CO_2 system Calculation Part 2

Using CO_2 system calculations for experimental CO_2 manipulations

USGS
science for a changing world

Introduction

- Impact of changing seawater chemistry as a result of OA on marine organisms is not well constrained
- Experimental data are needed to understand the consequences
- Perturbation experiments of seawater chemistry are key approaches to investigating biological responses to increasing pCO_2
- We will examine several techniques carried out in closed and open cell vessels and discuss pros and cons of these approaches

Main approaches to manipulate CO_2-system chemistry

Change TCO_2 at constant TA

- Gas bubbling
- Add high-CO_2 sea water
- Add CO_3^{2-} and/or HCO_3^- followed by strong acid

Change TA at constant TCO_2

- Add strong acids and base

Change TA & TCO_2

- Add CO_3^{2-} and/or HCO_3^-

Manipulate $[Ca^{2+}]$

We will follow modified Gattuso et al. 2009 examples

also section 2 of Guide to Best Practices

Assumptions:

Seawater pCO_2	= 384 µatm (Year = 2007)
Target pCO_2	= 793 µatm (Year = 2100)
Salinity	= 34.9
Temperature	= 18.9°C
Depth	= 0 m
Phosphate & Silicate	= 0.63 µmol/kg SW & 7.63 µmol/kg SW
TA	= 2325

Except we will use Lueker et al. 2000 K1,K2, Dickson 1990 KHSO4 constants ; pH-total scale ; Uppstrom et al., 2010 Boron constant

Bubbling gas in a vessel is fairly easy effective way to manipulate CO_2-system chemistry

Systems that have been used:

- control atmospheric CO_2 and then bubble that into container

- pH-stat- pH is monitored continuously and controller opens or closes valves when pH goes above or below the target value

Lets get started "bubbling"

- Scenario: You have a seawater sample that has the following conditions-"2007 condition"

Sal =34.9 T= 18.9C pH= 8.07 TA= 2325 µmol/kg

Nutrients : 0.63 umol/kgsw Tphos; 7.63 umol/kgsw TSi

Now, to "mimic" year 2100, you bubble in a CO_2 –air mixture of 793 µatm– what is your final pH? Note that we are assuming that TA will not change significantly over the next 100 years.

