CO_2 system calculations

Part 1. Using software to perform CO_2 system calculations

Part 2. Using CO_2 system calculations for experimental CO_2 manipulations

USGS
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CO_2 system Calculations Part 1

Using software to perform CO_2 system calculations

USGS
science for a changing world

CO_2-system Calculations

Mass-conservation equations[4]

$$C_T = [CO_2^*] + [HCO_3^-] + [CO_3^{2-}] \quad (17)$$

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] + [NH_3] + [HS^-] + \ldots - [H^+]_F - [HSO_4^-] - [HF] - [H_3PO_4] - \ldots \quad (18)$$

$$B_T = [B(OH)_3] + [B(OH)_4^-] \quad (19)$$

$$S_T = [HSO_4^-] + [SO_4^{2-}] \quad (20)$$

$$F_T = [HF] + [F^-] \quad (21)$$

$$P_T = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] \quad (22)$$

$$Si_T = [Si(OH)_4] + [SiO(OH)_3^-] \quad (23)$$

$$NH_{3T} = [NH_4^+] + [NH_3] \quad (24)$$

$$H_2S_T = [H_2S] + [HS^-] \quad (25)$$

Equilibrium constants

$$K_0 = [CO_2^*]/f(CO_2) \quad (26)$$

$$K_1 = [H^+][HCO_3^-]/[CO_2^*] \quad (27)$$

$$K_2 = [H^+][CO_3^{2-}]/[HCO_3^-] \quad (28)$$

$$K_B = [H^+][B(OH)_4^-]/[B(OH)_3] \quad (29)$$

$$K_W = [H^+][OH^-] \quad (30)$$

$$K_S = [H^+][SO_4^{2-}]/[HSO_4^-] \quad (31)$$

$$K_F = [H^+][F^-]/[HF] \quad (32)$$

$$K_{1P} = [H^+][H_2PO_4^-]/[H_3PO_4] \quad (33)$$

$$K_{2P} = [H^+][HPO_4^{2-}]/[H_2PO_4^-] \quad (34)$$

$$K_{3P} = [H^+][PO_4^{3-}]/[HPO_4^{2-}] \quad (35)$$

$$K_{Si} = [H^+][SiO(OH)_3^-]/[Si(OH)_4] \quad (36)$$

$$K_{NH_3} = [H^+][NH_3]/[NH_4^+] \quad (37)$$

$$K_{H_2S} = [H^+][HS^-]/[H_2S] \quad (38)$$

$$[HCO_3^-] = \frac{C_T K_1 [H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2} \quad (39)$$

$$[CO_3^{2-}] = \frac{C_T K_1 K_2}{[H^+]^2 + K_1[H^+] + K_1K_2} \quad (40)$$

$$[B(OH)_4^-] = B_T/(1 + [H^+]/K_B) \quad (41)$$

$$[OH^-] = K_W/[H^+] \quad (42)$$

$$[H_3PO_4] = \frac{P_T[H^+]^3}{[H^+]^3 + K_{1P}[H^+]^2 + K_{1P}K_{2P}[H^+] + K_{1P}K_{2P}K_{3P}} \quad (43)$$

$$[H_2PO_4^-] = \frac{P_T K_{1P}[H^+]^2}{[H^+]^3 + K_{1P}[H^+]^2 + K_{1P}K_{2P}[H^+] + K_{1P}K_{2P}K_{3P}} \quad (44)$$

$$[HPO_4^{2-}] = \frac{P_T K_{1P}K_{2P}[H^+]}{[H^+]^3 + K_{1P}[H^+]^2 + K_{1P}K_{2P}[H^+] + K_{1P}K_{2P}K_{3P}} \quad (45)$$

$$[PO_4^{3-}] = \frac{P_T K_{1P}K_{2P}K_{3P}}{[H^+]^3 + K_{1P}[H^+]^2 + K_{1P}K_{2P}[H^+] + K_{1P}K_{2P}K_{3P}} \quad (46)$$

$$[SiO(OH)_3^-] = Si_T/(1 + [H^+]/K_{Si}) \quad (47)$$

$$[NH_3] = NH_{3T}/(1 + [H^+]/K_{NH_3}) \quad (48)$$

$$[HS^-] = H_2S_T/(1 + [H^+]/K_{H_2S}) \quad (49)$$

$$[H^+]_F = [H^+]/(1 + S_T/K_S) \quad (50)$$

$$[HSO_4^-] = S_T/(1 + K_S/[H^+]_F) \quad (51)$$

$$[HF] = F_T/(1 + K_F/[H^+]) \quad (52)$$

Many Options

	CO2SYS								
OS & details	QBasic	Excel[a]	Matlab	CO2calc	ODV	csys	seacarb	swco2	mocsy
Linux/Unix			•		•	•	•		•
Windows	•	•	•	•	•	•	•	•	•
Mac OS		•	•	•	•	•	•		•
iOS				•					
Public source code	•	•	•			•	•		•
User programmable			•			•	•	•[c]	•
Software platform		E[d]	M[b]			M[b]	R[f, h]	E[e]	F[g, h]

[a] Both variants: CO2SYS-Excel-Pierrot and CO2SYS-Excel-Pelletier.
[b] Package runs under MATLAB (commercial software) or octave (free software).
[c] Spreadsheet interface is not code; core library is callable (Visual Basic) but not modifiable.
[d] Package runs under Excel.
[e] Package runs under Excel (commercial) or LibreOffice (free and open source).
[f] Package runs under R.
[g] Fortran 95 code.
[h] Also runs under Python.

Table 4. Available input pairs for each package.

