislabeled. The same package is the only one to produce significant subsurface discrepancies with the pressure correction at 2 °C, and those also concern other computed variables (e.g., pH and CO_3^{2-}). Another package (swco2) also produces significant subsurface discrepancies when the pressure correction is made at higher temperatures,

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which is of concern only for a warm marginal sea such as the Mediterranean. Furthermore, in those isolated warm deep waters, swco2 would produce significant subsurface discrepancies only for computed A_T or for other computed variables when A_T is a member of the input pair.

5 3.3 Chemical Factors

In Sect. 3.2, we compared differences among packages while varying physical input for different input pairs. Here we assess differences due to chemical factors, namely accounting for alkalinity from nutrients and opting for potentially important developments published since the publication of the best practices guide (Dickson et al., 2007).

10 3.3.1 Nutrients

Phosphate and silicate contribute to the total alkalinity when their concentrations are significant. Thus they affect computed carbonate alkalinity A_C when one of the input pairs is A_T . One of the packages, csys, neglects nutrient alkalinity, assuming PO_4^{3-} and SiO_2 concentrations are always zero. Out of the remaining six packages, four show negligible discrepancies relative to CO2SYS as nutrient concentrations are increased to the maxima observed in the ocean (Fig. 10). Discrepancies for the other 2 packages remain small: for swco2 they reach up to $-0.2 \mu\text{atm}$ in $p\text{CO}_2$, $+0.07 \mu\text{mol kg}^{-1}$ in CO_3^{2-} , and $+0.0002$ units in pH; for CO2calc, they remain less than $+0.3 \mu\text{atm}$ in $p\text{CO}_2$ and $-0.04 \mu\text{mol kg}^{-1}$ in CO_3^{2-} , while for pH they are not significantly different from zero.

20 These differences between packages are at least 70 times smaller than the actual changes in computed variables attributable to phosphate and silicate alkalinity. With the input pair A_T-C_T , nutrient alkalinity increases computed $p\text{CO}_2$ by $6 \mu\text{atm}$ for average surface waters in the Southern Ocean and by $12 \mu\text{atm}$ for average deep waters (below 2000 m); simultaneously, CO_3^{2-} is reduced by about $2 \mu\text{mol kg}^{-1}$ in the same waters
25 (Orr and Eptalon, 2014).

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3.3.2 Total Boron

Relative to the standard formulation for total boron (Uppström, 1974), the new formulation (Lee et al., 2010) represents a 4% increase of borate alkalinity throughout the ocean. Hence we first assessed whether or not packages gave consistent responses when changing from the standard to the new formulation. For the four packages that allow for the new formulation (CO2SYS, CO2calc, mocsy, and seacarb), their predicted changes agree within $0.15 \mu\text{atm}$ for $p\text{CO}_2$, $0.02 \mu\text{mol kg}^{-1}$ for CO_3^{2-} , and 0.00006 units for pH, i.e., with the A_T – C_T pair across observed ranges of T , S , and P (Fig. 11). With other input pairs, agreement is closer still but the comparison is limited to fewer packages (mocsy treats only A_T – C_T). Much larger are the actual changes themselves. With the A_T – C_T pair, given global average surface conditions ($T = 18^\circ\text{C}$, $S = 35$), changing from the standard to the new formulation for total boron increases $p\text{CO}_2$ by $5.7 \mu\text{atm}$, decreases CO_3^{2-} by $2.1 \mu\text{mol kg}^{-1}$, and decreases pH by 0.0056 units. Changes are generally smaller with the A_T –pH and A_T – $p\text{CO}_2$ pairs (e.g., -0.3 and $-0.4 \mu\text{mol kg}^{-1}$ for CO_3^{2-} , respectively). Conversely, with the C_T –pH and C_T – $p\text{CO}_2$ pairs, changes are negligible for all computed carbonate system variables, except total alkalinity.

3.3.3 K_1 and K_2

The formulations for K_1 and K_2 from (Lueker et al., 2000) are recommended for best practices (Dickson et al., 2007), but they are intended to be restricted to waters with S between 19 and 43 and T between 2 and 35°C . For waters with physical conditions outside of those ranges, there are no recommended K_1 and K_2 formulations. However, formulations exist, such as those from the most recent reassessment by Millero (2010), which are applicable over wider ranges of S (1–50) and T (0– 50°C).

With an analysis analogous to that shown in Fig. 5 (Sect. 3.2.1), we replaced formulations for K_1 and K_2 from Lueker et al. (2000) with those from Millero (2010) to assess the consistency of computed variables in the four packages that include this

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newer option (CO2SYS, CO2calc, seacarb, and mocsy). With the A_T - C_T pair, 2 of the 4 packages agree closely at surface pressure across ranges of T and S (Fig. 12). Conversely, CO2calc differs from the CO2SYS reference by up to $-12 \mu\text{atm}$ in $p\text{CO}_2$, $-1.2 \mu\text{mol kg}^{-1}$ in CO_3^{2-} , and $+0.006$ units in pH. Discrepancies are also found for seacarb, reaching up to $-20 \mu\text{atm}$ in $p\text{CO}_2$, $\pm 0.2 \mu\text{mol kg}^{-1}$ in CO_3^{2-} , and -0.0025 units in pH. However, seacarb's discrepancies at the surface are inconsistent with its negligible subsurface discrepancies. Pressure corrections alter CO2calc's discrepancies by less than $+1 \mu\text{atm}$ in $p\text{CO}_2$, $-0.05 \mu\text{mol kg}^{-1}$ in CO_3^{2-} , and -0.001 units in pH, changes that are notably less than its surface discrepancies. Overall, even though fewer packages offer the Millero (2010) formulations for K_1 and K_2 , the resulting differences between packages reach levels that are orders of magnitude larger than with the Lueker et al. (2000) formulations.

3.4 Computational efficiency

This study is primarily focused on assessing the accuracy and the precision of the different packages that compute carbonate system variables. Another concern, relevant for users with large data sets, is computational efficiency. To assess differences in computation time between packages, we chose to use the global gridded data set described in Sect. 3.1. With nearly 1 million grid points of input data, the computational time needed to compute all carbonate system variables varies by more than a factor of 3000 between packages (Table 2). The slowest of the seven packages (seacarb) required more than 1 day while the fastest (mocsy) needed 30 s. Except for seacarb, packages based on spreadsheets are generally slower than those run by directly calling routines with programming languages (Fortran 95, MATLAB, Visual Basic). The latter are usually coded so that the equilibrium calculations are made one time for each set of input data, whereas spreadsheets often repeat the same set of calculations for each computed variable (each cell). Fortunately, even with the slowest of the packages shown in Table 2, the computational time is trivial for most observational analysis

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efforts, because the number of samples is much smaller. Hence developers of most packages have not concerned themselves with computational efficiency. Nonetheless, for very large data sets and for models, which may have millions of grid cells to be treated every time step, computational efficiency is critical.

4 Discussion

To diagnose why computed variables differ between packages, we computed their sensitivities to each constant, assessed errors in individual constants, and used both to assign causes.

4.1 Sensitivity to individual constants

A computed variable y is affected by errors in all input variables (including constants as well as members of the input pair), each denoted here as x_i (for $i = 1, 2, \dots, n$). Thus, we calculated the sensitivity ratio as the relative change of y to the relative change in each x_i , namely $\partial y / y : \partial x_i / x$. These sensitivity ratios were determined numerically in three successive steps. First, we calculated variables with seacarb under our standard conditions ($S = 35$, $T = 18^\circ\text{C}$, $P = 0$ db, and zero nutrients, along with $C_T = 2058.185$ and $A_T = 2300 \mu\text{mol kg}^{-1}$). Then, we increased each input variable by 1% ($\partial x_i / x = 0.01$), individually, and recalculated output variables with seacarb for each perturbation. Finally, we took the difference between the first and second computations to obtain the proportional change in the computed variable $\partial y / y$.

Table 9 shows these sensitivity ratios for each variable and constant. Sensitivities of computed variables to input A_T , C_T , K_0 , and K_1 are much like those from Dickson and Riley (1978) who used the same approach, but with different software, input data, and values for constants. Yet our sensitivities to K_2 differ. Although only $\sim 30\%$ smaller for computed CO_2^* , ρCO_2 , and H^+ , they are 7 times larger for CO_3^{2-} as well as Ω_A and Ω_C . The former moderate reductions occur because the K_2 from Lueker et al.

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(2000) at standard conditions is 30 % greater than Dickson and Riley's ($pK_2 = 9.115$). Conversely, our seven-fold greater sensitivity of CO_3^{2-} to K_2 is inconsistent with the previous study. Further investigation suggests our results are accurate because (1) our code for this 3-step numerical calculation treats K_2 exactly as other constants (in a loop), (2) numerical derivatives have been verified by computing analytical solutions to the derivatives (by hand) in other pairs where such calculations are feasible, and (3) results are written directly to the electronic (L^AT_EX) version of Table 9, reducing room for transcription error.

With the A_T - C_T input pair, the sensitivities to K_1 and K_2 generally dominate, as expected from Dickson and Riley (1978). There is a similarly large sensitivity to K_0 when computing $p\text{CO}_2$ and $f\text{CO}_2$. The sensitivities to other constants have not been discussed previously. Here we find a surprisingly large sensitivity to K_B , even surpassing that to K_1 for computed H^+ , HCO_3^- , CO_3^{2-} , Ω_A , and Ω_C , i.e., with the A_T - C_T input pair. The sensitivity to K_W is also significant but remains 14 to 26 times smaller than that for K_B . The sensitivity to other constants remain small (absolute values less than 0.001), except for the solubility products K_A and K_C which are inversely proportional to Ω_A and Ω_C (large negative sensitivities of -1). Sensitivities differ with other input pairs as shown by Dickson and Riley (1978).

These sensitivities are fundamental to the classic propagation of relative errors that has already been applied to the carbonate system (Dickson and Riley, 1978; Dickson et al., 2007). In that, the uncertainty u of computed variable y is expressed as

$$\frac{u(y)}{y} = \sqrt{\sum_{i=1}^n \left(\frac{\partial y / y}{\partial x_i / x} \right)^2 \left(\frac{u(x_i)}{x} \right)^2}, \quad (4)$$

where the left-hand side is the relative error in y , a function of the right-hand side's individual relative errors of each input variable and constant ($u(x_i)/x$) multiplied by the square of the associated sensitivity term $(\partial y / y) / (\partial x_i / x)$ (Table 9). Hence to assess the relative importance of each input variable, we need not only its sensitivity but also

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its error. For the case where relative errors for each of the constants are assumed to be similar (Table 8), then it is largely the sensitivity term which determines the relative contribution of each constant to the overall error. Yet numerical errors in computed constants are neither identical nor entirely negligible in all packages.

