Florida Shelf Ecosystems Response to Climate Change Project

CO2calc: A User-Friendly Seawater Carbon Calculator for Windows, Mac OS X, and iOS (iPhone)

Open-File Report 2010–1280

U.S. Department of the Interior
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By L.L. Robbins, M.E. Hansen, J.A. Kleypas, and S.C. Meylan

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CO2calc: A User-Friendly Seawater Carbon Calculator for Windows, Mac OS X, and iOS (iPhone)

By L.L. Robbins,[1] M.E. Hansen,[1] J.A. Kleypas,[2] and S.C. Meylan[3]

Introduction

A user-friendly, stand-alone application for the calculation of carbonate system parameters was developed by the U.S. Geological Survey Florida Shelf Ecosystems Response to Climate Change Project in response to its Ocean Acidification Task. The application, by Mark Hansen and Lisa Robbins, USGS St. Petersburg, FL, Joanie Kleypas, NCAR, Boulder, CO, and Stephan Meylan, Jacobs Technology, St. Petersburg, FL, is intended as a follow-on to CO2SYS, originally developed by Lewis and Wallace (1998) and later modified for Microsoft Excel® by Denis Pierrot (Pierrot and others, 2006). Besides eliminating the need for using Microsoft Excel on the host system, CO2calc offers several improvements on CO2SYS, including:

- An improved graphical user interface for data entry and results
- Additional calculations of air-sea CO_2 fluxes (for surface water calculations)
- The ability to tag data with sample name, comments, date, time, and latitude/longitude
- The ability to use the system time and date and latitude/longitude (automatic retrieval of latitude and longitude available on iPhone® 3, 3GS, 4, and Windows® hosts with an attached National Marine Electronics Association (NMEA)-enabled GPS)
- The ability to process multiple files in a batch processing mode
- An option to save sample information, data input, and calculated results as a comma-separated value (CSV) file for use with Microsoft Excel, ArcGIS,® or other applications
- An option to export points with geographic coordinates as a KMZ file for viewing and editing in Google Earth™

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Background

While CO2calc expands on the functionality of CO2SYS, much of the code of the latter program was adopted with minimal changes to ensure back-compatibility. The Visual Basic.Net code for the Windows version of CO2calc is from the Excel VBA code of Pierrot and others (2006), which was in turn based on the Visual Basic program CO2SYS.BAS by Ernie Lewis. For questions about the original CO2SYS, the reader is referred to the CO2SYS documentation at *http://cdiac.ornl.gov/oceans/co2rprt.html#aboutco2sys*. For specific information regarding the Excel VBA code of Pierrot and others (2006), contact *dpierrot@rsmas.miami.edu* or *denis.pierrot@noaa.gov*. The modification of the CO2SYS program for CO2calc included the deletion of unused code, the addition of CO_2 constants from Lueker and others (2000) and Millero (2010), and the addition of code to calculate air-sea CO_2 fluxes. For the Mac OS® X and iOS versions, this augmented "core" code was translated to C++ and the interface for each platform was written in Objective-C, making use of Apple's Cocoa® (Mac OS X) and Cocoa Touch® (iOS) frameworks.

The Windows version of CO2calc runs on Windows XP, Vista, and 7. The Mac OS X version runs on computers with 64-bit-processors running Mac OS 10.5 (Leopard®) or 10.6 (Snow Leopard®). The iOS version runs on 2d, 3d, and 4th generation iPhones running iOS 3 and iOS 4. For GPS functionality in Windows, an attached GPS with NMEA output is required. For GPS functionality in iOS, an iPhone 3, 3GS, or 4 is required.

As in the Pierrot and others (2006) Excel VBA code, the user provides two of the five measurable CO_2 system parameters:

1. total alkalinity (TA),
2. total carbon dioxide (TCO_2),
3. pH, and
4. partial pressure of carbon dioxide (pCO_2) *or*
5. fugacity of carbon dioxide (fCO_2).

Along with these two, temperature (T), pressure (P), and salinity (S) must be entered. Concentrations of nitrate and phosphate are optional. CO2calc then calculates the concentrations

of the two remaining CO_2 system parameters, the Revelle factor, and the saturation states (Ω) for aragonite and calcite. An output temperature and pressure may be specified to calculate system parameters at in situ conditions. As is the case with the Excel version of CO2SYS, CO2calc does not calculate the sensitivity of the output to the input, referred to as "Partials" in the original program of Lewis and Wallace (1998).

The original developers of CO2SYS made special effort to provide a variety of constants for use in calculating carbonate parameters. In developing CO2calc we have left these original constants unchanged and added an additional two, as well as the ability to specify different scales for wind speed and different gas transfer velocities in the calculation of air-sea flux. All CO2SYS documentation has been replicated in the appendix, both for consistency and to ensure user access to this information. Where appropriate, it has been augmented. We kindly acknowledge Lewis and Wallace (1998) and Pierrot and others (2006) for permission to reproduce this documentation.

CO2calc follows CO2SYS by allowing for a variety of options and provides additional capabilities, including (new features are denoted with asterisks):

- The choice of various formulations for dissociation constants for carbonic acid (K1 and K2), *including Lueker and others (2000) and Millero (2010)
- Two distinct formulations for the dissociation constant for potassium sulfate ($KHSO_4$), including Dickson (1990a) and Khoo and others (1977)
- The choice of four pH scales (free, total, seawater, or NBS)
- The use of either fugacity (fCO_2) or partial pressure (pCO_2) of CO_2
- *The choice of using CO_2 gas transfer velocity as computed by Wanninkhof (1992), Nightingale and others (2000), or Ho and others (2006)
- The choice of any two CO_2 system parameters as input (except both fCO_2 and pCO_2)

As input, CO2calc accepts:

- salinity
- input temperature and pressure (or depth)
- concentrations of silicate and phosphate
- two known CO_2 system parameters at the input conditions
- *wind speed, in either knots or meters per second
- output temperature and pressure

If output temperature and pressure are not specified, CO2calc provides the following at input conditions:

- The remaining CO_2 system parameters
- TA and TCO_2 (invariant with temperature and pressure) are used to calculate the pH and fCO_2 (or pCO_2) at the output conditions
- fCO_2 and pCO_2
- contributions to the alkalinity and carbon speciation
- omega (the degree of saturation) for calcite and for aragonite
- the Revelle, or homogeneous buffer, factor
- pH values on the selected pH scale
- the values of pK_1, pK_2, pK_W, and pK_B
- *air-sea CO_2 flux (if wind speed and pCO_2 of air are provided)

If output pressure and (or) temperature is specified, CO2calc provides the aforementioned results at input conditions as well as a set adjusted for the specified output temperature and pressure. Note that there are slight differences in results between CO2calc and the Microsoft Excel/VBA version attributable to differences in rounding procedures. The results of CO2calc are consistent across platforms and are in all cases rounded to three digits after the decimal point.

Additional Features

Additional Constant from Lueker and Others (2000)

Based on the recommendations of Dickson and others (2007), we have added the option of using K_1 and K_2 of carbonic acid as determined by Lueker and others (2000). These constants are based on the total pH scale.

Taken directly from Dickson and others (2007):

The equilibrium constant …K_1… is given by the expression (Lueker and others, 2000):

$$\log_{10}(K_1/k^0) = \frac{-3633.86}{(T/K)} + 61.2172 - 9.67770 \ln(T/K) + 0.011555S - 0.0001152S^2 \quad (1)$$

where k^o, the gas transfer velocity = 1 mol kg-soln^{-1}, T is Kelvin, and S is salinity.