	CO2SYS[b]								
Pair	QBasic	Excel[a]	Matlab	CO2calc[b]	ODV[b]	csys	seacarb[c]	swco2[c]	mocsy
A_T–C_T	•	•	•	•	•	•	•	•	•
A_T–pCO_2	•	•	•	•	•		•	•	
A_T–pH	•	•	•	•	•	•	•	•	
A_T–CO_3^{2-}						•	•	•	
A_T–CO_2[b]						•	•	•	
A_T–HCO_3^-						•	•	•	
C_T–pCO_2	•	•	•	•	•		•	•	
C_T–pH	•	•	•	•	•	•	•	•	
C_T–CO_3^{2-}						•	•	•	
C_T–CO_2[b]						•	•	•	
C_T–HCO_3^-						•	•	•	
pCO_2–pH	•	•	•	•	•	•	•	•	
pCO_2–CO_3^{2-}							•	•	
pCO_2–HCO_3^-							•	•	
pH–CO_3^{2-}						•	•	•	
pH–CO_2[b]						•	•	•	
pH–HCO_3^-						•	•	•	
CO_3^{2-}–CO_2[b]						•	•	•	
CO_3^{2-}–HCO_3^-						•	•	•	
CO_2[b]–HCO_3^-						•	•	•	

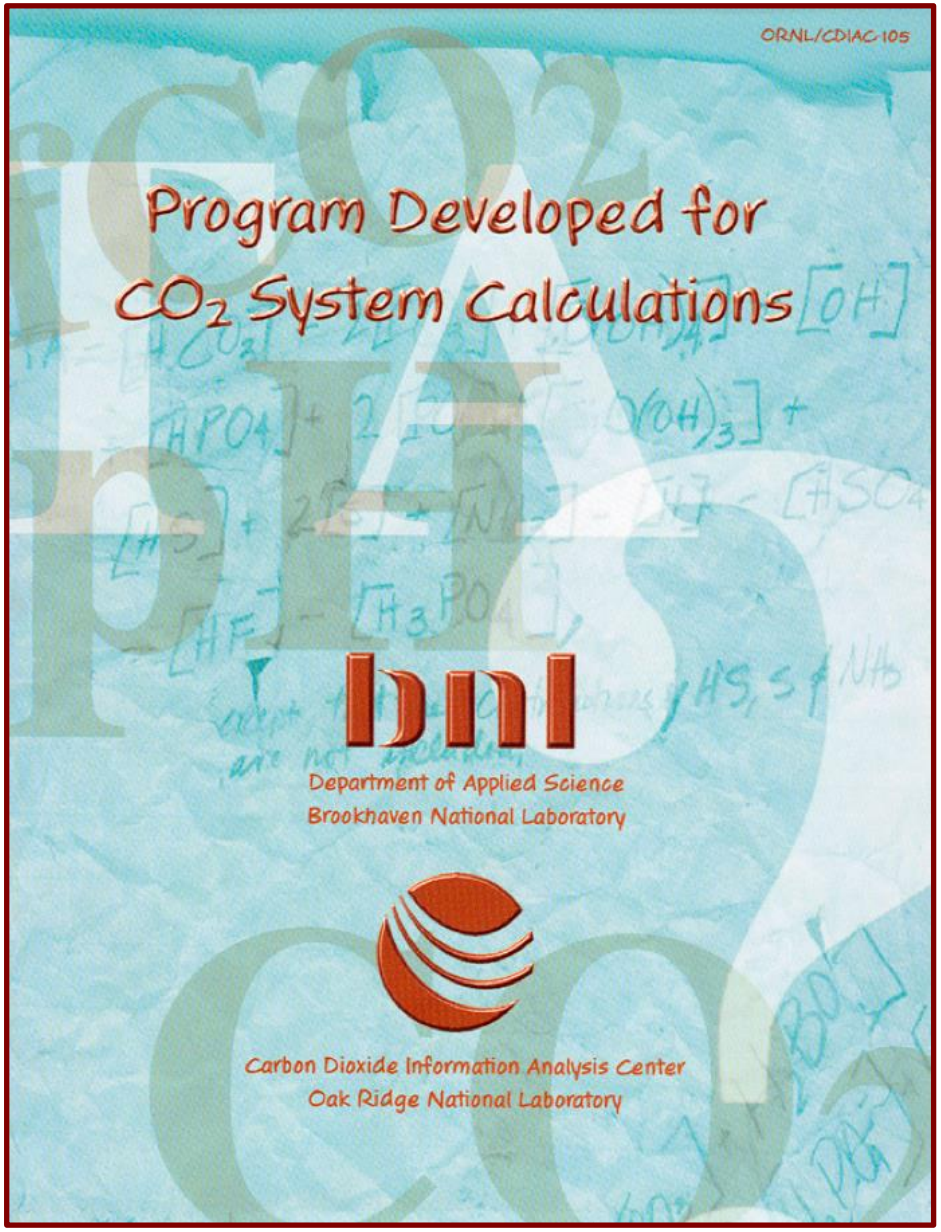
[a] Both variants: CO2SYS-Excel-Pierrot and CO2SYS-Excel-Pelletier.
[b] CO2SYS, CO2calc, and ODV also allow input pairs containing fCO_2 instead of pCO_2.
[c] seacarb and swco2 include user-callable functions to convert between pCO_2 and fCO_2.

From Orr et al., 2015 Biogeosciences

Table 1. Carbonate system software packages.

Package	Language	Version	Reference
CO2SYS[a]	QBasic	1.05	Lewis and Wallace (1998)
CO2SYS[b]	Excel	24	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	1.3.0	Robbins et al. (2010)
csys[d]	MATLAB	04–2014	Zeebe and Wolf-Gladrow (2001)
ODV[e]	C++	4.5.0	Schlitzer (2002)
mocsy[f]	Fortran 95	2.0	Orr and Epitalon (2015)
seacarb[g]	R	3.0.6	Gattuso et al. (2015)
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://www.ecy.wa.gov/programs/eap/models.html
[c] http://pubs.usgs.gov/of/2010/1280/
[d] http://www.soest.hawaii.edu
[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/