5 4.2 Errors in equilibrium constants

In order to identify sources of error, equilibrium constants were plotted in the same manner as computed variables. By characterizing errors graphically, we were able to use patterns in discrepancies to help isolate problems and eventually identify their causes, particularly in packages where source code was available. For packages with-
10 out source code, we attempted to reproduce error patterns by making temporary modifications to another package where source code was available.

4.2.1 K_0 , K_1 , and K_2 : best practices

The constants that have the greatest potential to cause the differences in computed variables seen in Figs. 5–6 are K_0 , K_1 , and K_2 (Table 9), simply because of their promi-
15 nence in the fundamental equilibria. For K_0 , all packages have negligible discrepancies relative to CO2SYS across ranges of T and S , and all packages agree with the check value from Dickson et al. (2007) (Table 11). For K_1 and K_2 with the Lueker et al. (2000) formulation, the story is almost the same, except that the csys package exhibits small discrepancies (Fig. 13). All packages agree at the surface, but csys's discrepancies
20 slowly increase with depth, e.g., reaching values that are 0.5 % larger than other packages at 4000 db. These discrepancies are caused by csys's pressure correction that is made on the total instead of the seawater pH scale.

Qualitatively, the patterns in csys's increasing discrepancies with depth for pK_1 and pK_2 resemble those already seen for computed $p\text{CO}_2$, CO_3^{2-} , and pH (e.g., Fig. 5).
25 To demonstrate, quantitatively, that pK_1 and pK_2 are responsible, we computed ratios between csys's three inorganic carbon species as a function of its K_1 and K_2 , while

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relating those to the same ratio and constants in CO2SYS. Using the definition of K_1 for package p and for the reference r , we can divide the first by the second and rearrange to obtain

$$\frac{[\text{HCO}_3^-]}{[\text{CO}_2^*]}|_p = \frac{(K_1)|_p}{(K_1)|_r} \cdot \frac{[\text{HCO}_3^-]}{[\text{CO}_2^*]}|_r. \quad (5)$$

This equation is applicable when $[\text{H}^+]$ does not differ between packages (e.g., A_T -pH and C_T -pH input pairs). Likewise for K_2

$$\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}|_p = \frac{(K_2)|_p}{(K_2)|_r} \cdot \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}|_r, \quad (6)$$

and for the product K_1K_2

$$\frac{[\text{CO}_3^{2-}]}{[\text{CO}_2^*]}|_p = \frac{(K_1K_2)|_p}{(K_1K_2)|_r} \cdot \frac{[\text{CO}_3^{2-}]}{[\text{CO}_2^*]}|_r. \quad (7)$$

With the A_T -pH pair, these derived ratios overlap with corresponding ratios directly determined from *csys*'s computed CO_2^* , HCO_3^- , and CO_3^{2-} (not shown). Thus subsurface discrepancies in *csys*'s computed variables are largely due to errors in the formulations for pressure corrections to K_1 and K_2 . Likewise, it follows from Eqs. (5) and (6) that packages without discrepancies in the $[\text{HCO}_3^-]/[\text{CO}_2^*]$ and $[\text{CO}_3^{2-}]/[\text{HCO}_3^-]$ ratios must have essentially identical K_1 's and K_2 's. Hence *swco2*'s discrepancies in individual carbonate system variables (Fig. 6) do not come from errors in K_1 and K_2 . Therefore only *csys* exhibits problems that can be traced back to its implementation of the Lueker et al. (2000) formulations for K_1 and K_2 .

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the seawater scale. In seacarb though, it is more complicated. At the surface, seacarb uses Millero's set of coefficients on the total scale to compute K_1 and K_2 ; conversely, below the surface seacarb uses Millero's coefficients for the seawater scale and then converts the resulting constants to the total scale after making the pressure correction (as is appropriate). Although the two approaches should yield equivalent results, seacarb's constants computed for the surface differ from those calculated by CO2SYS. Conversely, below the surface, the two packages agree. Because seacarb's formulations and coefficients are strictly identical to those published by Millero (2010), which we have verified closely, the surface discrepancies imply an inconsistency between Millero's sets of coefficients for the total and seawater scales. Both sets should yield the same results for K_1 and for K_2 , e.g., once the results from the seawater set are converted back to the total scale. Yet they do not. Indeed when K_1 and K_2 were computed separately from Millero's published sets of coefficients, we found similar patterns of surface discrepancies as between seacarb and CO2SYS (Fig. 15). Patterns matched exactly when we also accounted for the differences in K_F . That is, Millero converted pK_1 and pK_2 on the measured seawater scale to the total scale using K_F from Perez and Fraga (1987), whereas for this study all packages use K_F from Dickson and Riley (1979). In summary, seacarb shows surface discrepancies (relative to CO2SYS) primarily because it uses Millero's coefficients on the total scale, which are inconsistent with those on the seawater scale, and secondly because the K_F used by Millero is inconsistent with that used in this study.

The second package that differs substantially from CO2SYS is CO2calc, but only for K_2 . Although CO2calc's main code was taken from CO2SYS, the CO2calc developers included the Millero (2010) K_1 and K_2 formulations themselves, before they were available in CO2SYS. Lacking the CO2calc source code, we studied discrepancy patterns and with sensitivity tests found that they come from a different number of significant figures in one of the coefficients. More precisely, Fig. 15 compares the constants computed from the published set of coefficients (Millero, 2010, Tables 2 and 3) to those computed with the unpublished yet more precise set of coefficients used by Millero, i.e.,

his spreadsheet for the same publication (F. J. Millero, personal communication 2013). Only the α_5 coefficient differs, having one additional significant figure in the spreadsheet (Table 10). The difference between constants computed with the published coefficients and those computed with unpublished coefficients (Fig. 15) (seawater scale, spreadsheet coefficients) match the pattern and magnitude of the differences between CO2calc and CO2SYS (Fig. 14). Hence CO2calc developers appear to have used the set of coefficients (seawater scale) from Millero's spreadsheet. Given their greater precision and their consistency with original results (Millero, 2010, Fig. 3), it appears that the other package developers should also adopt this more precise set of coefficients designed for the seawater scale, and they should avoid using the sets of coefficients on the total and free scales based on inconsistencies identified in the previous paragraph and in Fig. 15.

Future work is needed though to assess if the number of significant figures of some of these seawater-scale coefficients from the spreadsheet still need to be extended further. The case for need of further improvement comes from our sensitivity tests that compared the analogous sets of coefficients on the total scale (for which the spreadsheet provides much greater precision). That scale's published α_1 for K_1 had to be extended from 4 to 5 significant figures, while corresponding α_5 's for both K_1 and K_2 had to be extended from 4 to 6 significant figures before the results matched those computed with the unpublished spreadsheet coefficients. The much worse agreement among packages found when changing from the Lueker et al. (2000) to the Millero (2010) formulations for K_1 and K_2 emphasizes the danger of applying conclusions from one comparison to cases with different sets of constants.

4.2.3 K_B and K_W : principal non-carbonate alkalinity constants

Previous comparison revealed substantial discrepancies in subsurface variables computed from the swco2 package (Fig. 5–6), which are not due to K_1 and K_2 (Figs. 13). These discrepancies occur only when A_T is a member of the input pair or when A_T is computed, suggesting that they stem from the need in these cases to correct from total

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to carbonate alkalinity. Moreover, carbonate alkalinity itself was ruled out previously. Hence the next most likely cause of these discrepancies is the correction for borate alkalinity. Indeed, comparison of K_B computed by the different packages does reveal discrepancies for swco2 (Fig. 16). Furthermore, swco2's divergence from CO2SYS increases linearly with depth, consistent with discrepancies in computed variables. Although we do not have access to the code for swco2, this discrepancy is consistent with a sign error in its a_2 pressure correction coefficient for K_B . This same error was only identified and corrected in other packages (e.g., in csys and seacarb) in 2010, whereas the current version of swco2 (v2) dates from 2007. Because the a_2 coefficient is multiplied by the square of T_c (Eq. 2), the swco2 discrepancies associated with the pressure correction of K_B are about two orders of magnitude smaller and become negligible when carried out at 2 °C rather than 13 °C.

Discrepancies in the pressure correction for K_B are also evident with csys, although its divergence from CO2SYS (at most ΔpK of 0.002) is 15 times less than for swco2. Inspection of the csys source code found no discrepancies in the related pressure-correction coefficients, but did reveal two other relatively minor code differences that could potentially contribute to the small divergence. First, pressure corrections for K_B and most other constants are designed to be effected on the seawater scale (Millero, 1995). Conversely, csys makes the K_B correction on the total scale. All other packages, convert K_B from the total to the seawater scale, make the pressure correction, and then reconvert K_B back to the total scale. Second, the value of the gas constant R used by csys in the pressure correction is $83.131 \text{ bar cm}^{-3} \text{ mol}^{-1} \text{ K}^{-1}$ instead of the recommended value of 83.14472 (Dickson et al., 2007). The other packages use values for R that are consistent to the third decimal place with the recommended value. However, sensitivity tests with seacarb show that these small differences in R have virtually no effect on computed results.

For related reasons, K_W in csys diverges significantly from CO2SYS, whereas in other packages it does not. These csys package's discrepancies for K_W are larger than for K_B , and they occur at surface conditions as well as at depth. Surface discrepancies

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reach up to $\Delta pK = 0.06$ at high temperatures and at low salinities. Perusal of the csys code reveals that its formulation for K_W corresponds exactly to that given by (Dickson and Goyet, 1994), which is identical to that from (Dickson et al., 2007). Furthermore, csys's computed K_W at $T = 25^\circ\text{C}$, $S = 35$, $P = 0$ db matches the best-practices' check value (Fig. 16). Nonetheless, the other packages prefer to use a more sophisticated formulation. The formulation for K_W is that from Millero (1995), on the seawater scale, for which the best-practice approach subtracts 0.015 as a simple way to convert to the total scale (Dickson and Goyet, 1994; Dickson et al., 2007, Chap. 5, footnote 5). The other packages use the same formulation but do not impose the simple constant offset. Instead, they use the more rigorous, classic approach to convert between the two scales (e.g., Millero, 2010, Eq. 6), resulting in an offset that varies with [HF]. For example, with K_F from Perez and Fraga (1987) the offset ranges from 0 to 0.032 across observed ocean temperatures and salinities; with K_F from Dickson and Riley (1979), it ranges from 0 to 0.024.

All packages but csys also use the variable-offset approach. Another reason for that is to defer the seawater-to-total scale conversion until after the pressure correction, which for K_W (and most other constants) should be done on the original seawater scale. In contrast, csys makes the K_W pressure correction on the total scale, explaining a portion of the discrepancy seen in Fig. 16. A greater part of that discrepancy stems from csys's a_0 , a_1 , and a_2 pressure correction coefficients for K_W , which are intended for fresh water. Conversely, the other packages use the seawater specific coefficients. The three freshwater coefficients from Millero (1983) were erroneously published in a table for seawater by the same author (Millero, 1995, Table 9). Although that artifact was identified in the documentation to CO2SYS (Lewis and Wallace, 1998, Appendix), it was buried among many others, perhaps explaining why other packages have been slow to make this correction. In the seacarb package this error was corrected in its version 2.3.4, released in 2010.