The equilibrium constant for …K_2… is given by the expression (Lueker and others, 2000):

$$\log_{10}(K_2/k^0) = \frac{-471.78}{(T/K)} - 25.9290 + 3.16967 \ln(T/K) + 0.01781S - 0.0001122S^2 \quad (2)$$

where k^o, the gas transfer velocity = 1 mol kg-soln^{-1}, T is Kelvin, and S is salinity.

Millero (2010) Constants for Estuarine Waters

(The following is new to the program)

We have added the option of using K_1 and K_2 of carbonic acid as determined by Millero (2010). The constants were based on the seawater scale. The following equations were taken from Millero (2010):

"$pK_i - pK^0_i = A_i + B_i/T + C_i \ln T$

where T is the absolute temperature and A_i, B_i, and C_i are salinity dependent constants.

"The values of pK^0_i in pure water are taken from Harned and Scholes (1941) and Harned and Bonner (1945), then fitted to the following equations (Millero and others, 2006):

$$pK^0_1 = -126.34048 + 6320.813/T + 19.568224 \ln T$$

$$pK^0_2 = -90.18333 + 5143.692/T + 14.613358 \ln T$$

"The values of the adjustable parameters A_i, B_i, and C_i are:

$$A_i = a_0S^{0.5} + a_1S + a_2S^2$$

$$B_i = a_3S^{0.5} + a_4S$$

$$C_i = a_5S^{0.5}$$"

Refer to Millero (2010) for further information.

Air-Sea CO_2 Flux

In that air-sea CO_2 flux calculations are new to this program, we include documentation of the constants and equations used in the relevant calculations both here and in a separate appendix (appendix H).

The calculation of air-sea fluxes is complex, and some familiarity with fluxes in seawater is assumed. The air-sea CO_2 flux will only be calculated for surface samples at 1 atmosphere (atm) pressure (P = 0 decibars, dbars) (that is, output conditions must be surface samples with wind measured at 10 meters (m) above the surface). CO2calc calculates the air-sea CO_2 flux (F) using the gas transfer velocity equations of Wanninkhof (1992), Nightingale and others (2000), or Ho and others (2006). The program requires the user to choose one of these gas transfer velocity equations, as well as input values of T, S, wind speed (meters per second, m s^{-1}), pCO_2sw, and pCO_2air. Specifically, the net air-sea CO_2 flux (in millimole per square meter per day) is estimated using:

$$F = k^*K_0\,\Delta pCO_2 \tag{3}$$

where k is the CO_2 gas transfer velocity (meters per second, m/s) (eqs. 4–6), K_0 is the solubility of CO_2 in seawater (moles per liter per atmosphere) (eq. 8), and $\Delta pCO_2 = (pCO_2sw - pCO_2air)$ in atmospheres as defined in Wanninkhof (1992). Velocity k is derived as a function of the wind speed using either Wanninkhof (1992), Nightingale and others (2000), or Ho and others (2006):

k from Wanninkhof (1992), denoted as k_{wa}:

$$k_{wa} = 0.31u^2\,(660/Sc)^{1/2} \tag{4}$$

k from Nightingale and others (2000), denoted as k_{ni}:

$$k_{ni} = (0.33u + 0.222u^2)(600/Sc)^{1/2} \tag{5}$$

k from Ho and others (2006), denoted as k_{ho}:

$$k_{ho} = 0.266u^2\,(600/Sc)^{1/2} \tag{6}$$

where u is the wind speed in m/s at 10 m above the surface, and Sc is the Schmidt number.

Note that in k_{ni} and k_{ho}, equations are for k_{600}, which is the gas transfer velocity normalized to a Schmidt number of 600. k_{wa} normalizes to a Schmidt number of 660 (Wanninkhof, 1992). The 600 is for freshwater at 20 °C, while 660 is for seawater at 20 °C.

The Schmidt number (Sc) is derived using:

$$Sc = A - Bt + Ct^2 - Dt^3 \tag{7}$$

where t is temperature in degrees Celsius and

$A = 2073.1$ $\quad C = 3.6276$
$B = 125.62$ $\quad D = 0.043219$

The Weiss solubility constant for CO_2 in seawater (K_0, in moles per liter per atmosphere) is calculated as:

$$K_0 = A_1 + A_2(100/T) + A_3\ln(T/100) + S[B_1 + B_2(T/100) + B_3(T/100)^2] \tag{8}$$

where T is temperature in Kelvin, S is salinity, and (from table 1 of Weiss, 1974)

A1 = –58.0931	A2 = 90.5069	A3 = 22.2940
B1 = 0.027766	B2 = –0.025888	B3 = 0.0050578

Finally, air-sea CO_2 flux is calculated:

$$\text{Flux (mmole/m}^2\text{/day)} = k * K_0 * (CO_{2SW} - CO_{2Air}) * 24 \tag{9}$$

where k is either k_{wa}, k_{ni}, or k_{ho}, and Temp is in degrees C. Celsius is converted to Kelvin by K = 273.15 + C

Running CO2calc on Windows or Mac OS X

The general look and functionality of the application are very similar between Windows and Mac OS X. Any differences between the two programs are noted here. On Windows, open the installer and follow the instructions in the installer. In OS X, mount the disk image and drag CO2calc.app into the Applications folder.

The first time CO2calc is opened (fig. 1), the user must choose the constants, seawater scale, gas transfer velocity, wind speed units, and pH scale (fig. 2).

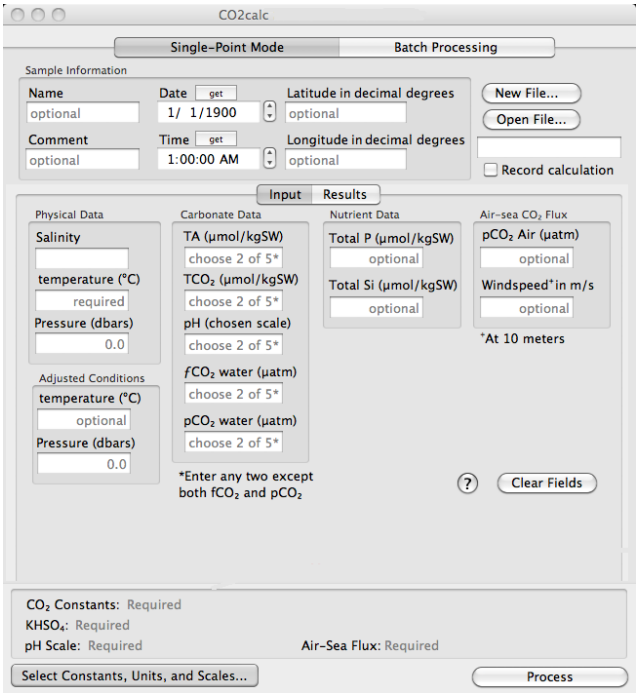

Figure 1. Input page of CO2calc for Windows and Mac OS X.