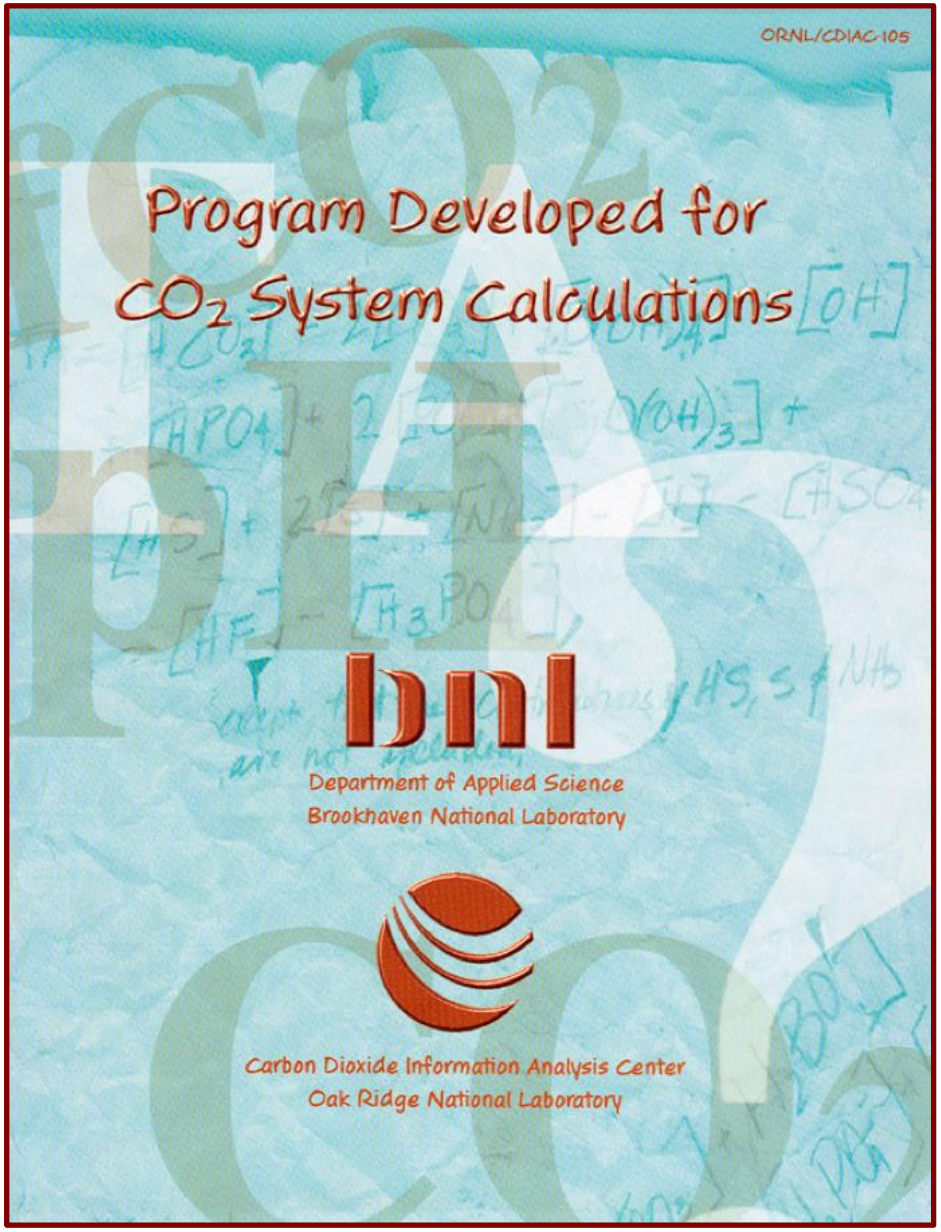
CO2sys

Original

Lewis, E, & DWR Wallace. 1998. *Program Developed for CO_2 System Calculations.*

ORNL/CDIAC-105. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee. doi: 10.3334/CDIAC/otg.CO2SYS_DOS_CDIAC 105

Microsoft QuickBASIC
– runs under DOS on PC's

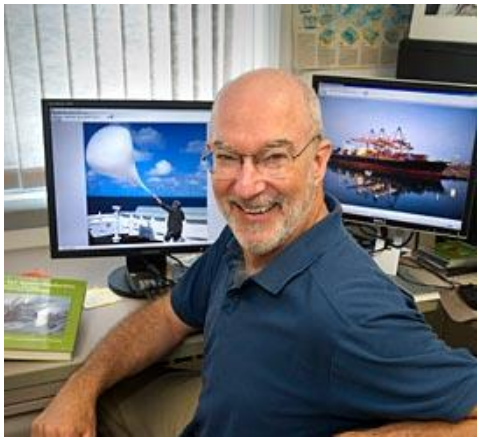


CO2sys

Original

Lewis, E, & DWR Wallace. 1998. *Program Developed for CO_2 System Calculations.*

Ernie Lewis



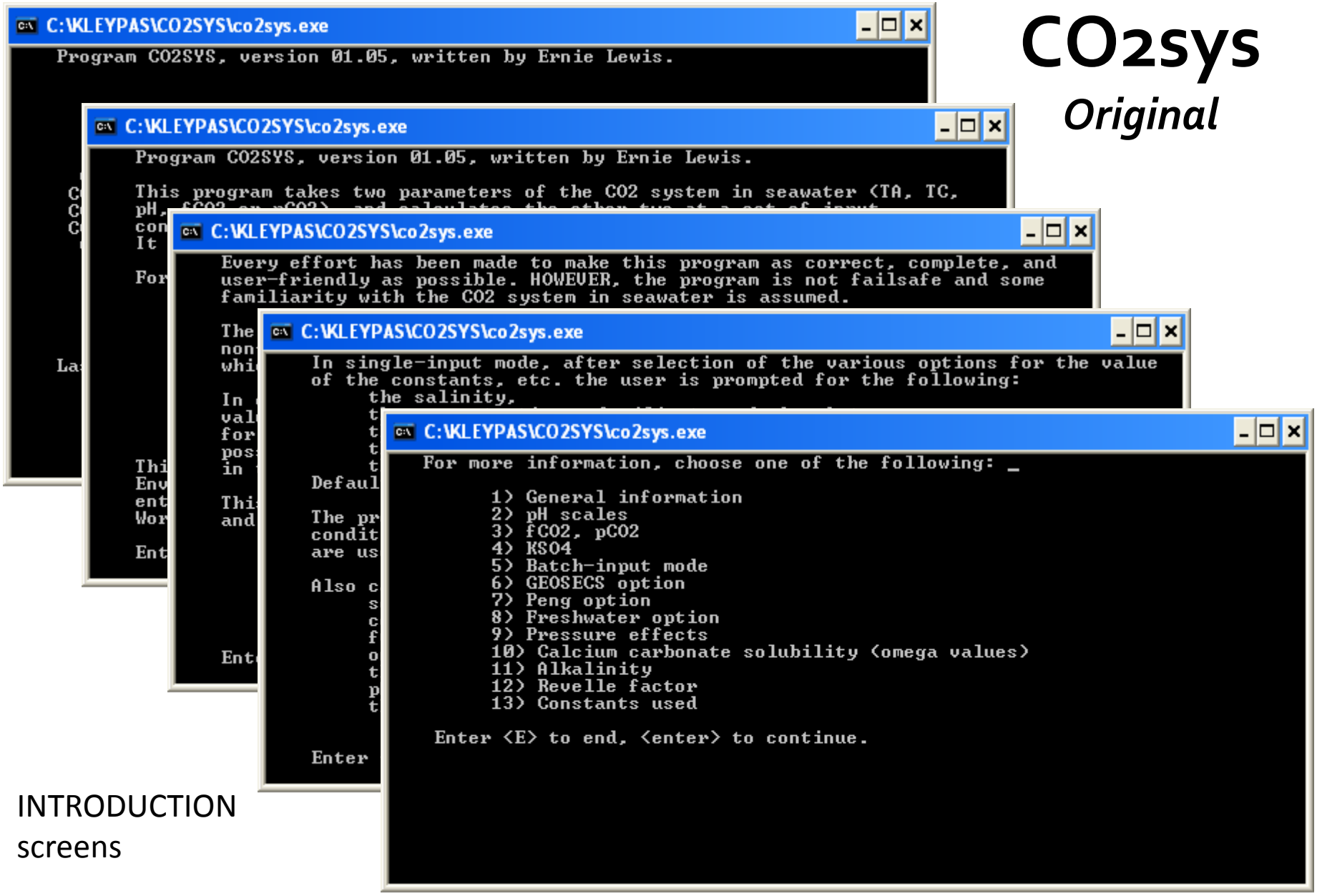
Brookhaven Nat. Lab

Doug Wallace

Dalhousie Univ.