4.2.4 K_F and K_S : constants to change pH scales

For K_F , two packages diverge substantially from CO2SYS under surface conditions, and one of those also exhibits discrepancies at depth. At the surface, csys and seacarb deviate substantially from CO2SYS for salinities below 20, a divergence that grows exponentially to $\Delta pK_F = -0.025$ as salinity approaches zero. Their identical discrepancies suggests that both have the same problem. Inspection of their code reveals that the source of the problem is an incorrect formulation for the ionic strength, which is necessary for the formulation of K_F chosen for this comparison (Dickson and Riley, 1979), i.e., the same as recommended by Dickson and Goyet (1994). Immediately adjacent to the incorrect formulation in both packages, there is another equation that computes the ionic strength correctly, as recommended for best practices, but that equation is not used.

In addition, the divergence for csys grows with depth, e.g., starting with near-zero ΔpK_F at surface pressure ($T = 13^\circ\text{C}$ and $S = 35$) and reaching $\Delta pK_F = -0.015$ at 4000 db. Study of the csys code and follow-up sensitivity tests reveal that this discrepancy is due entirely to an error in the conversion of K_F from the total to the free scale. The conversion between the two scales is straightforward using the classic approach

$$[\text{H}^+]_T = [\text{H}^+]_F (1 + S_T/K_S). \quad (10)$$

where S_T is the total sulfur concentration and K_S the equilibrium constant for bisulfate. The csys package properly incorporates this conversion in the formulation for K_F , but the pressure correction for K_S is done afterwards; the other packages do it beforehand. Hence the pH-scale conversion of K_F is inexact below the surface. That inconsistency explains virtually all of csys's subsurface discrepancy in K_F (Fig. 17). Other issues were also identified in the csys code, including an erroneous value for R and the K_F pressure correction being effected on the total scale instead of the free scale. The effect of former is entirely negligible, while the latter slightly compensates the lack of pressure effect on K_S (e.g., $\Delta pK_F = +0.002$ at 10 000 db). Although these ΔpK 's are

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generally larger than for other constants, they produce only minor consequences. They imply errors in K_F of up to several percent, but K_F is only important when converting between the seawater and total scales, a small difference to start with (e.g., 0.01 pH unit for average seawater).

5 For K_S , all packages essentially agree (ΔpK_S 's always less than 0.0002). There are visible differences for K_S computed from the different packages that merit further investigation (e.g., positive excursions under surface conditions for swco2 and a growing negative divergence with depth for csys) but they are quite small. Given the negligible consequences, we leave their resolution to the package developers.

10 4.2.5 K_A and K_C : solubility products

For K_A , the situation is similar at the surface but not at depth (Fig. 17). Under surface conditions, no packages have significant discrepancies. Although CO2calc appears to have discrepancies larger than other packages (average $\Delta pK_A \sim 0.0002$), they remain quite small; moreover, they may be exaggerated because we had to calculate them from computed variables with limited output precision (2 decimal places for CO_3^{2-}).
15 Pressure-correction discrepancies are negligible in all packages but one, swco2. At 4000 db, the discrepancy for 13 °C water reaches $\Delta pK_A = 0.015$, thereby biasing K_A to be 3.4 % too low and Ω_A to be 3.4 % too high. However, for more usual deep waters at 2 °C, those discrepancies are reduced by a factor of 7. The form of the swco2 discrepancy curve, quadratic with pressure, suggests an error in the b_1 pressure-correction coefficient. Without access to the swco2 source code, we made sensitivity tests with seacarb that confirmed that there is a sign error in swco2's b_1 coefficient for K_A . It should be +0.0003692 as in all other packages. The other swco2 pressure-correction coefficients for K_A appear to be correct.
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4.2.6 Constants for phosphoric and silicic acids

Constants for phosphoric and silicic acid enter into the calculations only when nutrient concentrations are significant and A_T is a member of the input pair. Under those conditions, A_T must be corrected for nutrient alkalinity to provide an accurate estimate of A_C , as needed to compute other variables. For K_{1P} , K_{2P} , and K_{3P} , two packages (seacarb and mocsy) agree with results from CO2SYS across ranges of T , S , and P (Fig. 18). Two other packages (CO2calc and ODV) do not provide these constants as output, nor could they be calculated from available variables.

The two remaining packages, csys and swco2, diverge significantly from CO2SYS, with discrepancies for each being consistent across all three constants. For csys, surface discrepancies in these nutrient constants have the same form and magnitude as already seen for csys's K_W (Fig. 16). The cause is also identical, the 0.015 constant offset proposed for best practices (Dickson et al., 2007) to convert from the seawater to the total scale; the other packages employ the more rigorous variable offset, which varies with T and S . For swco2, discrepancies under surface conditions remain constant across ranges of T and S . They are attributable to using the equations for K_{1P} , K_{2P} , and K_{3P} exactly as given by Dickson et al. (2007), i.e., with 0.015 subtracted from the constant term in each equation (to convert from the seawater to the total scale), but also applying the more rigorous, variable pH-scale correction afterwards. Effectively, swco2 errs by making both corrections instead of just one. The best remedy would be to remove the constant offset and keep the variable correction.

Away from the surface, only one package exhibits pressure-correction discrepancies in K_{1P} , K_{2P} , and K_{3P} , and those remain quite small. The results for csys demonstrate the minor error ($\Delta pK = 0.002$ over 10 000 db) that is associated with making pressure corrections on the total scale instead of the seawater scale, as intended by Millero (1995) and performed in all other packages. At very high pressures (10 000 db), that error partly compensates for taking the simplified approach (-0.015 offset) to change pH scales. Although this small discrepancy is only obvious when other errors are com-

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pletely negligible, it is also detectable in csys's previous results for K_1 , K_2 , and K_B (Figs. 13 and 16).

For K_{Si} , only the swco2 package reveals any discrepancies relative to CO2SYS (Fig. 16). Out of the other packages, two agree with K_{Si} from CO2SYS (seacarb and mocsy), two do not provide K_{Si} as output (CO2calc and ODV), and one does not compute K_{Si} (csys). Discrepancies for K_{Si} in swco2 under surface conditions are identical to those for its K_W , K_{1P} , K_{2P} , K_{3P} . The constant positive excursion of 0.006 is due to correcting K_{Si} from the seawater to the total scale two times, as mentioned for K_{1P} , K_{2P} , and K_{3P} . Below the surface, swco2's discrepancy for K_{Si} grows linearly with pressure, just as does its discrepancy for K_B (Sect. 4.2.3). The cause is identical, a sign error in the a_2 pressure correction coefficient: it should be -0.002608 instead of $+0.002608$. As for K_B , discrepancies in swco2's pressure correction for K_{Si} are lower when carried out at 2°C rather than at 13°C (e.g., ΔpK_{Si} 's of 0.007 and 0.015, respectively, at 4000 db).

5 Conclusions

To assess the consistency of carbonate chemistry software packages, we have compared computed variables from the seven publicly available distributions, identifying discrepancies and their causes. Packages generally agree when using the set of constants recommended for best practices (Dickson et al., 2007). The small discrepancies that do exist become significant in two packages and generally derive from a few constants. The only exception is csys's computed $p\text{CO}_2$, which is about $1\ \mu\text{atm}$ too low at the surface because it mislabels $f\text{CO}_2$ as $p\text{CO}_2$. When compared to $f\text{CO}_2$ in other packages, there is little disagreement. The csys package also has small errors in computed variables associated with pressure corrections of K_1 , K_2 , and K_B , which are carried out on the total scale instead of the seawater pH scale (leading to 0.5% greater values at 4000 db).

Pressure corrections do not contribute other significant differences when packages compute variables in the cold waters that pervade the deep ocean. For isolated warm

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5 deep waters though, such as found in the Mediterranean Sea, the swco2 package produces significant discrepancies, e.g., when $p\text{CO}_2$ and CO_3^{2-} are computed from the A_T-C_T input pair. Those discrepancies derive from a sign error in a pressure-correction coefficient for K_B . Similar sign errors in swco2's pressure-correction coefficients for K_A and K_C also cause Ω_A and Ω_C to be underestimated by 3 % at 4000 db when at 13 °C but only 0.5 % when at 2 °C.

10 Computed variables in the remaining packages (CO2calc, ODV, mocsy, and seacarb) do not differ significantly from CO2SYS, when used with the same set of constants recommended for best practices. Although significant discrepancies in some of those constants were identified, e.g., overestimates in K_F for $S < 10$ in both seacarb and csys (reaching +6 % at $S=0$) due to an error in ionic strength equation, much larger errors in K_F would be needed to significantly alter computed variables. Furthermore, if the best-practices set of constants are considered together, they should not be used at such low salinities nor at very low temperatures. That is, the associated formulations for K_1 and K_2 (Lueker et al., 2000) are not designed to be used in estuaries ($S < 19$) nor in the ocean's coldest waters ($T < 2^\circ\text{C}$), which comprise 11 % of its global surface area and 42 % of its global volume, based on an annual climatology (Locarnini et al., 2010).

20 Consequently, we also compared packages changing only the formulation for K_1 and K_2 to one designed for low-salinity and lower temperature waters (Millero, 2010). Out of the four packages where that newer option is available, mocsy agreed with the CO2SYS reference, whereas CO2calc and seacarb differed significantly, e.g., with surface $p\text{CO}_2$ lower by 5 and 7 μatm , respectively (at $S = 35$ and $T = 18^\circ\text{C}$). The seacarb package differs because it uses the set of published coefficients to compute the salinity-dependence of K_1 and K_2 on the total scale; conversely, CO2SYS and mocsy use another set to compute those constants on the seawater scale, later converting to the total scale. Although results from both approaches should be the same, they are not, indicating a fundamental inconsistency between the two published sets of coefficients. 25 The CO2calc package differs for another reason. Although it uses the set of coefficients

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for the seawater scale, one of its coefficients contains an additional significant figure. The latter comes from the unpublished spreadsheet provided by Millero that was used with the same publication (Millero, 2010). Unfortunately, some of the other published coefficients still appear to lack 1 or 2 significant figures, based on our tests with the spreadsheet coefficients on the total scale, for which there is much greater precision. Once this issue is resolved, the Millero (2010) formulations for K_1 and K_2 may well serve as better alternatives for low salinity waters.