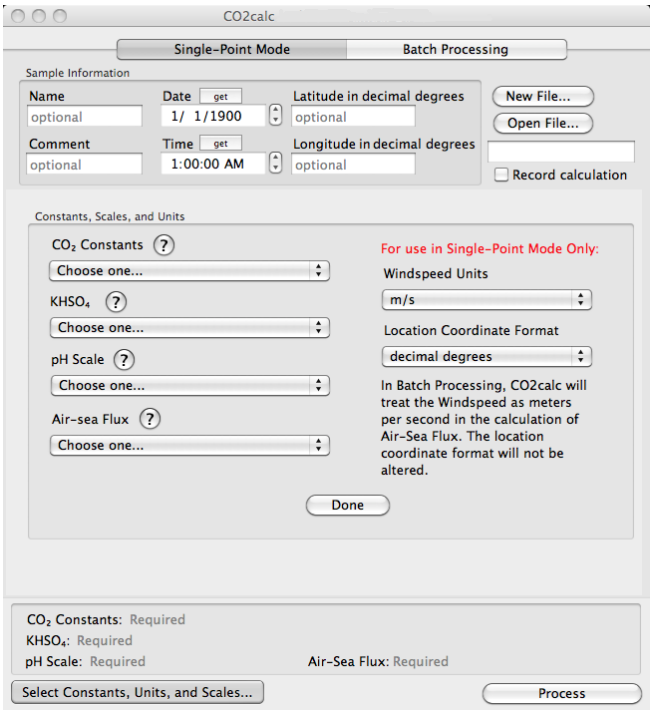

Figure 2. Constants, Scales, and Units page of CO2calc for Windows and Mac OS X.

These selections from drop-down menus (fig. 3) will be saved to disk automatically and retrieved on the application's next use. See the appendix for more information regarding constants and scales. Constants, units, and scales may be changed by clicking "Select" in the bottom section of the Input page or by clicking "File >> Constants, Scales, and Units…". CO2calc may be used in two modes, Single-Point Mode and Batch Processing. In Single-Point Mode, the user enters a set of parameters into text fields on the input tab; upon calculation, the remaining parameters for a single point are displayed in the Results at input conditions and Results at output conditions tabs. If desired, the input and output of these calculation may be saved incrementally to a CSV file. In Batch Processing Mode, the user selects an input CSV in a specified format and remaining parameters are calculated for all samples in that dataset and output as a CSV file (both platforms), a KML file (on OS X), or a KMZ or SHP file (in Windows).

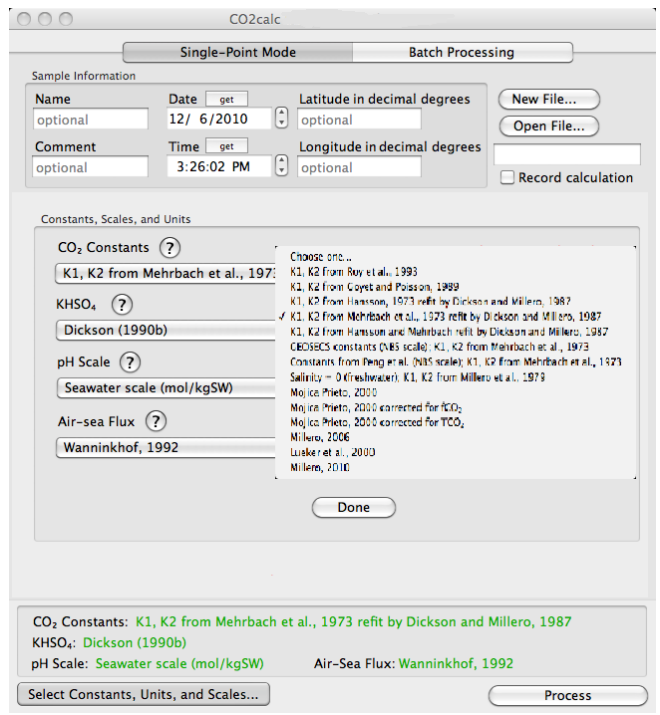

Figure 3. Changing the CO_2 constant using a drop-down menu on the Constants, Scales, and Units page.

Entering Sample Information

The sample information box allows the user to input a six character name, comment of unlimited length, date, time, latitude, and longitude. On either platform, the date and time may be automatically retrieved from the host system by clicking the "get" buttons.

Entering Input Data

Under the Input tab, groupings of data include Physical Data, Adjusted Conditions, Nutrient Data, Carbonate Data, and Air-Sea CO_2 Flux (fig. 1). Each box should be filled in unless labeled "optional." Under Carbonate Data, two of five carbonate parameters must be provided. If fields in Adjusted Conditions are left blank, Results at adjusted conditions will be the same as those in Results at input conditions. Use only pCO_2 or fCO_2, not both. If more than two parameters are provided, the program will analyze the first two fields from the top down. If air-sea CO_2 flux is desired, both parameters (air pCO_2 and wind speed) must be provided. Clicking the "clear" button will clear all input fields.

Viewing and Exporting Output Data

To calculate the results, click the "Process" button in lower right of CO2calc. An error message will be displayed if there are insufficient input data, if there are commas in the sample name or comment (which would interfere with the creation of a comma-delimited output), or if any constants, units, and scales have not been selected. Results are then shown on the Results tab (fig. 4). There are two sub-tabs, Results (input conditions) and Results (adjusted), which correspond to the Results In and Results Out sections of the CO2SYS program of Pierrot and others (2006).

Recording Calculations

Clicking the "Record" checkbox will launch a Save File dialog. A default file name is suggested based on the name field in the sample information section, if present. The path and filename of the new/selected file are displayed next to the checkbox. While a file is selected, the sample information, input data, results at input conditions, results at adjusted conditions, flags for the constants and scales used in calculation, and the sample comment are then appended to the file (for the exact format and units, refer to table 1). On subsequent calculations, results are appended to the file incrementally. To close the current file, uncheck the "Record" checkbox; to write to another file, uncheck and re-check the "Record" checkbox.

Batch Processing

To process a CSV file that contains multiple data points, click the "Batch Processing" tab at the top of the CO2calc window (fig. 5).

Upon clicking the "Input File" button the user is prompted with an Open File dialog to select a file as input to CO2calc. The user must also select an output data file by clicking "Output File," which opens up a Save File dialog. We have provided a template CSV file with CO2calc that can be filled with the appropriate numbers and saved under

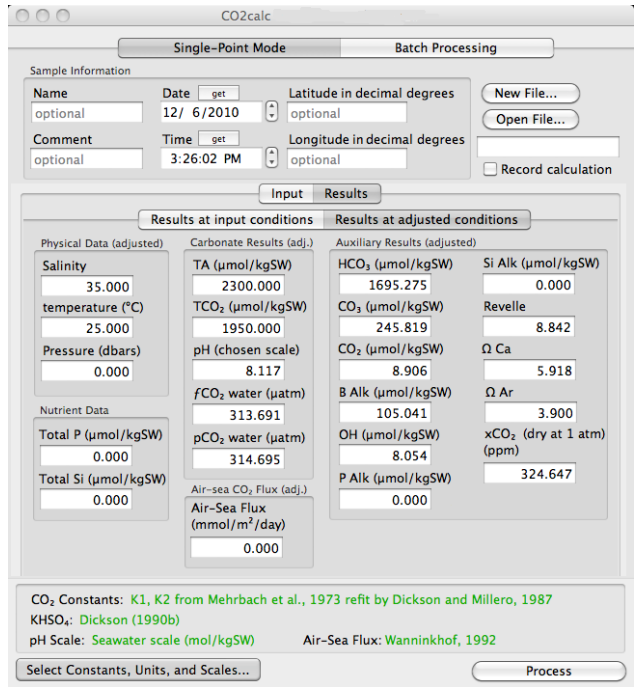

Figure 4. Results (adjusted) page following a calculation in CO2calc for Windows and Mac OS X.