CO2sys

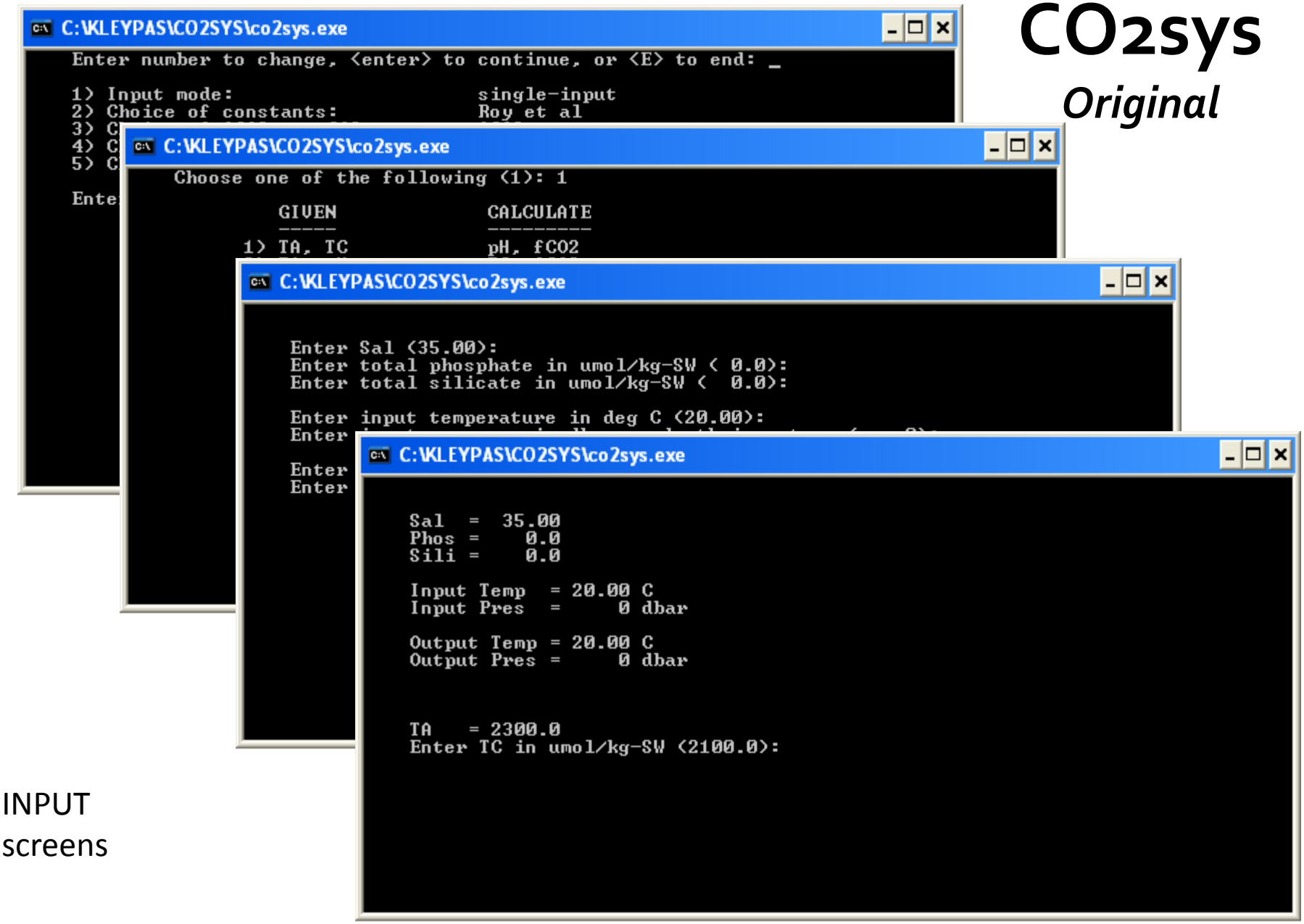
Original



INTRODUCTION screens

CO2sys

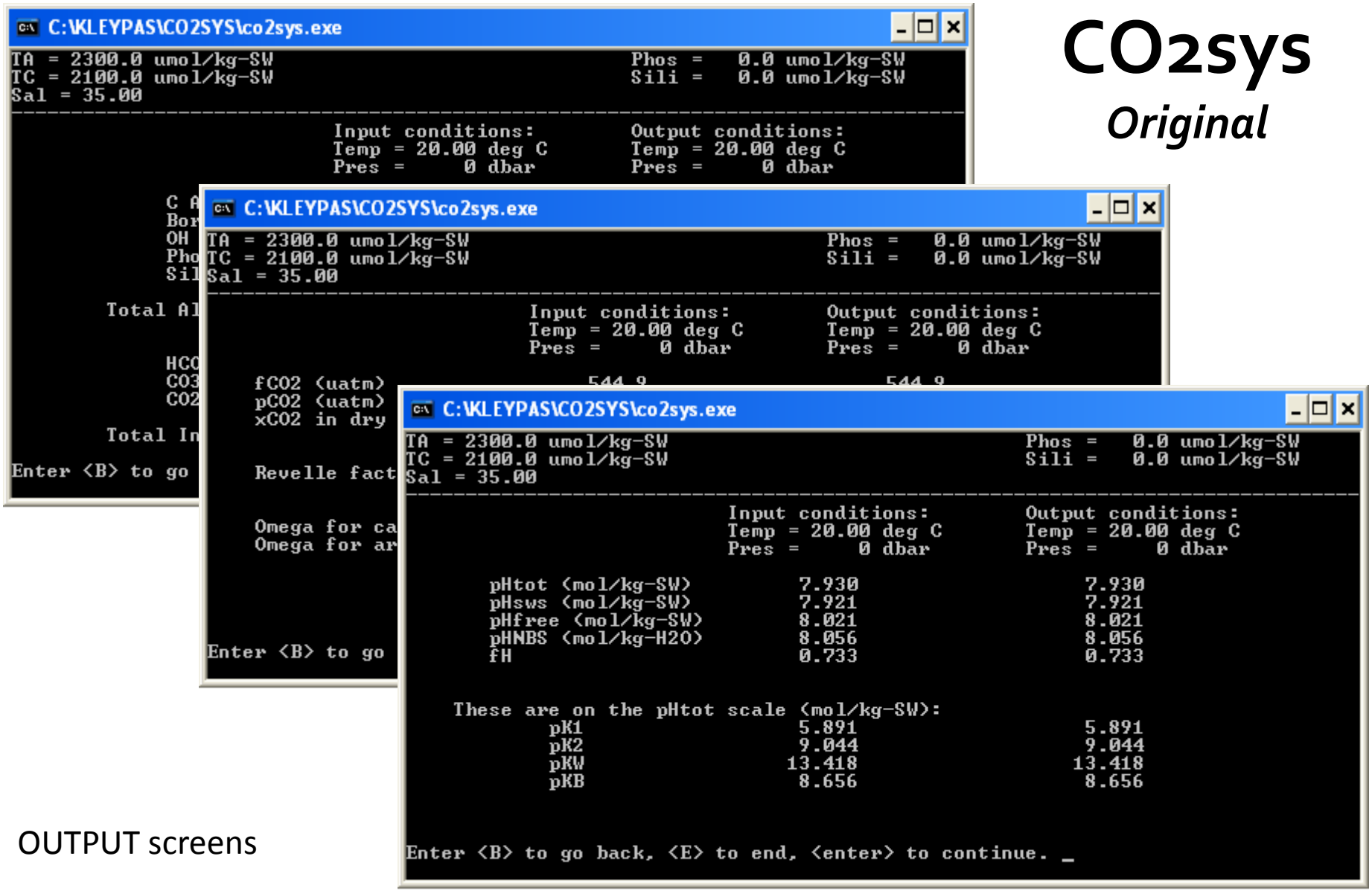
Original



INPUT screens

CO2sys

Original



OUTPUT screens

CO2Sys EXCEL Macro

Pierrot, D, E Lewis & DWR Wallace. 2006. MS Excel Program Developed for CO_2 System Calculations. ORNL/CDIAC-105a. doi: 10.3334/CDIAC/otg.CO2SYS_XLS_CDIAC105a

	A	B	C	D	E	F	G	H
1	SUBJECT							
2	About this Macro		Previous versions (2007): CO2sys_macro_PC.xls and CO2sys_macro_MAC.xls					
3	General Information		. Two separate files for PC and MAC versions.					
4	pH Scales		Version 1.0 (10 Octobre 2011): CO2sys_2011.xls					
5	fCO2, pCO2							
6	KSO4		. Combined PC and MAC versions of previous macro into one file working on both platforms.					
7	Freshwater Option							
8	GEOSECS Option		Version 2.0 (19 July 2012): CO2sys_2011.xls					
9	Peng Option							
10	Pressure Effects		. New R formulation from "NIST Physical Reference Data (http://physics.nist.gov/cgi-bin/cuu/Value?r)"					
11	Calcium Carbonate Solubility (Omega Values)		Difference with old formulation is not numerically significant.					
12	Alkalinity		. Matched formulation of Uppstrom's Total Boron with Matlab program (same numerical results).					
13	Revelle Factor		. Added option of Total Boron from Lee et al., 2010					
14	Constants		. Added a few formulations for K1, K2:					
15	Macro Version History		- Cai and Wang, 1998					
16			- Lueker et al., 2000					
17			- Mojica Prieto et al., 2002					
18			- Millero et al., 2002					
19			- Millero et al., 2006					
20			- Millero, 2010					
21			. Updated the "INFO" section					
22			. Added the "Macro Version History" option in "INFO" Sheet.					
			. Version number is displayed in cell B2 when the "About this Macro" option in "INFO" Sheet is selected.					
			Version 2.1 (18 September 2012): CO2sys_v2.1.xls					