This comparison of computed variables, constants, and source code from the different packages leads us to make several recommendations for both developers and users. Developers would facilitate future validation and improvements by providing computed constants as output and, if possible, by releasing their source code. Developers would enhance reproducibility by providing access to all older versions of their package along with a detailed history of changes. Developers are encouraged to offer the option, if not already available, to use the revised total boron to salinity ratio (Lee et al., 2010), which now appears preferable. Users would facilitate reproducibility by citing in their publications not only the name of the package but also its version number. Larger differences were found here between versions of one package than between all up-to-date packages. Users should use the best-practices set of constants (Dickson et al., 2007) by default, reporting exceptions along with rationale. Although our focus has been on public packages, it is just as necessary to validate privately developed code. To facilitate such validation, we provide a subset of the data that was produced for this comparison in the Supplement.

Supplementary material related to this article is available online at
**[http://www.biogeosciences-discuss.net/11/5327/2014/
bgd-11-5327-2014-supplement.zip](http://www.biogeosciences-discuss.net/11/5327/2014/bgd-11-5327-2014-supplement.zip)**

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Table 1. Carbonate system software packages.

Package	Language	Version	Reference
CO2SYS ^a	DOS	1.05	Lewis and Wallace (1998)
CO2SYS ^b	Excel	14	Pelletier et al. (2007)
CO2SYS ^a	Excel	2.1	Pierrot et al. (2006)
CO2SYS ^a	MATLAB	1.1	van Heuven et al. (2011)
CO2calc ^c	Visual Basic	1.2.0	Robbins et al. (2010)
csys ^d	MATLAB	3	Zeebe and Wolf-Gladrow (2001)
ODV ^e	C++	4.5.0	Schlitzer (2002)
mocsy ^f	Fortran 95	1.2	Orr and Epitalon (2014)
seacarb ^g	R	2.4.8	Lavigne and Gattuso (2011)
swco2 ^h	Excel	2	Hunter (2007); Mosley et al. (2010)
swco2 ^h	Visual Basic	2	Hunter (2007)

^a <http://cdiac.ornl.gov/oceans/co2rprt.html>

^b <http://envsci.rutgers.edu/~reinfelder/aquaticnotes/co2sys.xls>

^c <http://pubs.usgs.gov/of/2010/1280/>

^d http://www.soest.hawaii.edu/oceanography/faculty/zeebe_files/CO2_System_in_Seawater/csyes.html

^e <http://odv.awi.de/>

^f <http://ocmip5.ipsl.jussieu.fr/mocsy>

^g <http://cran.r-project.org/package=seacarb>

^h http://neon.otago.ac.nz/research/mfc/people/keith_hunter/software/swco2/

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**Table 2.** Computational time needed to process global 3-D GLODAP gridded data product.

Package	Total time	Run time	Write time
secarb (R)	1665.3		
swco2 (Excel)	897.1		
CO2calc	91.2		
ODV	73.3		
swco2 (Visual Basic)	28.0		
csys (MATLAB)	7.7		
CO2SYS (MATLAB)	5.9	5.5	0.4
mocsy (Fortran 95)	0.5	0.2	0.3

^a Time in minutes required to treat 958 557 unmasked records

^b All packages run on a 2.0 GHz Intel Pentium dual-core T4200 under Linux or Windows Vista.

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Table 3. Operating system and code details for each package.

OS & details	CO2SYS									
	DOS	Excel	Matlab	CO2calc	ODV	csys	seacarb	swco2	mocsy	
Linux/Unix			•		•	•	•		•	
Windows	•	•	•	•	•	•	•	•	•	
Mac OS		•	•	•	•	•	•		•	
iPhone				•						
Public source code	•	•	•			•	•		•	
User programmable			•			•	•	• ^b	•	
Required software		E ^c	M ^a			M ^a	R	E ^c	F95 ^d	

^a Package works with MATLAB (commercial software) or octave (free software)

^b Spreadsheet interface is not code; Core library is callable (Visual Basic) but not modifiable

^c Package works with Excel (commercial) or LibreOffice (free and open source)

^d Fortran 95 code, which is also callable via python

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Table 4. Available input pairs for each package.

Pair	CO2SYS								
	DOS	Excel	Matlab	CO2calc	ODV	csys	seacarb	swco2	mocsy
A_T-C_T	•	•	•	•	•	•	•	•	•
A_T-pCO_2	•	•	•	•	•		•	•	
A_T-pH	•	•	•	•	•		•	•	
$A_T-CO_3^{2-}$						•	•	•	
A_T-CO_2						•	•	•	
$A_T-HCO_3^-$						•	•	•	
C_T-pCO_2	•	•	•	•	•		•	•	
C_T-pH	•	•	•	•	•		•	•	
$C_T-CO_3^{2-}$						•	•	•	
C_T-CO_2						•	•	•	
$C_T-HCO_3^-$						•	•	•	
pCO_2-pH	•	•	•	•	•	•	•	•	
$pCO_2-CO_3^{2-}$							•	•	
$pCO_2-HCO_3^-$							•	•	
$pH-CO_3^{2-}$						•	•	•	
$pH-CO_2$						•	•	•	
$pH-HCO_3^-$						•	•	•	
$CO_3^{2-}-CO_2$						•	•	•	
$CO_3^{2-}-HCO_3^-$						•	•	•	
$CO_2-HCO_3^-$						•	•	•	

¹ CO2SYS, CO2calc, and ODV also allow input pairs containing fCO_2 instead of pCO_2

² seacarb and swco2 include user callable functions to convert between pCO_2 and fCO_2

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Table 5. Available pH scales for each package.

pH scale	CO2SYS									
	DOS	Excel	Matlab	CO2calc	ODV	csys	seacarb	swco2	mocsy	
NBS	•	•	•	•				•		
Free	•	•	•	•	•	•	•	•		
Total	•	•	•	•	•	•	•	•		•
Seawater	•	•	•	•	•		•	•		
Convert pH between scales			•				•	•		
Convert K's between scales	•						•			

¹ All packages convert pH and K's between scales, internally

² Some packages have user-callable routines to make these conversions between scales

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Table 6. Available constants for each package.

Constant	CO2SYS								
	DOS	Excel ^a	Matlab	CO2calc	ODV	csys	seacarb	swco2	mocsy
K_1 and K_2		•	•	•	•	•	•	•	•
(Lueker et al., 2000)		•	•	•	•	•	•	•	•
(Roy et al., 1993)	•	•	•	•	•	•	•	•	•
(Goyet and Poisson, 1989)	•	•	•	•	•	•	•	•	•
(Hansson, 1973a, b) ^b	•	•	•	•	•	•	•	•	•
(Mehrbach et al., 1973) ^b	•	•	•	•	•	•	•	•	•
(Millero, 1979)	•	•	•	•	•	•	•	•	•
(Mojica Prieto and Millero, 2002)		•	•	•	•	•	•	•	•
(Cai and Wang, 1998)		•	•	•	•	•	•	•	•
(Millero et al., 2006)		•	•	•	•	•	•	•	•
(Millero, 2010)		•	•	•	•	•	•	•	•
K_0 (Weiss, 1974)	•	•	•	•	•	•	•	•	•
K_B (Dickson, 1990b)	•	•	•	•	•	•	•	•	•
K_F (Perez and Fraga, 1987)		•	•	•	•	•	•	•	•
K_F (Dickson and Riley, 1979)	•	•	•	•	•	•	•	•	•
K_W (Millero, 1995)	•	•	•	•	•	•	•	•	•
K_S (Dickson, 1990a)	•	•	•	•	•	•	•	•	•
K_S (Khoo et al., 1977)	•	•	•	•	•	•	•	•	•
K_{1P} , K_{2P} , K_{3P} (Millero, 1995)	•	•	•	•	•	•	•	•	•
K_{Si} (Millero, 1995)	•	•	•	•	•	•	•	•	•
K_A (Mucci, 1983)	•	•	•	•	•	•	•	•	•
K_C (Mucci, 1983)	•	•	•	•	•	•	•	•	•

^a Excel version of CO2SYS from Pierrot et al. (2006)

^b refit by Dickson and Millero (1987)

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Table 7. Coefficients used in Eqs. (2) and (3) to correct for effect of pressure on equilibrium constants.

K	a_0	a_1	a_2	b_0	b_1	b_2
K_1	-25.50	0.1271	0	-0.00308	0.877×10^{-4}	0
K_2	-15.82	-0.0219	0	0.00113	-1.475×10^{-4}	0
K_B	-29.48	0.1622	-0.002608	-0.00284	0	0
K_W	-20.02	0.1119	-0.001409	-0.00513	0.794×10^{-4}	0
K_S	-18.03	0.0466	0.000316	-0.00453	0.900×10^{-4}	0
K_F	-9.78	-0.0090	-0.000942	-0.00391	0.540×10^{-4}	0
K_C	-48.76	0.5304	0	-0.01176	3.692×10^{-4}	0
K_A	-46.00	0.5304	0	-0.01176	3.692×10^{-4}	0
K_{1P}	-14.51	0.1211	-0.000321	-0.00267	0.427×10^{-4}	0
K_{2P}	-23.12	0.1758	-0.002647	-0.00515	0.900×10^{-4}	0
K_{3P}	-26.57	0.2020	-0.003042	-0.00408	0.714×10^{-4}	0
K_{hs}	-14.80	0.0020	-0.000400	0.00289	0.540×10^{-4}	0
K_n	-26.43	0.0889	-0.000905	-0.00503	0.814×10^{-4}	0
K_{Si}	-29.48	0.1622	-0.002608	-0.00284	0	0

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Table 8. Desired measurement and numerical uncertainties.

Variable	Uncertainties		Units
	Measurement	Numerical	
A_T	1	0.1	$\mu\text{mol kg}^{-1}$
C_T	1	0.1	$\mu\text{mol kg}^{-1}$
$p\text{CO}_2$	1	0.1	μatm
CO_3^{2-}	1	0.1	$\mu\text{mol kg}^{-1}$
pH	0.003	0.0003	
pK_0	0.002	0.0002	
pK_1	0.01	0.001	
pK_2	0.02	0.002	
pK_i (other)	0.01	0.001	

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Table 9. Ratio of relative change between output and input variables $(\partial y/y) / (\partial x/x)$.

Output	Input											
	A_T	C_T	K_0	K_1	K_2	K_B	K_W	K_S	K_F	K_A	K_C	
CO_2^*	-9.5	11.7		-0.92	0.63	0.28	0.02					
HCO_3^-	-0.7	1.7		0.01	-0.03	0.02						
CO_3^{2-}	8.8	-7.4		-0.05	0.30	-0.24	-0.01					
H^+	-8.8	9.8		0.06	0.66	0.26	0.01					
$p\text{CO}_2$	-9.5	11.7	-0.99	-0.92	0.63	0.28	0.02					
$f\text{CO}_2$	-9.5	11.7	-0.99	-0.92	0.63	0.28	0.02					
Ω_A	8.8	-7.4		-0.05	0.30	-0.24	-0.01			-0.99		
Ω_C	8.8	-7.4		-0.05	0.30	-0.24	-0.01					-0.99

¹ Percent change in output (dy/y) computed from a 1 % change in input (dx/x) .