Table 1. CSV input format for CO2calc for Mac OS X and Windows.

Name	Format/Unit
SampleID	N/A
Name	N/A
Time	HH:MM:SS
Date	MO/DD/YYYY
Latitude	decimal degrees
Longitude	decimal degrees
Salinity	Practical salinity units
Temperature	degrees Celsius
Pressure	decibars
Total P	Micromole per kilogram seawater
Total Si	Micromole per kilogram seawater
Temperature adjusted	degrees Celsius
TA	Micromole per kilogram seawater
TCO2	Micromole per kilogram seawater
pH	Chosen scale
fCO2	Microatmospheres
Seawater pCO2 in	Microatmosphere
Air pCO2	Microatmosphere
Windspeed	chosen units (knots or meters per second)
Comment	Chosen by user

a different name and used as the input file. Input files should be UTF8-encoded CSV files that include a header line (see below) or a blank line first line; the following lines will be treated as comma-delimited data lines. As in Single-Point mode, if more than two carbonate parameters are entered, only the first two from the left will be used. If "Adjusted Conditions" fields are left blank, Results at input conditions will be equal to Results at adjusted conditions.

Example Header Line:

SampleID,Name,Time,Date,Lat,Lon,Salinity (psu), temperature(C),P (dbars), Total P (µmol/kgSW),Total Si (µmol/kgSW),temperature(C) adjusted,P (dbars) adjusted,TA (µmol/kgSW),TCO_2 (µmol/kgSW),pH,fCO_2 (µatm), pCO_2 Water (µatm),pCO_2 Air (µatm),Wind speed (m/s), Comment

Example Input data line:

1,"SAMP",16:30:50, 4/13/2010, 25.183, –82.367, 35.0, 22.0, , , , ,550.0, 8.1, , , , , 300.0, 5.0, "This is a comment"

In this example, Input fields are:

Sample ID (1),sample ID ("SAMP"),time (16:30:54),date (4/13/2010),latitude (25.183),longitude (–82.367),Salinity (35.000),temperature(26.0),TCO_2(550.000),pH(8.1),pCO_2 Air (300.0),Wind speed (5.0),Comment ("This is a comment")

Output data have the same format described in the previous section and listed in table 1.

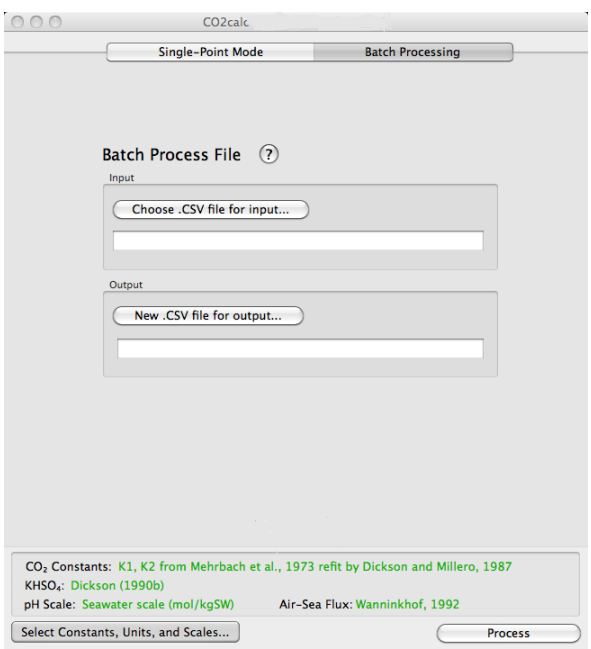

Figure 5. Batch Process File page of CO2calc for Mac OS X and Windows.

CSV to KML/KMZ Translation

CO2calc allows the user to translate CSV files in the input format described above into Google Earth KML or KMZ files by clicking "File >> Convert CSV to KML…". The user is prompted with an Open dialog to select one or more input files, and then a succession of save dialogs equal to the number of input files. On Mac OS X, the output files are simple KML files. On Windows, the output files are KMZ archives that include the CO2calc icon as a placemarker for datapoints when displayed. This KMZ may be opened directly using Google Earth, or, alternatively opened to view the contents by changing the file extension to .zip and unzipping it. In Google Earth, clicking a datapoint will display a popup containing a table with all post-calculation output data and sample information (table 2).

Running CO2calc on iOS (iPhoneOS)

CO2calc may be downloaded to an iOS device (iPhone, iPad,® or iPod Touch®) from the Apple App Store. While the calculations within the iOS version of CO2calc are identical to those of the desktop version, the user interface is necessarily different given the handheld-optimized iOS platform. After a splash screen displays the credits, the user is presented with an Input page with text boxes for entering carbonate system parameters, salinity, temperature, and pressure.

Entering Sample Information

Sample information can be edited by pressing a disclosure button in the top right corner, which takes the user to the sample information page with text fields for name, number, comment, latitude, and longitude and pickers for date and time (fig. 6). When done, click "Input" to return to the Input page.

Entering Input Data

On the Input page, the user is presented with a table with groupings of data including Physical Data, Nutrient Data, Adjusted Conditions, Carbonate Data, and Air-Sea CO_2 Flux (fig. 7). Each field should be filled in unless labeled "optional." Under Carbonate Data, two of five carbonate parameters must be provided. Use only pCO_2 or fCO_2, not both. If more than two parameters are provided, the program will analyze the first two fields from the top down. If air-sea CO_2 flux is desired, both air pCO_2 and wind speed must be provided.

Table 2. CSV output format for CO2calc for Mac OS X and Windows.

Name	Format/Unit
SampleID	N/A
Name	N/A
Time	HH:MM:SS
Date	MO/DD/YYYY
Latitude	decimal degrees
Longitude	decimal degrees
Salinity	Practical salinity units
Temperature	degrees Celsius
Pressure	decibars
Total P	Micromole per kilogram seawater
Total Si	Micromole per kilogram seawater
TA	Micromole per kilogram seawater
TCO2	Micromole per kilogram seawater
pH	Chosen scale
fCO2	Microatmospheres
HCO3	Micromole per kilogram seawater
CO3	Micromole per kilogram seawater
CO2	Micromole per kilogram seawater
B Alk	Micromole per kilogram seawater
OH	Micromole per kilogram seawater
P Alk	Micromole per kilogram seawater
Si Alk	Micromole per kilogram seawater
Revelle	N/A
Omega Ca	N/A
Omega Ar	N/A
xCO2	Parts per million dry at 1 atmosphere
Temperature out	degrees Celsius
Pressure out	Decibars
Total P out	Micromole per kilogram seawater
Total Si out	Micromole per kilogram seawater
TA out	Micromole per kilogram seawater
TCO2 out	Micromole per kilogram seawater
pH out	Chosen scale
fCO2 out	Microatmospheres
HCO3 out	Micromole per kilogram seawater
CO3 out	Micromole per kilogram seawater
CO2 out	Micromole per kilogram seawater
B Alk out	Micromole per kilogram seawater
OH out	Micromole per kilogram seawater
P Alk out	Micromole per kilogram seawater
Si Alk out	Micromole per kilogram seawater
Revelle out	N/A
Omega Ca out	N/A
Omega Ar out	N/A
xCO2 out	Parts per million dry at 1 atmosphere
pCO2_air	Microatmosphere
Windspeed	chosen units (knots or meters per second)
Air-sea CO2flux input	Millimole per square meter per day
Air-sea CO2flux output	Millimole per square meter per day
CO2 constants	Set of constants used
KHSO4	Constant used
Air-Sea Flux	Constant used
Windspeed Units	Unit used
pH scale	Scale used
Comment	Chosen by user

Figure 6. The Sample Info page of CO2calc for iOS.