			. Corrected an error in the code which affected the results when the constants of 'Millero et. al., 2002' and 'Millero, 2010' were selected.					
			. References to 'Cai and Wang, 2008' have been corrected to 'Cai and Wang, 1998'					
			. Incorporated version number in the name of the file and removed it from the 'INFO' sheet (see v.2.0)					

CO2Sys EXCEL Macro

	A	B	C	D
1	***Set of Constants***	***$KHSO_4$***	***pH Scale***	***$[B]_T$ Value***
2	K1, K2 from Roy, et al., 1993	Dickson	Total scale (mol/kg-SW)	Uppstrom, 1974
3	K1, K2 from Goyet and Poisson, 1989	Khoo et al	Seawater scale (mol/kg-SW)	Lee et al., 2010
4	K1, K2 from Hansson, 1973 refit by Dickson and Millero, 1987		Free scale (mol/kg-SW)	
5	K1, K2 from Mehrbach et al., 1973 refit by Dickson and Millero, 1987		NBS scale (mol/kg-H2O)	
6	K1, K2 from Hansson and Mehrbach refit by Dickson and Millero, 1987			
7	GEOSECS constants (NBS scale); K1, K2 from Mehrbach et al., 1973			
8	Constants from Peng et al. (NBS scale); K1, K2 from Mehrbach et al.			
9	Salinity = 0 (freshwater); K1, K2 from Millero, 1979			
10	K1, K2 from Cai and Wang, 1998			
11	K1, K2 from Lueker et al., 2000			
12	K1, K2 from Mojica Prieto et al., 2002			
13	K1, K2 from Millero et al., 2002			
14	K1, K2 from Millero et al., 2006			
15	K1, K2 from Millero, 2010			
16				

The Recommended Constants

K1, K2: Mehrbach et al. (1973) refit by Dickson & Millero (1987)
Lueker et al. (2000)
Millero (2010)

1. Lee et al. (2000) recommend using Mehrbach et al. (1973) as refit by Dickson & Millero for a wide range of salinities.

2. Dickson et al. (2007) and Dickson (2010, table 1.1) recommend using the Lueker et al. (2000) constants.

3. Millero (2010) cautions against using the Lueker et al. constants where salinities are below 15. Note: Orr et al., 2015 cautions against using Millero until publication/spreadsheet discrepancy has been taken care of

NOTE: Many of the other constants are included because they are useful when working with older data.