² Missing values indicate changes of less than 0.001 %.

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Table 10. Coefficients from Millero (2010) for K_1 and K_2 formulations (seawater scale).

	K_1	K_2
α_0	13.4038	21.3728
α_1	0.03206	0.1218
α_2	-5.242×10^{-5}	-3.688×10^{-4}
α_3	-530.659	-788.289
α_4	-5.8210	-19.189
α_5	-2.0664	-3.374 ^a

^a Value is -3.3738 in Millero's spreadsheet (F. J. Millero, personal communication 2013).

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Table 11. Check values vs. computed equilibrium constants (pK 's) at $T = 25^\circ\text{C}$, $S = 35$, $P = 0$.

	pK_0	pK_1	pK_2	pK_B	pK_W	pK_S^1	pK_F^1
Check value	1.5468	5.8472	8.966	8.5975	13.217	0.999	2.627
swco2	1.54680	5.84720	8.96600	8.59750	13.2204	0.9987	2.6261
mocsy	1.54680	5.84720	8.96600	8.59750	13.2173	0.9987	2.6261
CO2SYS	1.54681	5.84715	8.96595	8.59747	13.2204	0.9987	2.6261
csys	1.54681	5.84715	8.96595	8.59747	13.2173	0.9987	2.6260
seacarb	1.54681	5.84715	8.96595	8.59747	13.2206	0.9987	2.6260
CO2calc	1.54681	5.85643	8.97522	8.59697	13.2200		
ODV	1.54681	5.84715	8.96595				

¹ free scale (all other pK s are on total scale)

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Table 11. Continued.

	pK_C	pK_A	pK_{1P}	pK_{2P}	pK_{3P}	pK_{Si}
Check value			1.61	5.962	8.79	9.39
swco2	6.3693	6.1883	1.6220	5.9715	8.799	9.394
mocsy	6.3693	6.1883	1.6120	5.9618	8.789	9.384
CO2SYS	6.3693	6.1883	1.6150	5.9649	8.793	9.387
csys	6.3693	6.1883	1.6119	5.9618	8.789	
seacarb	6.3693	6.1883	1.6152	5.9652	8.7927	9.3872
CO2calc	6.3696	6.1884				
ODV	6.3693	6.1883				

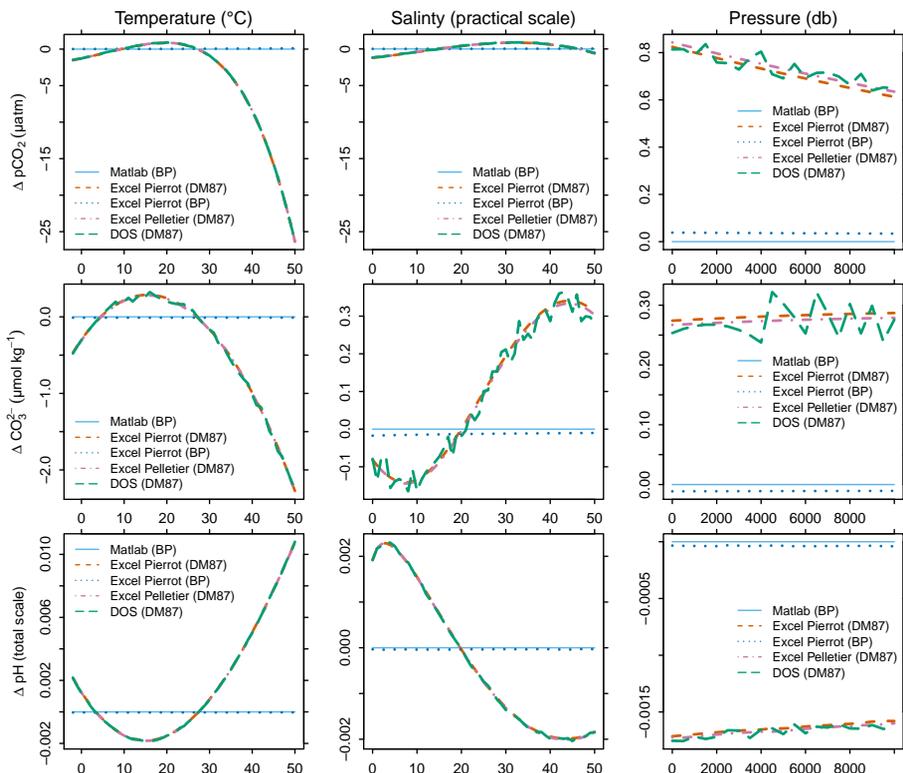


Fig. 1. Differences (Δ) between the 4 versions of CO2SYS relative to the reference (MATLAB code) for variables computed from C_T and A_T . Differences are shown across ranges of T (left), S (center), and P (right) for $p\text{CO}_2$ (top), CO_3^{2-} (middle), and pH (bottom). The two most recent versions (MATLAB and Pierrot's Excel version) are run with constants recommended for best practices (BP). The two legacy codes (DOS and Pelletier's Excel version) do not offer the same K_1 and K_2 , so we used an earlier refit by Dickson and Millero (1987) of the same data (DM87).

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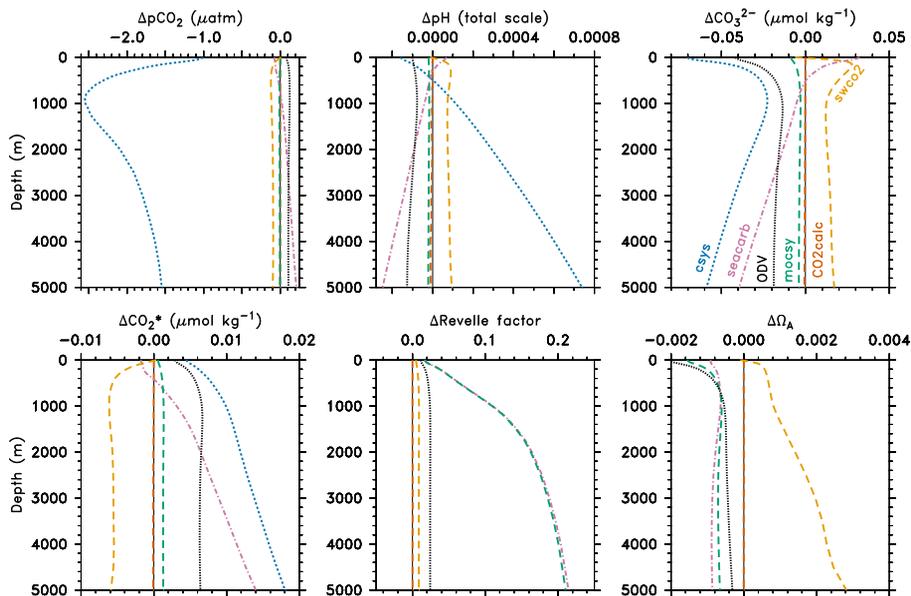


Fig. 2. Global-mean vertical profiles of variables computed from gridded data products for C_T and A_T from GLODAP (Key et al., 2004) combined with T , S , and nutrients from the 2009 World Ocean Atlas (WOA2009) (Locarnini et al., 2010; Antonov et al., 2010; Garcia et al., 2010). Results are shown for each software package after subtracting off corresponding results from the reference (CO2SYS-MATLAB). The csys package does not provide results for R and Ω_A (bottom center and right).

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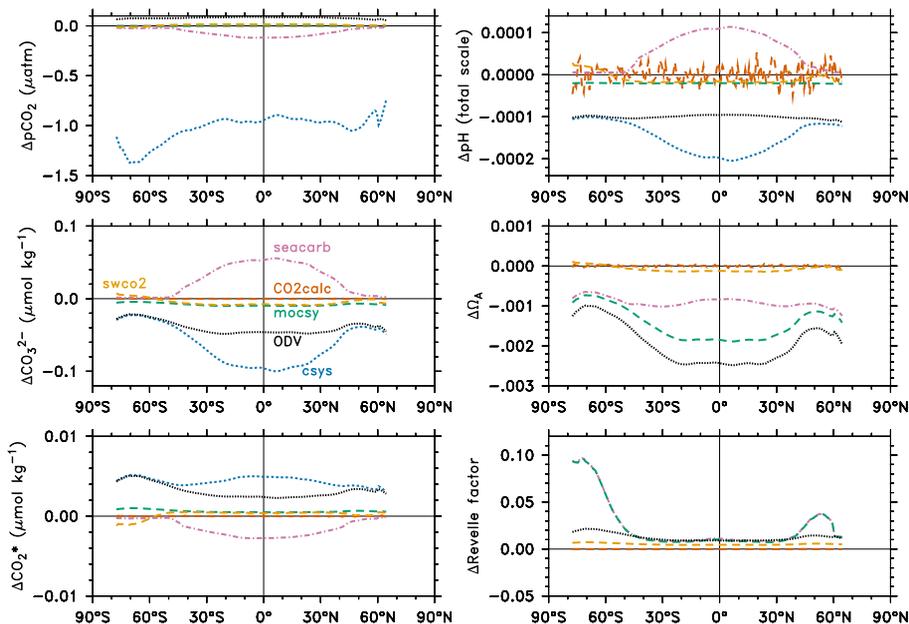


Fig. 3. Global zonal-mean surface values for variables computed from GLODAP C_T and A_T as in Fig. 2. Curves are shown for each package and variable after subtracting off corresponding results for the CO2SYS reference. The csys packages does not provide results for Ω_A and R (middle right and bottom right).

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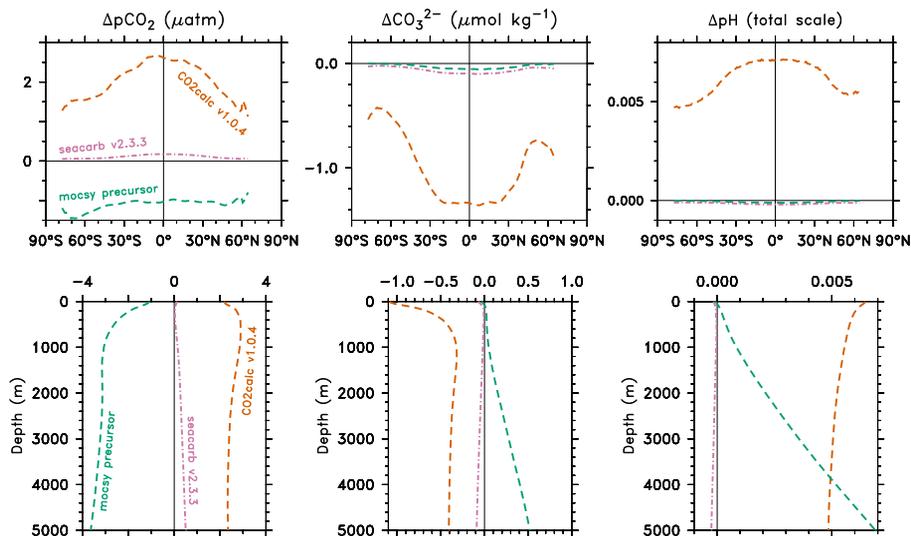


Fig. 4. Global zonal-mean surface values (top) and global-mean vertical profiles (bottom) from outdated versions of packages for $p\text{CO}_2$ (left), CO_3^{2-} (middle), and pH (right) as computed from GLODAP C_T and A_T as in Figs. 2 and 3. The three older versions include CO2calc (v1.0.4), seacarb (v2.3.3), and mocsy (non public precursor from Orr et al., 2005). As before, results are shown after subtracting off corresponding results from the same CO2SYS reference.