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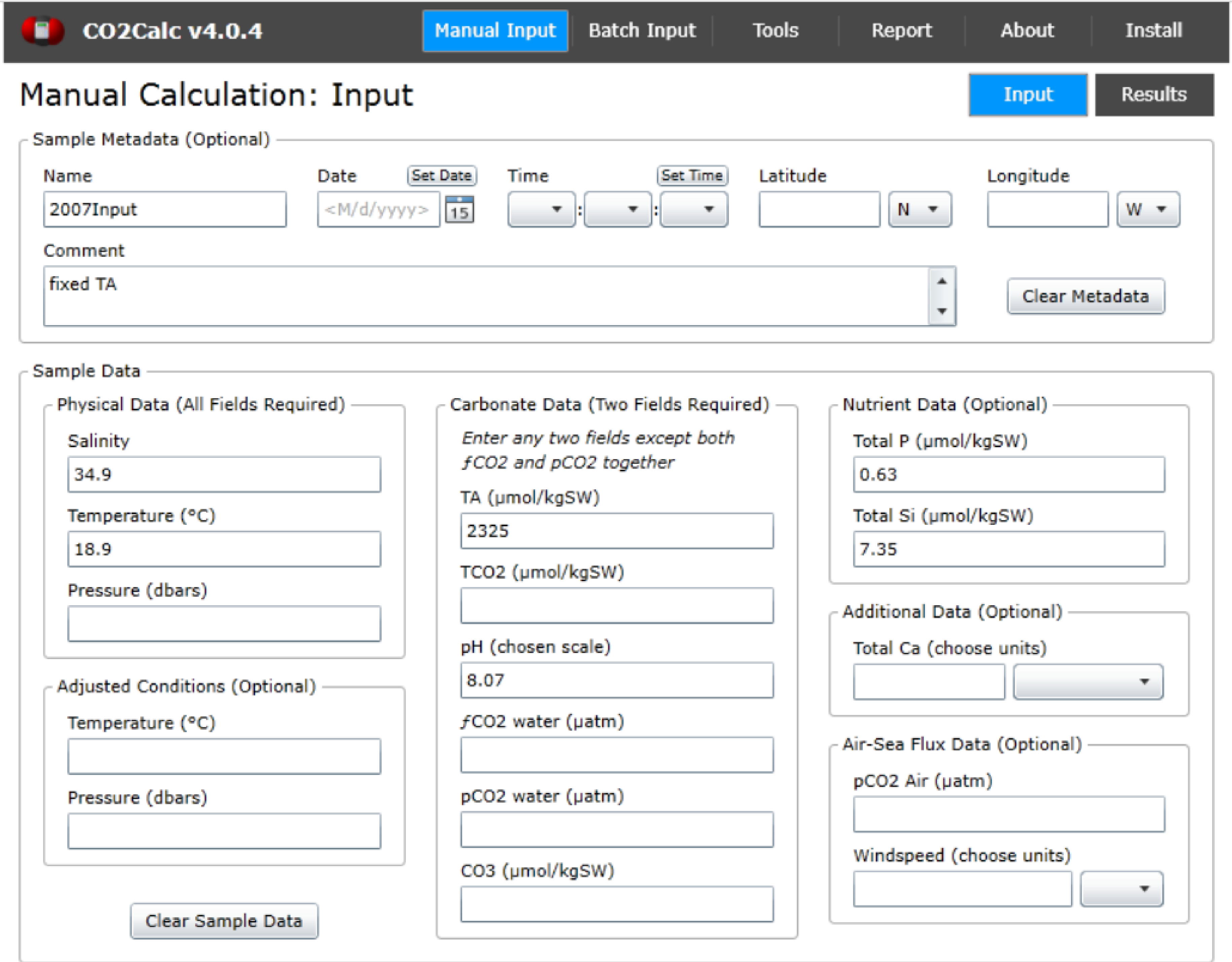
Constants: K1,K2:Leuker, KSO4: Dickson, pHtot, Bt: Uppstrom


CO2Calc v4.0.4
Manual Input
Batch Input
Tools
Report
About
Install
Manual Calculation: Input
Input
Results
Sample Metadata (Optional)
Name
2007Input
Date
Set Date
<M/d/yyyy>
15
Time
Set Time
Latitude
N
Longitude
W
Comment
fixed TA
Clear Metadata
Sample Data
Physical Data (All Fields Required)
Salinity
34.9
Temperature (°C)
18.9
Pressure (dbars)
Adjusted Conditions (Optional)
Temperature (°C)
Pressure (dbars)
Clear Sample Data
Carbonate Data (Two Fields Required)
Enter any two fields except both ƒCO2 and pCO2 together
TA (µmol/kgSW)
2325
TCO2 (µmol/kgSW)
pH (chosen scale)
8.07
ƒCO2 water (µatm)
pCO2 water (µatm)
CO3 (µmol/kgSW)
Nutrient Data (Optional)
Total P (µmol/kgSW)
0.63
Total Si (µmol/kgSW)
7.35
Additional Data (Optional)
Total Ca (choose units)
Air-Sea Flux Data (Optional)
pCO2 Air (µatm)
Windspeed (choose units)

"2007 CONDITIONS"

Sample Results

Input Conditions | Computed Constants

Physical Parameters

Salinity	34.900
Temperature (°C)	18.900
Pressure (dbars)	0.000
Density (kg m^3)	1024.971

Nutrient Data

Total P (µmol/kgSW)	0.630
Total Si (µmol/kgSW)	7.350

Air-Sea CO2 Flux

Flux (mmol/m^2/d)	

Carbonate

TA (µmol/kgSW)	2325.000
TCO2 (µmol/kgSW)	2061.391
pH (chosen scale)	8.070
ƒCO2 water (µatm)	377.975
pCO2 water (µatm)	379.279
CO3 (µmol/kgSW)	188.004