The Recommended Constants

K1, K2: Mehrbach et al. (1973) refit by Dickson & Millero (1987)
Lueker et al. (2000)
Millero (2010)- discrepancies amongst programs Therefore, Orr et al 2015 suggests to wait until resolved

$KHSO_4$: Dickson 1990

pH scale: Total
Free

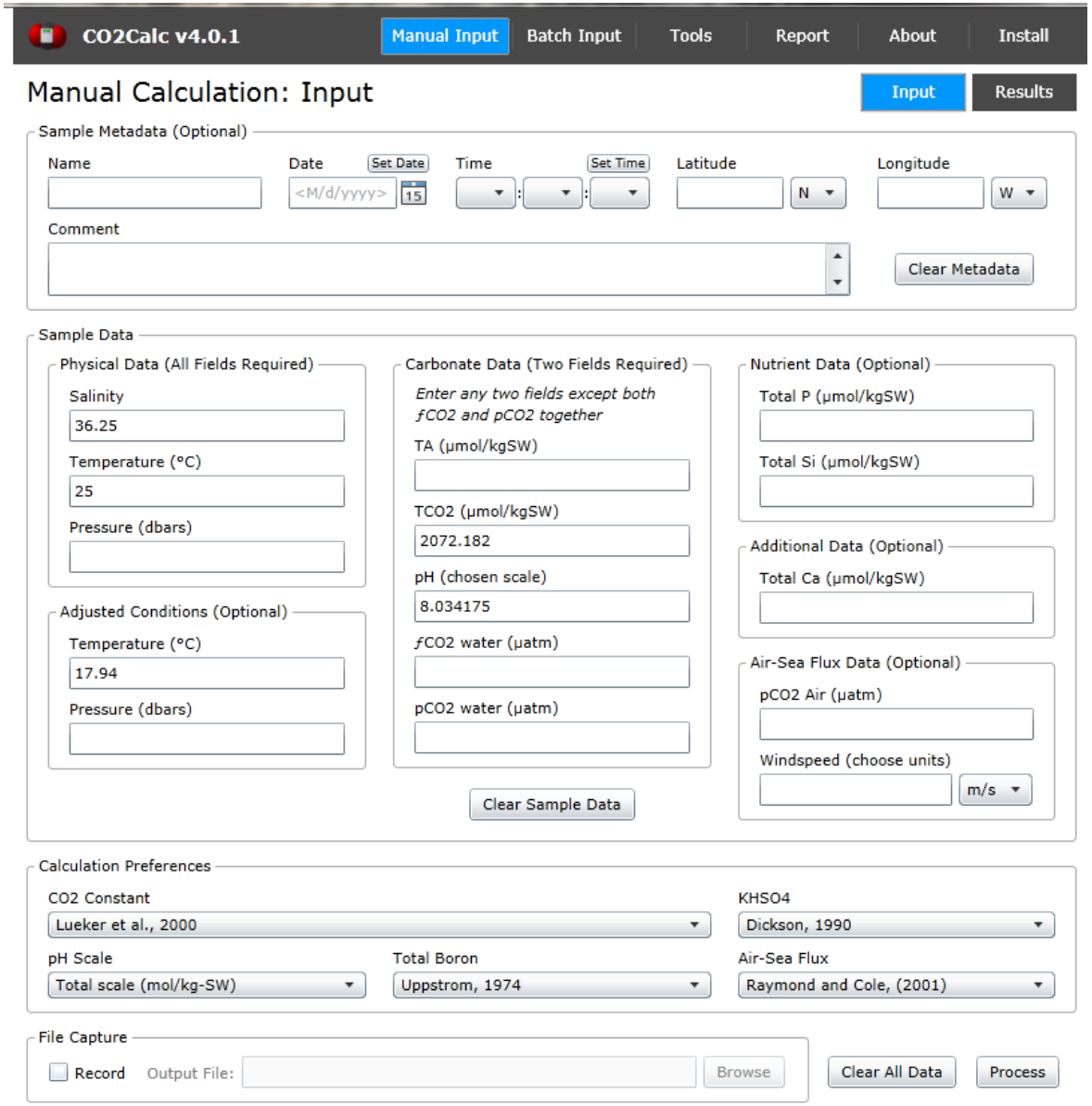
B_T: Uppström 1974

NOTE: Cite Software Program and version number

CO2calc

CO2calc application for PC and Mac desktop and iPhone

Robbins, LL, ME Hansen, JA Kleypas, & SC Meylan (2010) CO2calc - A user-friendly seawater carbon calculator for Windows, Max OS X, and iOS (iPhone): U.S. Geological Survey Open-File Report 2010 - 1280, 17 p.