Viewing Output Data

To perform the calculation, click "Compute" in the top navigation bar of the Input page. If the record switch at the top of the Input page is set to "ON," the output will be recorded to a file. The user is then taken to the Results Adj. page (fig. 8) corresponding to the Results at Output Conditions section of CO2SYS.

A navigation bar at the bottom of the screen allows the user to switch at any time between Input, Results (corresponding to the "Results at Input Conditions" of CO2SYS), Results (adj) (corresponding to the "Results at Output Conditions" of CO2SYS), Constants (labeled "K") and Information (labeled "More…."). On the Constants page (fig. 9), the user may select constants, units, and scales that are used in performing the calculation. For each selection, a link is provided to the appropriate appendix that provides information on the options.

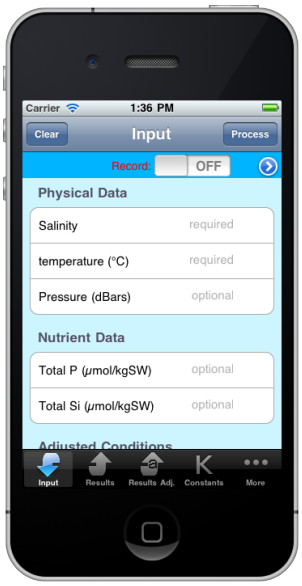

Figure 7. Input page of CO2calc for iOS.

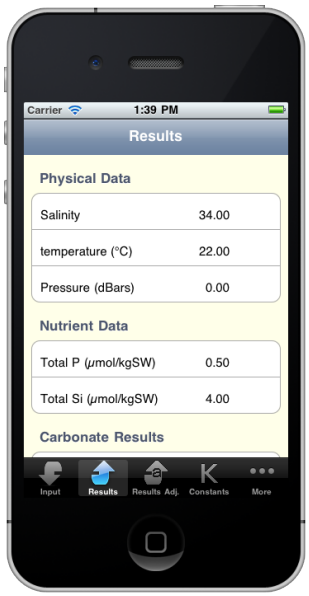

Figure 8. Results page of CO2calc for iOS.

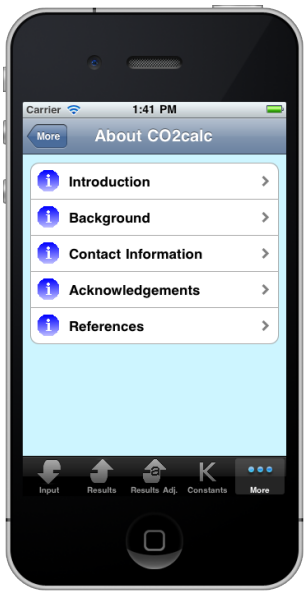

Figure 10. The About (information) page for CO2calc for iOS.

The About (information) page of CO2calc (fig. 10) presents a menu from which the user may access citation information for publications and contact information if the user has questions. The user may also access the appendixes that describe the various aspects of the application. For the most part, these appendixes have been adapted from those provided by Pierrot and others (2006); one major addition is the section "Air-sea CO_2 Flux" that describes the equations, constants, and references used in the air-sea CO_2 flux calculations of CO2calc.

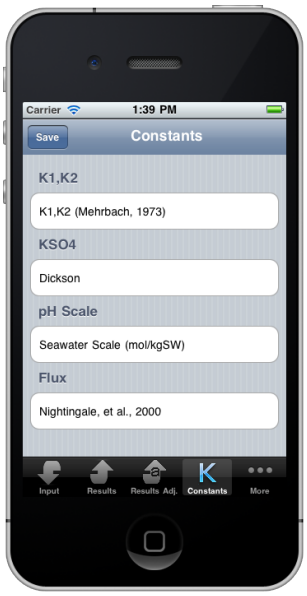

Figure 9. Constants and scales page for CO2calc for iOS.

Deleting and Emailing Stored Calculations

If the record switch on the input page is set to "On" and a filename is provided on the sample information page, the results of the calculation are recorded to a file each time "Process" is clicked. The user can choose to delete these files or send them as an attachment to an email message by clicking on "More" in the lower right hand corner and then selecting the topmost navigation button, entitled "Data Management." The user selects one or more files from the list and chooses either "Delete" or "Mail" from a bar that appears at the bottom of the screen once a file is selected. "Delete" permanently removes the calculations from the iPhone's memory. "Mail" opens up an email with the selected file or files attached; thereafter the user fills in the To: and Subject: fields and sends the email. A confirmation of the completed operation ("File(s) Sent!" or "Files Deleted!") appears on the file management page upon successful completion of the operation. The user may return to the input page at any time by clicking the appropriate navigation button in the upper left corner. Note that a data file is not created until the first point is processed while the record switch is set to "On."

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Appendixes

The following appendixes are excerpts from Lewis and Wallace (1998) as reported in Pierrot and others (2006) so that the reader has easy access to the original document when using CO2calc. Only minor grammatical or typographical technical edits have been made to these documents.

Appendix A. – Constants

The recommended dissociation constants vary depending on which parameters are measured, the pH scale being used, and on salinity. The user of the program needs to consider these issues when choosing which set of constants to use. For example:

(1) Lee and others (2000) recommend using Mehrbach (1973) as refit by Dickson and Millero [noted simply as K1,K2 (Mehrback, 1973) in CO2calc] for a wide range of salinities.

(2) Dickson and others (2007) and Dickson (2010, table 1.1) recommends using the Lueker and others (2000) constants.

(3) However, Millero (2010) cautions against using the Lueker constants in dilute seawater (i.e., estuarine waters) where salinities are below 15. Within CO2calc, we have added Millero (2010) to the list of possible constants. These constants were modified from Millero and others (2006).

The following section, except for the Lueker and Millero equilibrium constants section, is an excerpt from Lewis and Wallace (1998) as reported in Pierrot and others (2006). Note that the notations K1, K2, KW, etc., are printed exactly as written, but obviously refer to K_1, K_2, K_W, etc. :