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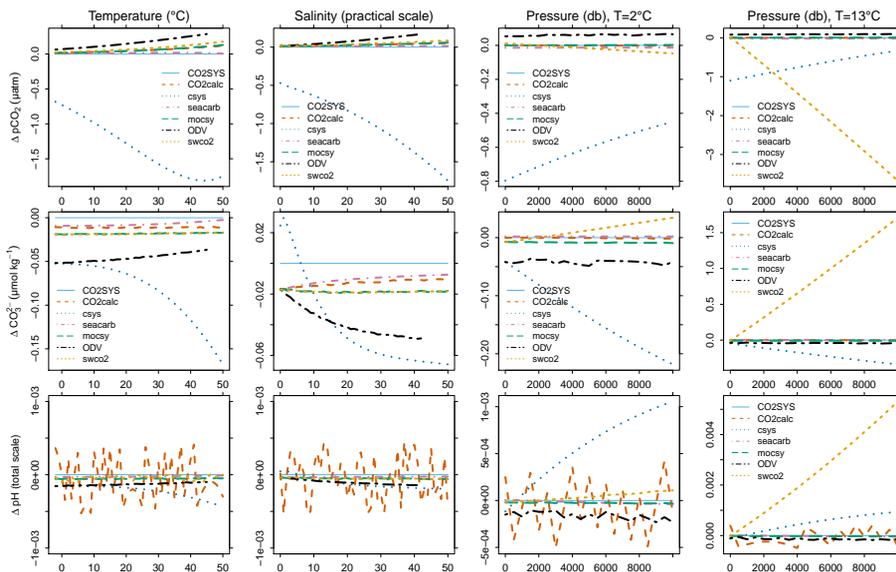


Fig. 5. Variables computed from A_T-C_T for each package minus corresponding results from CO2SYS. The computed $p\text{CO}_2$ (top), CO_3^{2-} (middle), and pH (bottom) are shown across ranges of T (column 1), S (column 2), and P when $T = 2^\circ\text{C}$ (column 3), and when $T = 13^\circ\text{C}$ (column 4). For each range, there is one curve per package and per variable.

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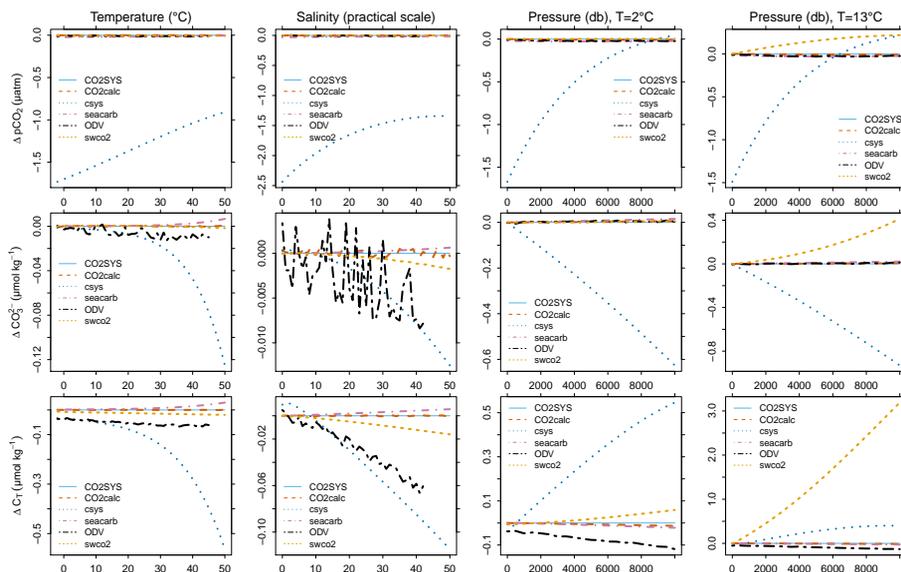


Fig. 6. Variables computed from A_T - pH with each package minus corresponding results from CO2SYS. Shown are computed pCO_2 (top), CO_3^{2-} (middle), and C_T (bottom) across ranges of T (column 1), S (column 2), and P when $T = 2^\circ C$ (column 3) and when $T = 13^\circ C$ (column 4).

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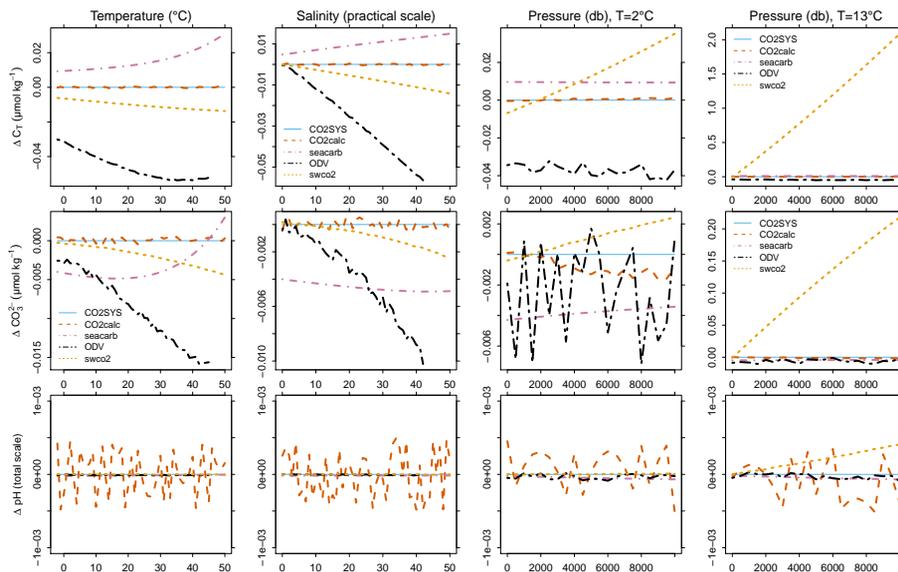


Fig. 7. Variables computed from A_T – $p\text{CO}_2$ with each package minus corresponding results from CO2SYS. Shown are computed C_T (top), CO_3^{2-} (middle), and pH (bottom) across ranges of T (column 1), S (column 2), and P when $T = 2^\circ\text{C}$ (column 3) and when $T = 13^\circ\text{C}$ (column 4) for each of the six software packages. Packages not included are mocsy, which allows only the A_T – C_T pair, and csys, which does not allow $p\text{CO}_2$ as an input variable.

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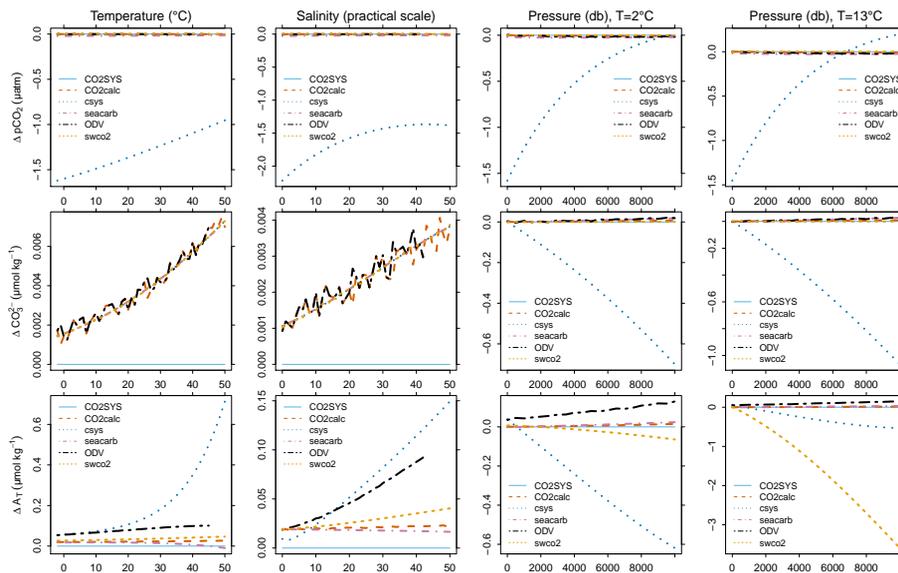


Fig. 8. Variables computed from C_T -pH with each package minus corresponding results from CO2SYS. Shown are computed $p\text{CO}_2$ (top), CO_3^{2-} (middle), and A_T (bottom) across ranges of T (column 1), S (column 2), and P when $T = 2^\circ\text{C}$ (column 3) and when $T = 13^\circ\text{C}$ (column 4) for the six software packages.

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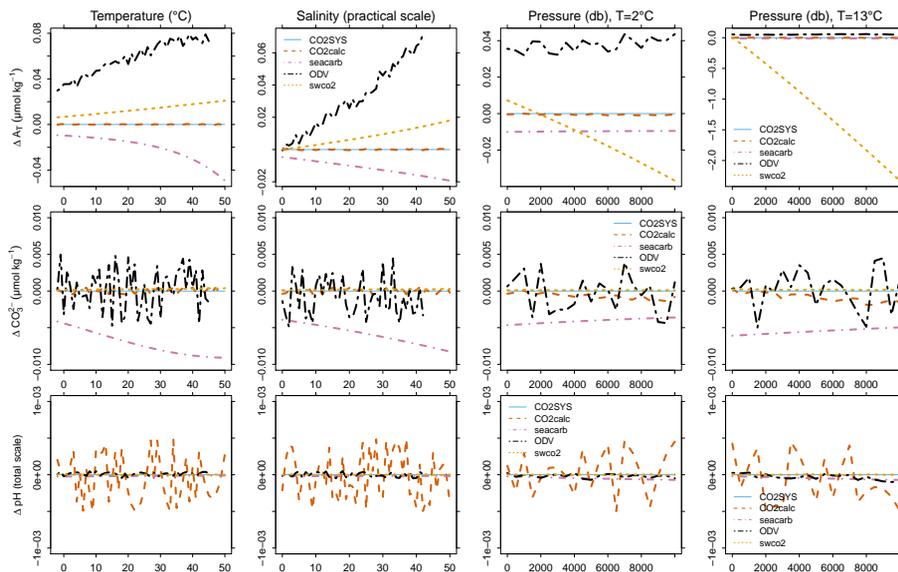


Fig. 9. Variables computed from C_T – $p\text{CO}_2$ with each package minus corresponding results from CO2SYS. Shown are computed A_T (top), CO_3^{2-} (middle), and pH (bottom) across ranges of T (column 1), S (column 2), and P when $T = 2^\circ\text{C}$ (column 3) and when $T = 13^\circ\text{C}$ (column 4) for six software packages.