CO2calc

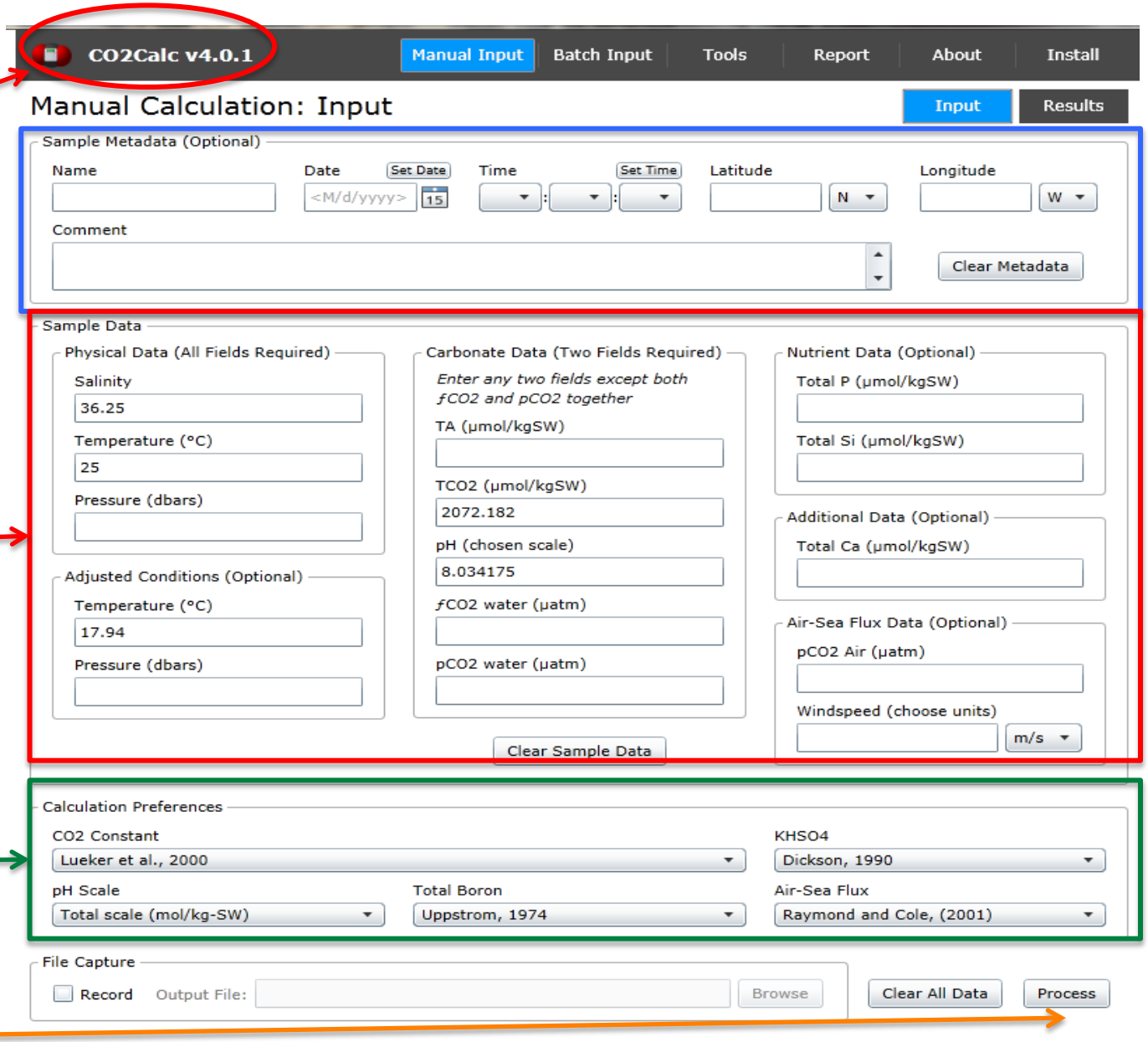
VERSION #

SAMPLE INFO

INPUTS

CONSTANTS

RUN SAMPLE



Getting Started

(1) Open CO2calc

(2) Input SAMPLE INFORMATION

(3) Set up an output file for recording calculations

Example 1

(1) Open CO2calc

(2) Select Constants, Units and Scales

CO_2 constants:	Lueker et al. (2000)
$KHSO_4$:	Dickson (1990b)
pH Scale:	Total Scale
Boron:	Lee et al., 2010

(3) Input

Salinity =	35.0
Temperature =	25.0
Pressure =	0.0
TA =	2300
TCO_2 =	2000

(4) Results

pH =	8.040
fCO_2 =	401.419
pCO_2 =	402.704
xCO_2 =	415.439
Ω Ar =	3.347

Example 1: now add pH

(1) Open CO2calc

(2) Select Constants, Units and Scales

CO_2 constants:	Lueker et al. (2000)
$KHSO_4$:	Dickson (1990b)
pH Scale:	Total Scale
Boron:	Lee et al. (2010)

(3) Input

Salinity =	35.0
Temperature =	25.0
Pressure =	0.0
TA =	2300
TCO_2 =	2000
pH =	7.900

(4) Results

pH =	8.040
fCO_2 =	401.419
pCO_2 =	402.704
xCO_2 =	415.439
Ω Ar =	3.347

Example 1

(1) Open CO2calc

(2) Select Constants, Units and Scales

CO_2 constants:	Lueker et al. (2000)
$KHSO_4$:	Dickson (1990b)
pH Scale:	Total Scale

(3) Input

Salinity =	35.0
Temperature =	25.0
Pressure =	0.0
TA =	2300
~~TCO_2 =~~	~~2000~~
pH =	7.900 ≠

(4) Results

pH =	7.900
fCO_2 =	591.591
pCO_2 =	593.484
xCO_2 =	612.253
Ω Ar =	2.586
TCO_2 =	2076.748

CO2calc uses the first two parameters it sees

Example 2

http://andrew.ucsd.edu/co2qc/

University of California, San Diego
Scripps Institution of Oceanography
Marine Physical Laboratory
9500 Gilman Drive
La Jolla, CA 92093-0244

Certificate of Analysis

Reference material for oceanic CO_2 measurements

Batch 93 (Bottled on December 18, 2008)

This reference material consists of natural sea water sterilized by a combination of filtration, ultra-violet radiation and addition of mercuric chloride.

Analysis Results

The various procedures used for these analyses are detailed overleaf.

Salinity	33.615	
Total dissolved inorganic carbon	2020.34 ± 0.89 μmol·kg^{-1}	(9; 9)
Total alkalinity	2230.06 ± 0.56 μmol·kg^{-1}	(25; 10)

http://andrew.ucsd.edu/co2qc/batches.html

Input:

Salinity = 33.615
PO_4 = 0.33
SiO_4 = 4.7
TCO_2 = 2020.34
TA = 2230.06
But Lab pCO_2 = 390.0
T = 20°C

Results:

pH = 7.972
fCO_2 = 477.138
pCO_2 = 478.761
xCO_2 = 489.852
Ω Ar = 2.368

Example 2

http://andrew.ucsd.edu/co2qc/

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Salinity	33.615	
Total dissolved inorganic carbon	2020.34 ± 0.89 $\mu mol \cdot kg^{-1}$	(9; 9)
Total alkalinity	2230.06 ± 0.56 $\mu mol \cdot kg^{-1}$	(25; 10)

http://andrew.ucsd.edu/co2qc/batches.html

Input:

Salinity = 33.615
PO_4 = 0.33
SiO_4 = 4.7
~~TCO_2 = 2020.34~~
TA = 2230.06
pCO_2 = 390.0
T = 20°C

Results:

pH = 8.047
fCO_2 = 388.677
TCO_2 = 1982.986
xCO_2 = 399.034
Ω Ar = 2.729

Example 3

Determine the carbonate chemistry for a discrete water sample taken at 2952 m depth off South Atlantic

Input:

In situ:	T	= 1.55°C
	Salinity	= 34.661
	Depth	= 2952 m
Lab:	Phos.	= 2.64
	Silicate	= 159.4
	TCO_2	= 2345
	TA	= 2419
	T	= 20.0°C
	Depth	= 0 m

Results:

	input (lab)	output (in situ)
pH =	7.594	7.742
fCO_2 =	1360.466	618.271
pCO_2 =	1365.096	620.943
xCO_2 =	1396.699	625.076
Ω Ar =	1.213	0.566

Example 3a

What are the effects of the nutrients on the carbonate chemistry?