> "Constants are converted to the appropriate pH scale and concentration scale, if needed, before calculations are made.
>
> "The value of K_0 (the solubility coefficient of CO_2) and the conversion between the fugacity and the partial pressure of CO_2 are from Weiss (1974).
>
> "The vapor pressure of H_2O above seawater is from Weiss and Price (1980). The concentrations of sulfate and fluorine are from Morris and Riley (1966) and Riley (1965), respectively.
>
> "The value of KSO_4, the dissociation constant for HSO_4, is from either Khoo and others (1977) or Dickson (1990a).
>
> "KF, the dissociation constant for HF, is from Dickson and Riley (1979). Constants for calcium solubility and for pressure effects are given in other information sections.
>
> "The value of KB (for boric acid), in constant choices 1 to 5, is from Dickson (1990b).
>
> GEOSECS and Peng and other (1987) choices use Lyman's KB, the fit being from Li and others (1969).
>
> "The boron concentration in constant choices 1 to 5 is from Uppstrom (1974).
>
> "The GEOSECS and Peng choices, are from Culkin (1965).
>
> "Values of KW (for H_2O), KP1, KP2, and KP3 (for phosphoric acid), and KSi (for silicic acid) are from (Millero, 1995) (in constant choices 1 to 5) (note that some typos and inconsistencies from this paper were corrected).
>
> "The Peng choice uses KP2 and KP3 from Kester and Pytkowicz (1967), and KSi from Sillen and others (1964). For the Peng and the freshwater choice, KW is from Millero (1979). For the freshwater choice, the fit is a refit of data from Harned and Owen (1958).
>
> "Several determinations of K1 and K2 of carbonic acid have been made: Hansson (1973a, b) on the total pH scale, Mehrback and others (1973) on the NBS pH scale, Goyet and Poisson (1989) on the seawater pH scale, Roy and others (1993) on the total pH scale, and Lueker and others (2000) on the total pH scale.
>
> "The data of Hansson (1973a,b) and Mehrbach and others (1973), both separately and together, have been refit by Dickson and Millero (1987) on the seawater scale.
>
> GEOSECS and Peng and others (1987) used the fit given in Mehrbach and others (1973). For freshwater, Millero (1979) refit data from Harned and Davis (1943) for K1 and Harned and Scholes (1941) for K2."

The following are approximate precisions of the fits of the data:

Author	K_1	K_2
Roy and others (1993)	2%	1.5%
Goyet and Poisson (1989)	2.5%	4.5%
Hansson (1973 a,b) refit by Dickson Millero (1987)	3%	4%
Mehrbach and others (1973) refit by Dickson Millero (1987)	2.5%	4.5%
Dickson and Millero (1987) combined fit	4%	6%
Mehrbach and others (1973) fit	1.2%	2%
freshwater choice	0.5%	0.7%

Lueker Equilibrium Constants

(The following is new to the program)

Based on the recommendations of Dickson and others (2007), we have added the option of using K_1 and K_2 of carbonic acid as determined by Lueker and others (2000). These constants are based on the total pH scale.

Taken directly from Dickson and others (2007):

"The equilibrium constant …K_1… is given by the expression (Lueker and others, 2000):

$$\log_{10}(K_1 / k^0) = \frac{-3633.86}{(T/K)} + 61.2172 - 9.67770$$
$$\ln(T/K) + 0.011555S - 0.0001152S^2$$

where k^o = 1 mol kg-soln^{-1}, T is Kelvin, and S is salinity at S = 35 and T= 25 °C (298.15 K), $\log_{10}(K_1/k^o) = -5.8472$.

The equilibrium constant for …K_2… is given by the expression (Lueker and others, 2000):

$$\log_{10}(K_2 / k^0) = \frac{-471.78}{(T/K)} - 25.9290 + 3.16967$$
$$\ln(T/K) + 0.01781S - 0.0001122S^2$$

where k^o = 1 mol kg-soln^{-1} at S = 35 and T= 25 °C (298.15 K), $\log_{10}(K_2/k^o) = -8.9660$."

Millero (2010) Constants for Estuarine Waters

(The following is new to the program)

We have added the option of using K_1 and K_2 of carbonic acid as determined by Millero (2010). The constants were based on the seawater scale. The following equations were taken from Millero (2010):

"$pK_i - pK^0_i = A_i + B_i/T + C_i \ln T$

where T is the absolute temperature and A_i, B_i and C_i are salinity dependent constants.

"The values of pK^0_i in pure water are taken from Harned and Scholes (1941) and Harned and Bonner (1945), then fitted to the following equations (Millero and others, 2006):

$pK^0_1 = -126.34048 + 6320.813/T + 19.568224 \ln T$

$pK^0_2 = -90.18333 + 5143.692/T + 14.613358 \ln T$

"The values of the adjustable parameters A_i, B_i and C_i are:

$A_i = a_0S^{0.5} + a_1S + a_2S^2$
$B_i = a_3S^{0.5} + a_4S$
$C_i = a_5S^{0.5}$"

Refer to Millero (2010) for further information.

Appendix B. – About pH

The following is an excerpt from Pierrot and others (2006):

"The various pH scales are inter-related by the following equations:

$$\alpha H = 10^{-pHNBS} = fH * Hsws$$

$$Hfree = \frac{Htot}{1 + TS/KSO4} = \frac{Hsws}{1 + TS/KSO4 + TF/KF}$$

where αH is the activity and fH the activity coefficient of the H+ ion (this includes liquid junction effects), TS and TF are the concentrations of SO_4^- and fluorine, and KSO_4 and KF are the dissociation constants of HSO_4 and HF in seawater.

"These conversions depend on temperature, salinity, and pressure. At 20 °C, Sal 35, and 1 atm, pH values on the total scale are (about) 0.09 units lower than those on the free scale, 0.01 units higher than those on the seawater scale, and 0.13 units lower than those on the NBS scale. The concentration units for αH on the NBS scale are mol/kg-H_2O. The concentration units used here for [H] on the other scales is mol/kg-SW (note that the free scale was originally defined in units of mol/kg-H_2O). The difference between mol/kg-SW and mol/kg-H_2O is about 0.015 pH units at salinity 35 (the difference is nearly proportional to salinity).

"The seawater scale was formerly referred to as the total scale, and each is still sometimes referred to as the other in the literature. The fit of fH used here is valid from salinities 20 to 40. fH has been found to be electrode-dependent, and does NOT equal 1 at salinity 0 due to the liquid junction potential.

"Values on the NBS pH scale are only accurate to (at best) 0.005. All work on pressure effects on pH has assumed that fH is independent of pressure. Some of the pH scale conversions depend on pressure.

"For discussions of the various pH scales, see Culberson (1981), Dickson (1984), Butler (1992), Dickson (1993), and Millero and others (1993). Attention is required because in some of these papers the distinction between the total and seawater pH scales was not made."

Appendix C. – fCO_2, pCO_2

The following is an excerpt from Pierrot and others (2006):

"The fugacity of CO_2 (fCO_2) in water is defined to be the fugacity of CO_2 in wet (100% water-saturated) air which is in equilibrium with the water. pCO_2, the partial pressure of CO_2, is defined to be the product of the mole fraction of CO_2 in WET air and the total pressure. This is the same as the product of the mole fraction of CO_2 in DRY air (xCO_2 (dry)) and (pTot – pH2O), where pH_2O is the vapor pressure of water above seawater. At pressures of order 1 atm fCO_2 in air is about 0.3% lower than the pCO_2 due to the non-ideality of CO_2 (see Weiss, 1974). This program assumes a pressure near 1 atm (where most equilibrators function) for the conversion between partial pressure and fugacity. fCO_2 is related to TC and pH by the following equation:

$$fCO_2 = \frac{[CO_2*]}{K0} = \frac{TC}{K0} * \frac{H*H}{H*H + K1*H + K1*K2}$$

where $[CO_2*]$ is the concentration of dissolved CO_2, K0 is the solubility coefficient of CO_2 in seawater, and K1 and K2 are the first and second dissociation constants for carbonic acid in seawater.

"Units for fCO_2 and pCO_2 in this program are µatm (micro-atmospheres). The value of xCO_2 (dry) given in this program assumes pTot = 1 atmosphere. GEOSECS and Peng and others (1985) did not distinguish between fCO_2 and pCO_2, nor did some other programs that we have evaluated."