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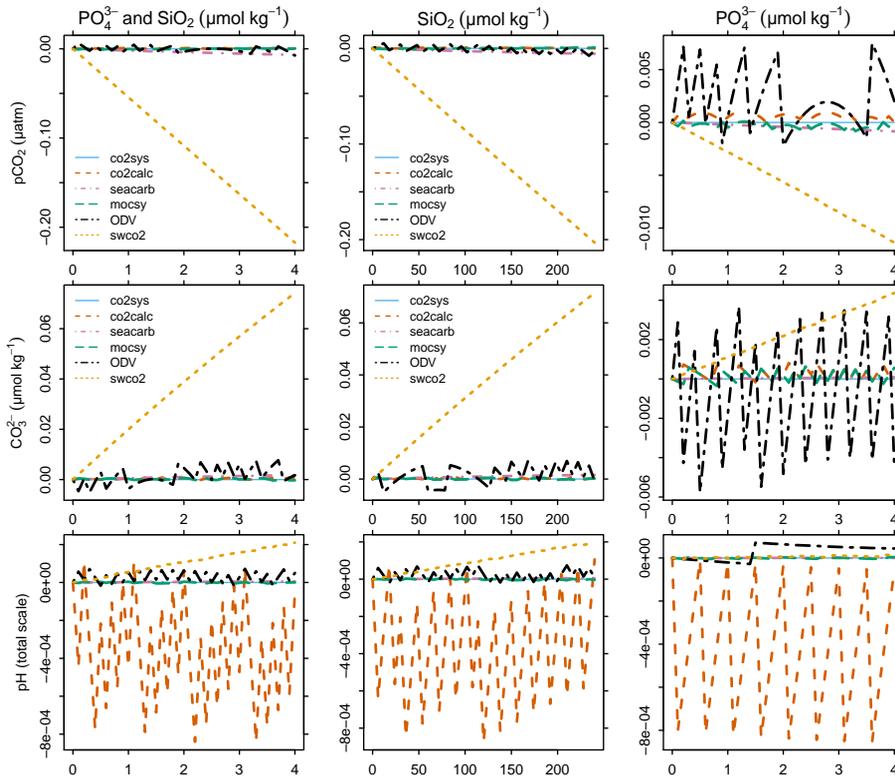


Fig. 10. Effect of nutrients on variables computed from $C_T - A_T$ with each package minus results for CO2SYS. Shown are effects on computed $p\text{CO}_2$ (top), CO_3^{2-} (middle), and pH (bottom) across the observed oceanic ranges of PO_4^{3-} (right), SiO_2 (center), and their combined effect (left) for six software packages. Results for csys are not included as it assumes that nutrient concentrations are always zero.

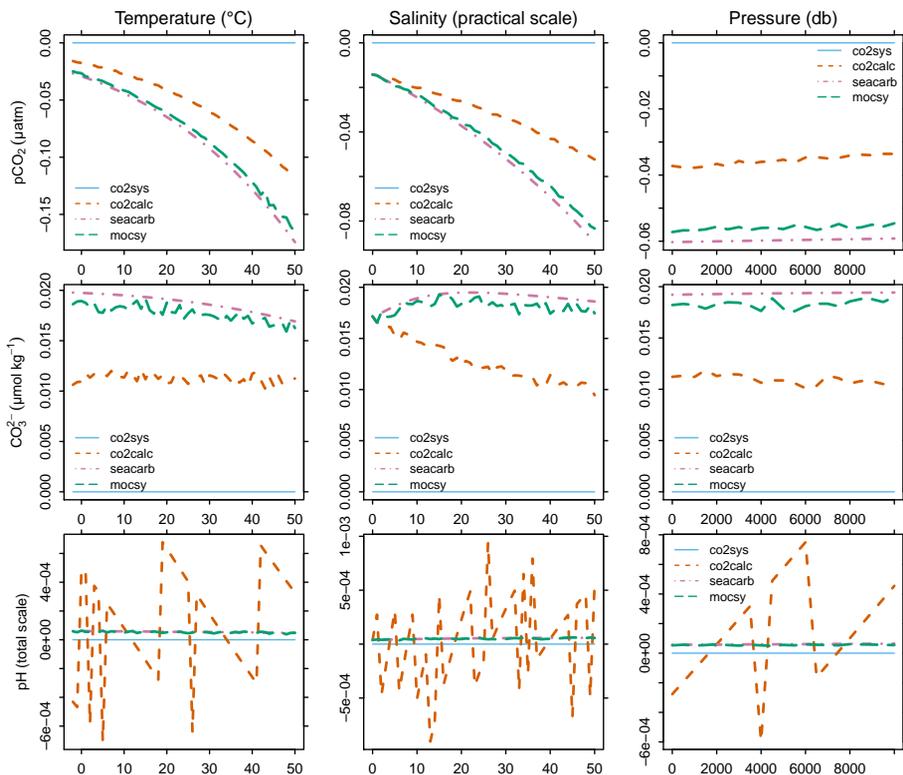


Fig. 11. Effect of increased total boron on variables computed from $C_T - A_T$. Shown are the effects of the increased boron (Lee et al., 2010 minus Uppström, 1974) on computed $p\text{CO}_2$ (top), CO_3^{2-} (middle), and pH (bottom) across ranges of T (left), S (center), and P (right). The Lee et al. (2010) formulation is included in 3 packages (CO2SYS, seacarb, and mocsy). The recommendation to use the Uppström (1974) formulation by Dickson et al. (2007) came before the Lee et al. (2010) study.

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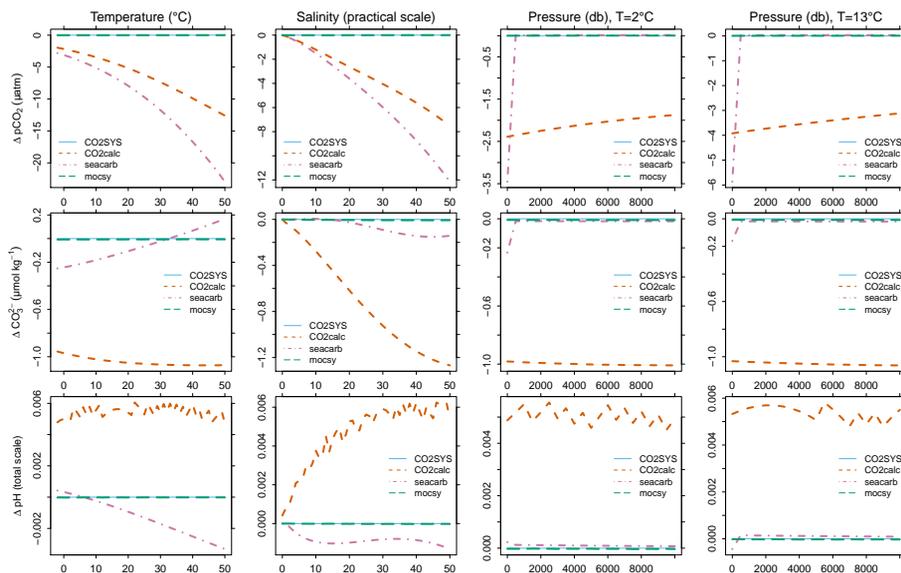


Fig. 12. Variables computed from $C_T - A_T$ with each package minus corresponding results from CO2SYS, as in Fig. 9 but with K_1 and K_2 from Millero (2010) instead of from Lueker et al. (2000). Shown are computed $p\text{CO}_2$ (top), CO_3^{2-} (middle), and pH (bottom) across ranges of T (column 1), S (column 2), and P when $T = 2^\circ\text{C}$ (column 3) and when $T = 13^\circ\text{C}$ (column 4). Only four packages (CO2SYS, CO2calc, seacarb, and mocsy) include this newer option.

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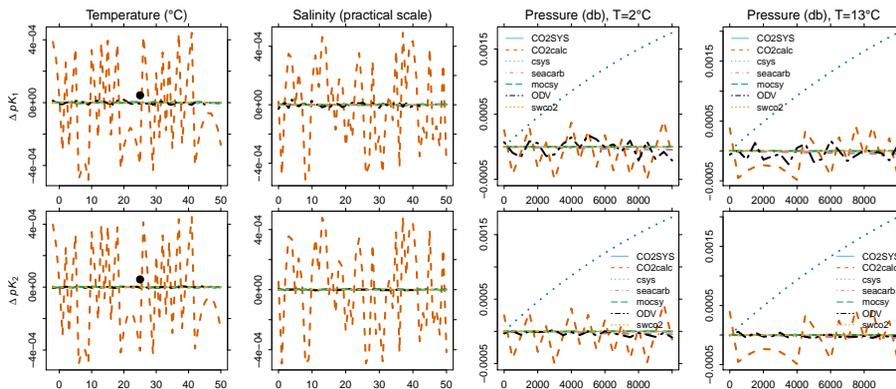


Fig. 13. The pK_1 (top) and pK_2 (bottom) computed with each package minus corresponding values for CO2SYS. Formulations are those recommended for best practices, namely K_1 and K_2 from (Lueker et al., 2000). Constants were computed across the same ranges of T (column 1), S (column 2), and P when $T = 2^\circ\text{C}$ (column 3) and when $T = 13^\circ\text{C}$ (column 4) as used in previous figures. Constants from CO2calc and ODV were not directly available but are estimated from variables computed with the A_T – C_T pair. The filled black circles indicate the check values (Table 11).

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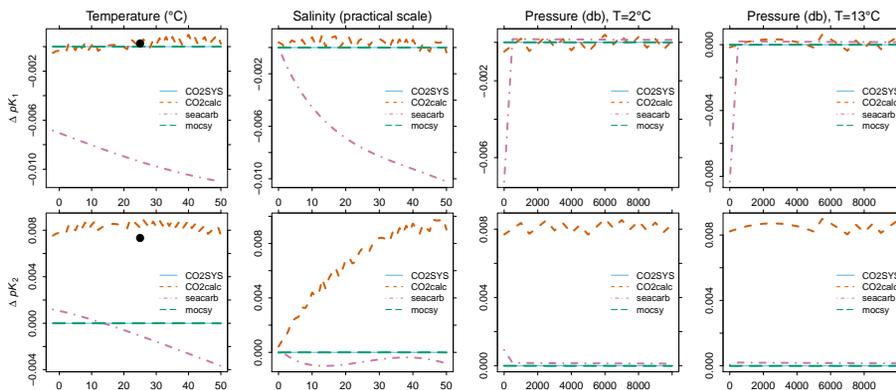


Fig. 14. The pK_1 (top) and pK_2 (bottom) computed in each of four packages minus corresponding values for CO2SYS, as in Fig. 13 except that formulations are from Millero (2010), not Lueker et al. (2000). The filled black circles indicate the check values (Table 11).