Input:

In situ:	T	= 1.55°C
	Salinity	= 34.661
	Depth	= 2952 m
Lab:	Phos.	= 0
	Silicate	= 0
	TCO_2	= 2345
	TA	= 2419
	T	= 20.0°C
	Depth	= 0 m

Results:

	with nutrients	without nutrients
pH =	7.742	7.756
fCO_2 =	618.27	598.360
pCO_2 =	620.947	600.946
xCO_2 =	625.076	604.947
Ω Ar =	0.566	0.585

Batch Files

Input files tend to be in XCL or CSV format

For CO2calc, the file must be saved in UTF8-encoded CSV format. On a Mac, this can be problematic. Open the CSV file in a text editor and save with Unicode (UTF-8) encoding (may have to set this under preferences).

Once you have an input file that works, you can use this as a template for future files.

Example 4

Batch Files: use a batch file to compare effects of using different K1,K2 constants

(1) Select Lueker 2000 constants

Input file: batchin_example_sal_gradient.csv

Output file: batchout_Lueker2000

(2) Select Millero 2010 constants

Input file: batchin_example_sal_gradient.csv

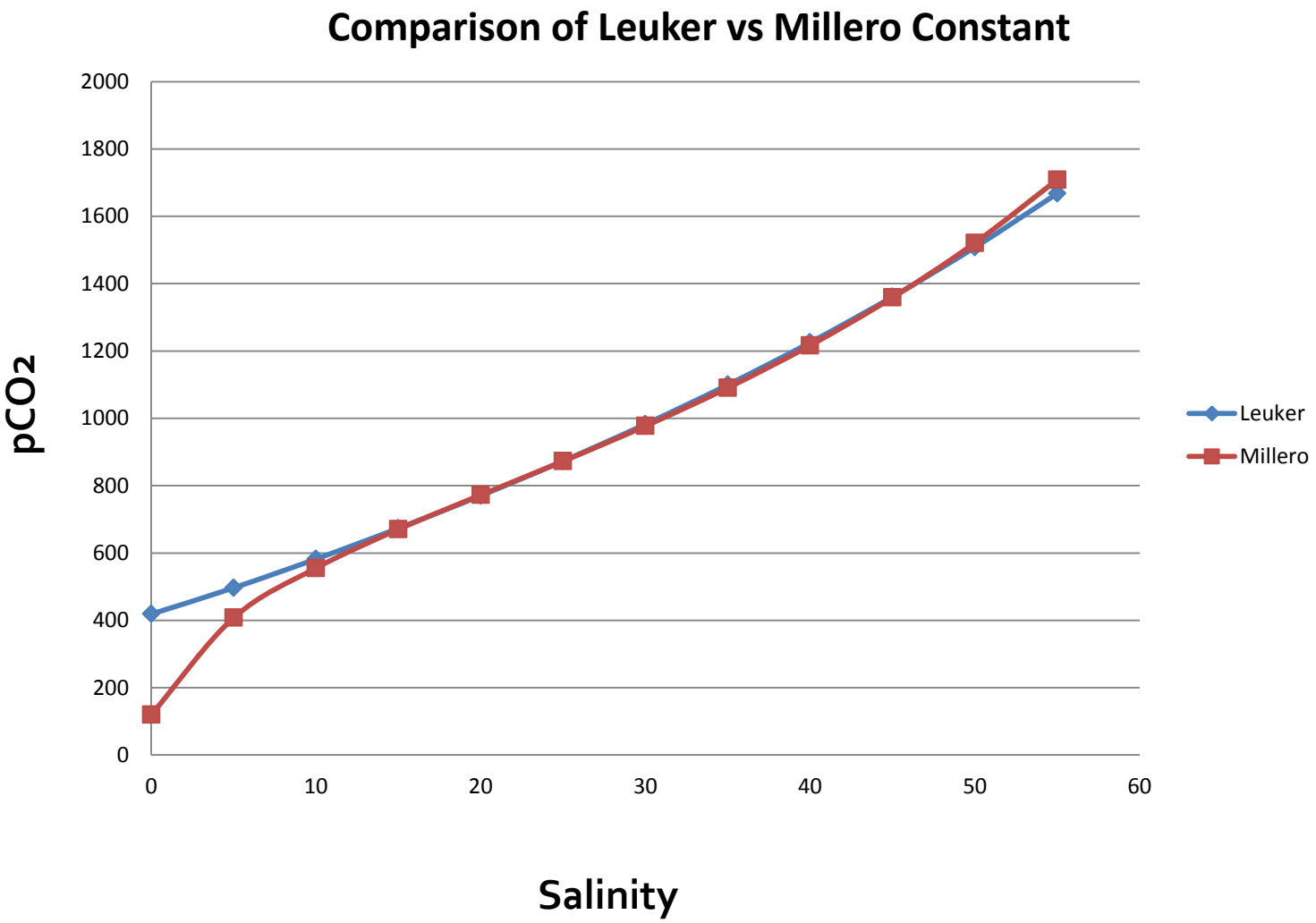
Output file: batchout_Millero2010

(3) Combine the two output (.txt) files into a single spreadsheet

(4) Plot pCO_2 versus Salinity for both data sets.

Example 4

Batch Files: use a batch file to compare effects of using different K1,K2 constants



Example 5

Comparing old data with new data

Old data:

T = 25.1

S = 34.2

Z = 0.1

Total P = 0.1

Total Si = 1.1

pH_{SW} = 8.15

TCO_2 = 2032

TA = 2414.467

pCO_2 = 302.658

Your data:

T = 23.0

S = 34.2

Z = 0.1

Total P = 0.1

Total Si = 1.1

pH_T = 8.15

TCO_2 = 2032

TA = 2407.069

pCO_2 = 310.315

Check UNITS, CONSTANTS, SCALES !!!

Pitfalls

(1) Know your constants

(2) Don't use 3 carbon parameters at the same time

(3) Don't compare data that have used different constants unless you can confidently recalculate the data using the same constants

(4) Make sure that you carefully input lab vs insitu (adjusted) data

A word about data reporting….

- When reporting data, metadata should include: info on units (and pH scale), estimated uncertainties, thermodynamic constants used to compute carbonate parameters, and QC procedures applied to data set. Essential
  - Units of measurements
  - In situ and measurement temp
  - Salinity