Appendix D. – KSO_4

The following is an excerpt from Pierrot and others (2006):

"KSO_4 is defined to be the dissociation constant for the reaction

$$HSO_4^- = H^+ + SO_4^{--}$$

"Thus,

$$KSO_4 = [H] * [SO_4] / [HSO_4].$$

"Two formulations of this are still in current usage: Khoo and others (1977) and Dickson (1990).

The values of Dickson (1990) are now recommended, though many older papers used values of Khoo and others (1977). They are between 15 to 45% lower than those of Dickson (1990b), depending on temperature (mostly).

"The main effect of this difference will occur when converting from one pH scale to another, or when working on a scale for which equilibrium constants must be converted (e.g., most constants were determined on either the total scale or the seawater scale). Use of the Dickson (1990) values when converting from the total pH scale to the free pH scale will result in pH values which are 0.015 to 0.03 units lower than those obtained using values of Khoo and others (1977)."

Appendix E. – Options

The following is an excerpt from Lewis and Wallace (1998) as reported by Pierrot and others (2006):

The Freshwater Option

"For the freshwater option only [HCO3], [CO3], [OH], and [H] are included in the definition of alkalinity: TA = $[HCO_3] + 2[CO_3] + [OH] - [H]$.

fH, the activity coefficient of H^+, does NOT equal 1 at salinity 0 due to liquid junction effects (included in its definition). It is also found to be electrode dependent. Thus, while the values of pH on the free, total, and seawater scales will coincide at salinity 0, the value on the NBS scale will differ. For these reasons, for this choice only a pH value is given without reference to a pH scale. Constants used for this choice (K1, K2, and KW) are from Millero (1979); pressure effects on these constants are from Millero (1983)."

The GEOSECS Option

"The GEOSECS option was designed to replicate the calculations performed in Takahashi and others (1982). That work used the NBS pH scale, the values of K1 and K2 from Mehrbach and others (1973), and the value of KB from Lyman [1957]. It did not include effects of OH, silicate, or phosphate, nor was there a correction for the non-ideality of CO_2 (i.e., implying fCO_2 and pCO_2 are the same). Their boron concentration was about 1% lower than that used for the other choices in this program (except the choice of Peng and others (1985).

"In GEOSECS, TA and TC values from titration were used to determine pCO_2,

$[H_2CO_3]$, $[HCO_3^-]$, $[CO_3^{--}]$, and pH, at P = 1 atm and in situ T; and $[H_2CO_3]$, $[HCO_3^-]$, $[CO_3^{--}]$, aH, pH, ICP, and delta CO_3^{--} for calcite and aragonite at in situ T and P, where aH = 10^(-pH), ICP = $[Ca^{++}]$ $[CO_3^{--}]$, and delta CO_3^{--} is the difference between $[CO_3^{--}]$ and its saturation level. These last three parameters were used to describe the saturation states of calcite and aragonite. In this program only omegas, dimensionless ratios, are output for this. A fit for fH was also given (for salinities 20 to 40) and is used to convert between pH scales in this program.

"Some typographic errors in the GEOSECS report were noted and corrected:

in the pressure dependence of K2 the given value 26.4 should be 16.4, and the expression for ln KW should have C*ln T, not C/ln T. That these are correct can be seen by checking the original references. The ratio of Ksp(aragonite) / Ksp(calcite) is given as 1.48 in the original reference (Berner, 1976), but the value of 1.45 given in GEOSECS was used both in that work and in this program as well for this choice.

"The GEOSECS report also contains a discussion on the effects of OH, phosphate, and silicate (see p. 79–82, especially Table 1 on p. 81, of Chapter 3, Carbonate Chemistry, Takahashi and others (1982). From this, it can be seen how important these can be, especially for calculated values of fCO_2 (or pCO_2). This table has a typo: 17.8 for Aw in Pacific Surface Water should be 7.8.

The choice of Peng and others (1985) is very similar, and should be used instead if the values of OH, etc. are desired with these constants."

Peng and others (1987) Option

"This choice replicates the calculation scheme of Peng and others (1987), which is similar to GEOSECS. Peng and others (1987) worked on the NBS pH scale and included effects of phosphate, silicate, and OH, but did not distinguish between fCO_2 and pCO_2. The values of K1 and K2 from Mehrbach and others (1973) and the value of KB from Lyman [1957] were used.

"They did not treat calcite and aragonite solubility or pressure effects, but these are included in this program for this choice using GEOSECS values for solubility and pressure dependence of K1, K2, and KB, and the same values for the pressure dependence of OH and phosphate and silicate dissociation as are used in constant choices 1 to 5. The concentration of boron they used was about 1% lower than that used for other choices in this program (except for GEOSECS choice).

"The value of fH given in their paper was NOT the same as that given in the GEOSECS report as claimed, rather it had been rounded off and was therefore about 1% higher, corresponding to a change of 0.003 in pH. Note that the check value given in the paper does not match either fit.

"Their definition of alkalinity (TA) differs from that of Dickson (1981) in that it is greater by an amount equal to the total phosphate (TP). This seems insignificant, but can affect the calculated fCO_2 appreciably."

Appendix F. – Pressure Effects

The following is an excerpt from Lewis and Wallace (1998):

"The equilibrium constants depend on pressure as well as on temperature and salinity. Data are scarce on the effects of pressure on these constants in seawater, and most values are estimated from molal volume data. Few measurements have been made for K_1 and K_2 (of carbonic acid) and K_B (of boric acid) at only a few combinations of temperature, salinity, and pressure in seawater (mostly in artificial seawater). All of the work assumed that f_H, the activity coefficient of H^+ (including liquid junction effects), is independent of pressure. Some of the *pH scale* conversions do depend on pressure, however. Values of the constants should be (1) converted to the seawater or NBS pH scale WITHOUT pressure-corrected pH scale conversions, (2) then corrected for pressure, and (3) then converted to the desired pH scale WITH pressure-corrected pH scale conversions. Measurements have also been made for the effects of pressure on the solubility of calcite and aragonite in seawater.

"Depth in meters and pressure in decibars are used interchangeably in this program. They differ by only 3% at 10,000 dbar and less at lower pressures—well within the uncertainties of the pressure effects on the constants. No salinity dependence of the pressure corrections is used in this program.

"For the *Freshwater Choice*, the effects of pressure on K_1, K_2, and K_W are from Millero (1983).

"Peng and others (1987) did not consider the effects of pressure, but they are included in the program CO2SYS for the *Peng Choice*. For *Constant Choices 1 through 5* and the *Peng Choice*, the effects of pressure on the values of K_{P1}, K_{P2}, and K_{P3} are from Millero (1995). The only mention of K_{Si} was in Millero (1995), where it is stated that the values have been estimated from the values of boric acid, but they are not listed in the table. In the program CO2SYS, the values used are the same as those for the pressure effects on K_B given in Millero (1995). For the effects of pressure on K_W, the fit given in Millero (1983) is used. GEOSECS did not include the effects of OH, phosphate, or silicate, so these are irrelevant for that choice.

"For the GEOSECS Choice and the Peng Choice, the effects of pressure on K1, K2, and KB are those given in the GEOSECS report (Takahashi and others, 1982). The reference given there is Culberson and Pytkowicz (1968), but the fits are actually those from Edmond and Gieskes (1970) who in turn quote Li (personal communication). In the fit for the correction for K2 due to pressure, the GEOSECS report had the value 26.4, but the value 16.4 was used, which was consistent with their calculations as well as with the fit given in Edmond and Gieskes (1970). The effects of pressure on the solubility of calcite and aragonite are also those from Takahashi and others (1982). [The original reference given in that work for the pressure corrections is not valid and the fit used appears to be new to Takahashi and others (1982)].