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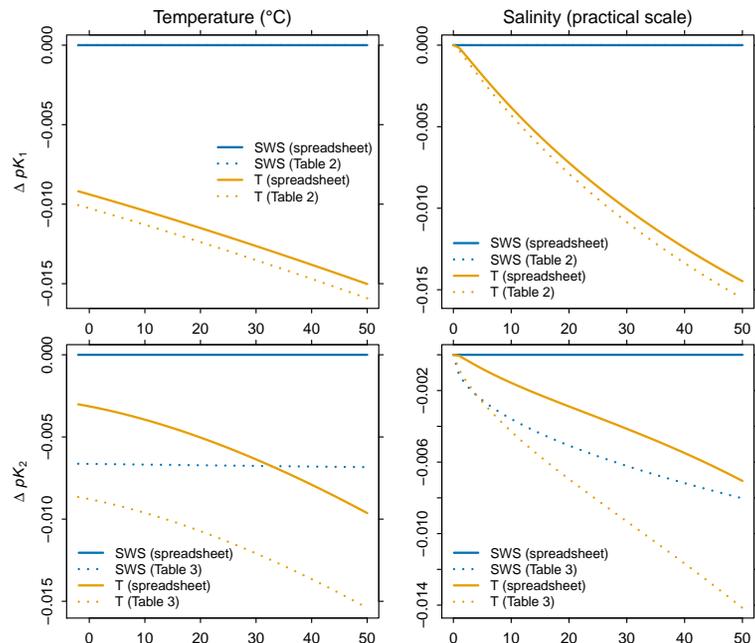


Fig. 15. Relative differences between four formulations for pK_1 (top) as well as pK_2 (bottom), i.e., between values computed from four different sets of coefficients from Millero (2010) over ranges of T (left) and S (right). Two sets of coefficients are from Millero’s (2010) Tables 2 and 3, i.e., for the total scale (T , orange dotted line) and the seawater scale (SWS, blue dotted line). The two other sets, also on the T and SWS scales (solid lines), have greater precision, coming from the spreadsheet used for calculations in the same publication (F. J. Millero, personal communication 2013). For consistent comparison, both SWS curves were converted to the total scale using the standard approach (Millero, 2010, Eqs. 11 and 12) and K_F from Perez and Fraga (1987). Curves are shown after subtracting values from the preferred formulation (spreadsheet coefficients for the SWS scale converted to the T scale).

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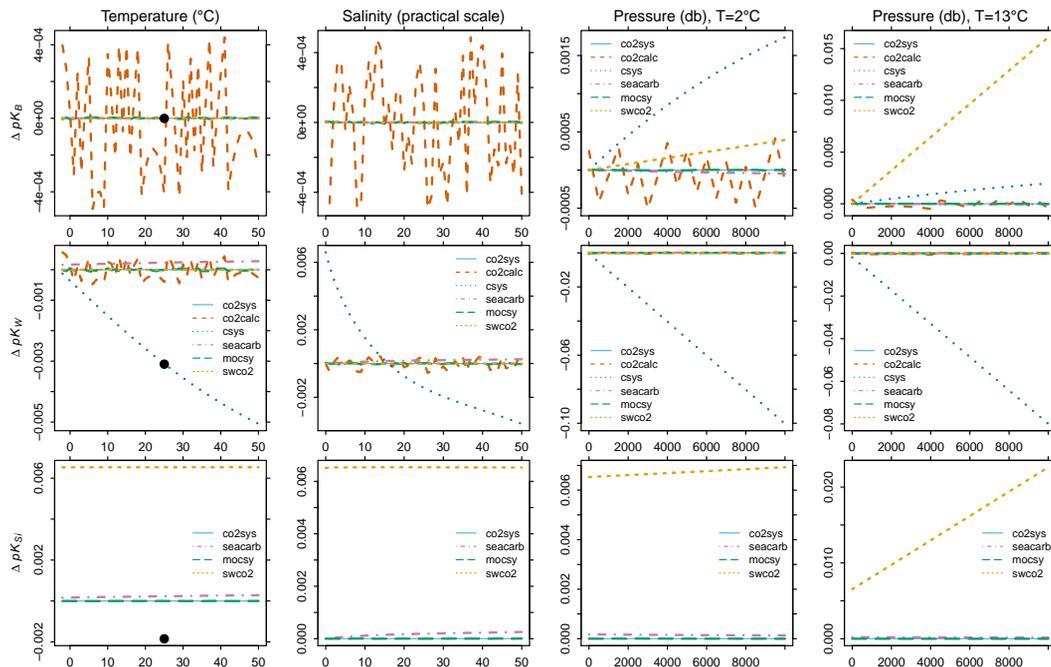


Fig. 16. The pK_B (top), pK_W (middle) and pK_{Si} (bottom) computed from each package minus corresponding values from CO2SYS. Formulations are from Millero (1995), as recommended for best practices. The filled black circles indicate the check values (Table 11).

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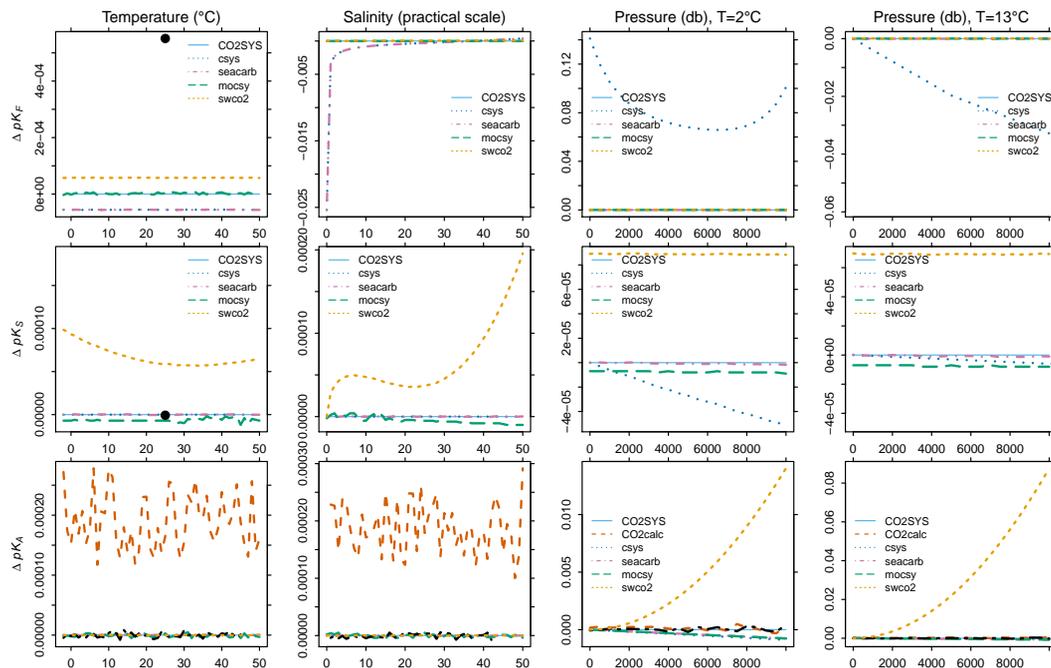


Fig. 17. The pK_F (top), pK_S (middle) and pK_A (bottom) computed from each package minus corresponding values from CO2SYS. The formulation for K_F is from Dickson and Riley (1979) as recommended by Dickson and Goyet (1994), with all packages on the free scale. The formulation for K_S is from Dickson (1990a) and on the free scale, while that for K_A is from Mucci (1983) with no scale, as recommended for best practices. The filled black circles indicate check values (Table 11).

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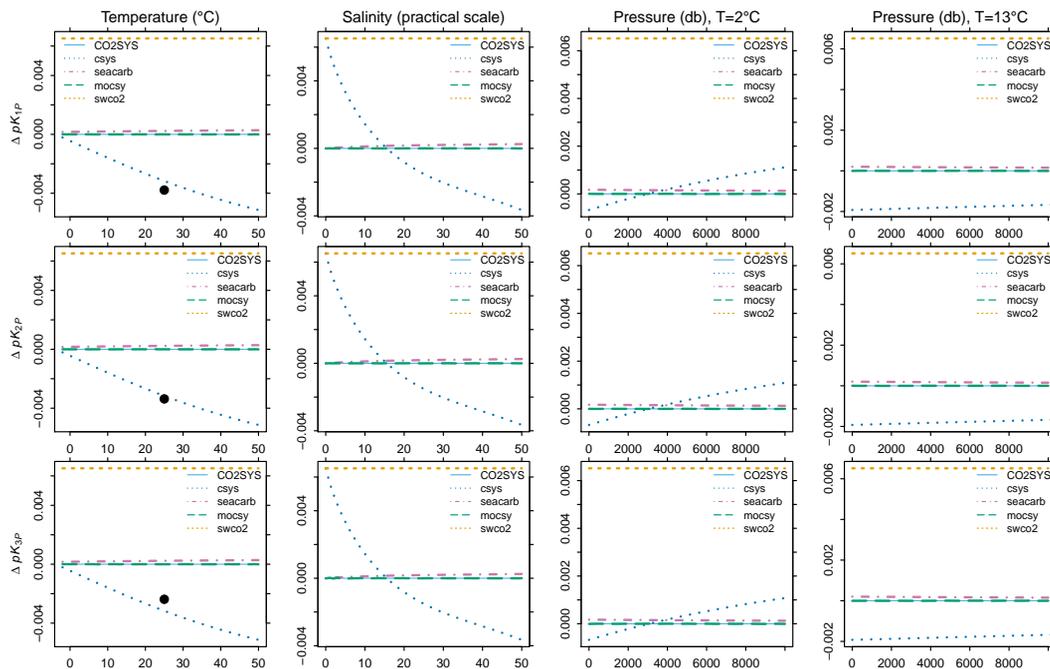


Fig. 18. The pK_{1P} (top), pK_{2P} (middle) and pK_{3P} (bottom) computed from each package minus corresponding values from CO2SYS. Formulations are from Millero (1995), as recommended for best practices. Constants are computed across the same ranges of T (column 1), S (column 2), and P when $T = 2^\circ\text{C}$ (column 3) and when $T = 13^\circ\text{C}$ (column 4) as used in previous figures. The filled black circles indicate the check values (Table 11).

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