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

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Comment on "Comparison of seven packages that compute ocean carbonate chemistry," by J. C. Orr, J.-M. Epitalon, and J.-P. Gattuso, in Biogeosciences Discuss., 11, 5327-5397, 2014, by Ernie R. Lewis and Douglas. W. R. Wallace.

We read with interest the manuscript comparing the various packages that calculate parameters of the CO2 system in seawater and would like to commend the authors for their authoritative comparison of these programs. We found the review insightful, balanced, and informative, and were amused to see that conversions among pH scales and pressure corrections remain a source of mystery, error, and ambiguity, as they have for the last 20-odd years. We have one minor comment on the manuscript: that the programming language for the original CO2SYS be listed as QBasic rather than

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

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

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

The online help feature in the original CO2SYS, albeit perhaps a bit crude by today's

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

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

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it readily illustrates how accurately the calculated quantities can be determined.

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

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

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Version 1.03 only cosmetically (typos corrected, more efficient codes, etc.), and no differences exist between calculations performed using these versions and Version 1.03. The original CO2SYS was written in QBasic, which we chose because it ran on any 80x86 computer with the DOS operating system by typing the program name on the command line. We intended that the program could be used for decades: in our infinite wisdom, despite the advent of early versions of Windows, we felt that DOS would be the operating system of the future and we placed our bets on this. In our defense, it was probably the best choice at the time: an executable file could be created and distributed and it would run on any DOS-based computer without the necessity to install anything else (the same cannot be said for MATLAB or other programs, which require more than merely an executable to run). The program did not run on Macs, although they were not as common back then. Computers were very different back then, in ways that are probably difficult for younger programmers to understand. CO2SYS had to be broken into two parts and compiled separately, then combined. Lest this give the impression that it was a large program, consider the following text from the program: "PROGRAMMER'S NOTE: This program is DANGEROUSLY close to the DOS-imposed 64K limit . . . Don't make any unnecessary changes or the limit will be exceeded."

As stated above, there was a large section in the CO2SYS report on typographic errors in the literature. One common feature in oceanographic papers not seen in other fields is the use of check values for expressions for dissociation constants and other quantities; i.e., the value of the expression at a specified set of conditions (salinity, temperature, pressure). These check values are of immense help in determining if coefficients are listed correctly in the manuscript and if they are incorporated correctly in computer codes. Errors in listed coefficients on if their transcription can cost hours of time, in addition to leading to incorrect values. Thus, a compilation of such errors would be very useful for the community. We had compiled such a list while writing CO2SYS, which we were originally hesitant about presenting publicly, for several obvious reasons. However, Rik Wanninkhof convinced us that making this list available would be a service to the community, and we think that it has been. Considering how often such

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typographic errors continue to appear in the literature, we recommend that the outdated version on the CDIAC website (http://cdiac.ornl.gov/oceans/co2rprt.html#typos) be updated and made available. Perhaps this manuscript will prompt those who have updated CO2SYS or similar programs by including more recent constants will make those available and someone will come forward to collate and publish them.

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