"For the Constant Choices 1 to 5, the effects of pressure on K_1 and K_2 are from Millero (1995), and those for K_B are from Millero (1979) but without the salinity dependence. These fits are from the data of Culberson and Pytkowicz (1968). The effects of pressure on K_{SO4} and K_F are from Millero (1995). Note that *typographical errors* in Millero (1995) include a factor of 1000 left out of the definition of Kappa and an incorrect value and incorrect units for the gas constant R. The pressure correction for K_{sp} for calcite is from Ingle (1975) and that for aragonite is from Millero (1979)."

Appendix G. – Calcium Carbonate Solubility (Ω), Alkalinity, and the Revelle Factor

The following is an excerpt from Pierrot and others (2006):

"The solubility product (Ksp) is calculated for both calcite and aragonite and the saturations states are given in terms of Omega, the solubility ratio, defined as Omega = $[CO_3^{--}]*[Ca^{++}]$ / Ksp. Thus, values of Omega < 1 represent conditions of undersaturation, and values of Omega > 1 represent conditions of oversaturation. The concentration of calcium, $[Ca^{++}]$, is assumed to be proportional to the salinity, and the carbonate, $[CO_3^{--}]$, is calculated from TC, pH, and the values of K1 and K2 for carbonic acid. The values used in this program are from: Mucci (1983), Ingle and others (1973), Millero (1979) Takahashi and others (1982), and Berner (1976)."

Alkalinity

The following is an excerpt from Pierrot and others (2006):

"The definition of alkalinity (TA) used in this program for constant choices 1 to 5 is the same as that of Dickson (1981) and Roy and others (1993):

$$TA = [HCO_3] + 2[CO_3] + [B(OH)_4] + [OH] + [HPO_4] + 2[PO_4] + [SiO(OH)_3] + [HS] + 2[S] + [NH_3] - [H] - [HSO_4] - [HF] - [H_3PO_4]$$

except that the contributions of HS, S, and NH3 are not included.

"For the choice of Peng, the definition of Peng and others (1987) is used. The main difference is that it is greater by an amount equal to the total phosphate:

$$TP = [PO_4^{---}] + [HPO_4^{--}] + [H_2PO_4^{-}] + [H_3PO_4]$$

"Though this seems small, it can have a large effect on the calculated fCO_2. Each µmol/kg-SW of TA results in a change in about 0.5% in fCO_2, so a value of TP = 3 µmol/kg-SW (a modest amount) can result in a difference of 5 to 20 µatm (or more) in fCO_2 between the two definitions. "The definition used for the GEOSECS choice is:

$$TA = [HCO_3] + 2[CO_3] + [H_2BO_3]$$

and for the freshwater choice is:

$$TA = [HCO_3] + 2[CO_3] + [OH] - [H]$$

"In this program values of alkalinity are given in micro-moles per kilogram of seawater (µmol/kg-SW)."

The Revelle Factor

"The Revelle Factor, or homogeneous buffer, factor is the % change in fCO_2 (or pCO_2) caused by a 1% change in TC at constant alkalinity. It depends on temperature, salinity, and the total alkalinity and TC (or any combination of the two CO_2 system parameters) of the sample. It is calculated at both the input and output conditions using:

Revelle factor = $(df CO_2/dTC) / (fCO_2/TC)$ at constant TA. Normal seawater values are between 8 and 20."

Appendix H. – Air-Sea CO_2 Flux and Conversions

Air-sea CO_2 flux calculations were not originally incorporated into CO2SYS, and as such the following documentation is provided.

The calculation of air-sea fluxes is complex, and some familiarity with fluxes in seawater is assumed. The air-sea CO_2 flux will only be calculated for surface samples at 1 atm pressure (P = 0 dbars) (that is, output conditions must be surface samples with wind measured at 10 m above the surface). CO2calc calculates the air-sea CO_2 flux (F) using the gas transfer velocity equations of Wanninkhof (1992), Nightingale and others (2000) or Ho and others (2006). The program requires the user to choose one of these gas transfer velocity equations, as well as input values of T, S, wind speed (m s^{-1} at 10 m above surface), pCO_2sw, and pCO_2air. Specifically, the net air-sea CO_2 flux (in mmol m^{-2} d^{-1}) is estimated using:

$$F = k*K_0 \Delta pCO_2 \qquad \text{(H-1)}$$

where k is the CO_2 gas transfer velocity (m/sw) (eqs. 4–6), K_0 is the solubility of CO_2 in seawater (moles per liter per atmosphere) (eq. 8), and $\Delta pCO_2 = (pCO_{2sw} - pCO_{2air})$ in atmospheres as defined in Wanninkhof (1992). Velocity, k, is derived as a function of the wind speed using either Wanninkhof (1992), Nightingale and others (2000), or Ho and others (2006):

k from Wanninkhof (1992), denoted as k_{wa}:

$$k_{wa} = 0.31u^2 (660/Sc)^{1/2} \quad \text{(H-2)}$$

k from Nightingale and others (2000), denoted as k_{ni}:

$$k_{ni} = 0.33u + 0.222u^2 (600/Sc)^{1/2} \quad \text{(H-3)}$$

k from Ho and others (2006), denoted as k_{ho}:

$$k_{ho} = 0.266u^2 (600/Sc)^{1/2} \quad \text{(H-4)}$$

where u is the wind speed at 10 m above surface in m s^{-1}, and Sc is the Schmidt number.

Note that in k_{ni} and k_{ho}, equations are for k_{600} ,which is the gas transfer velocity normalized to a Schmidt number of 600. k_{wa} normalizes to a Schmidt number of 660 (Wanninkhof, 1992). The 600 is for freshwater at 20 °C, while 660 is in seawater at 20 °C.

The Schmidt number (Sc) is derived using:

$$Sc = A - Bt + Ct^2 - Dt^3 \quad \text{(H-5)}$$

where t is temperature in degrees Celsius and

$A = 2073.1$ $C = 3.6276$
$B = 125.62$ $D = 0.043219$

The Weiss solubility constant for CO_2 in seawater (K_0, in moles per liter per atmosphere) is calculated as:

$$K_0 = A_1 + A_2(100/T) + A_3\ln(T/100) + S[B_1 + B_2(T/100) + B_3(T/100)^2] \quad \text{(H-6)}$$

where T is in Kelvin and S is salinity, and (from table 1 of Weiss, 1974):

A1 = –58.0931 A2 = 90.5069 A3 = 22.2940
B1 = 0.027766 B2 = –0.025888 B3 = 0.0050578

Finally, air-sea CO_2 flux is calculated:

$$\text{Flux (mmole/m}^2\text{/day)} = k * K_0 * (CO_{2SW} - CO_{2Air}) * 24 * (1 + \text{Sigma(Temp, Sal)} / 1000) * 0.01 \quad \text{(H-7)}$$

where k is either k_{wa}, k_{ni} or k_{ho} and Temp is in degrees C.

Conversions

xCO_2 is converted to pCO_{2a} according to

$$pCO_{2a} = (P - pH_2O) \text{ x } CO_2 \quad \text{(H-8)}$$

Celsius is converted to Kelvin by $K = 273.15 + C$.