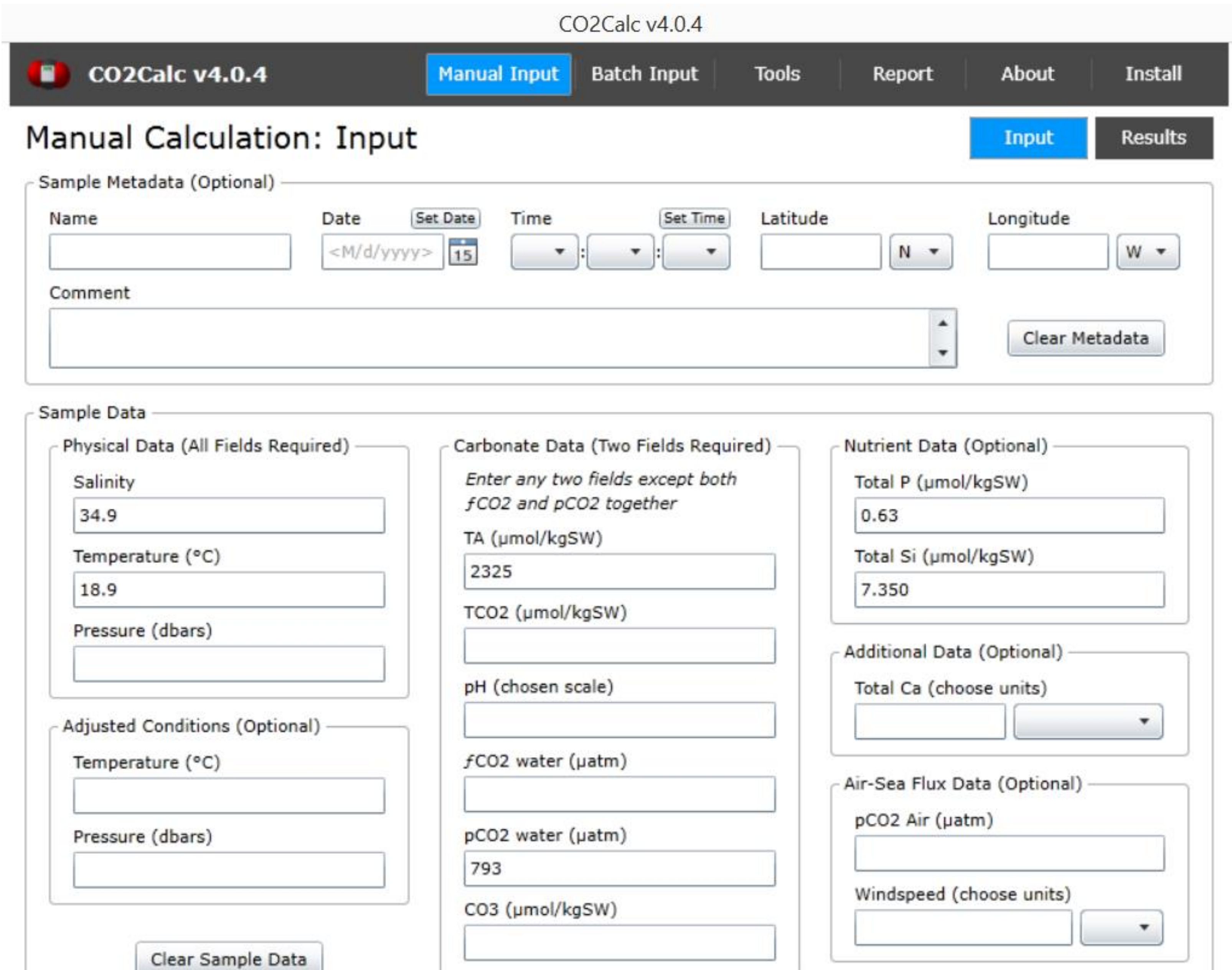
Calcium

Calculated (µmol/kgSW)	10255.185
User Value	

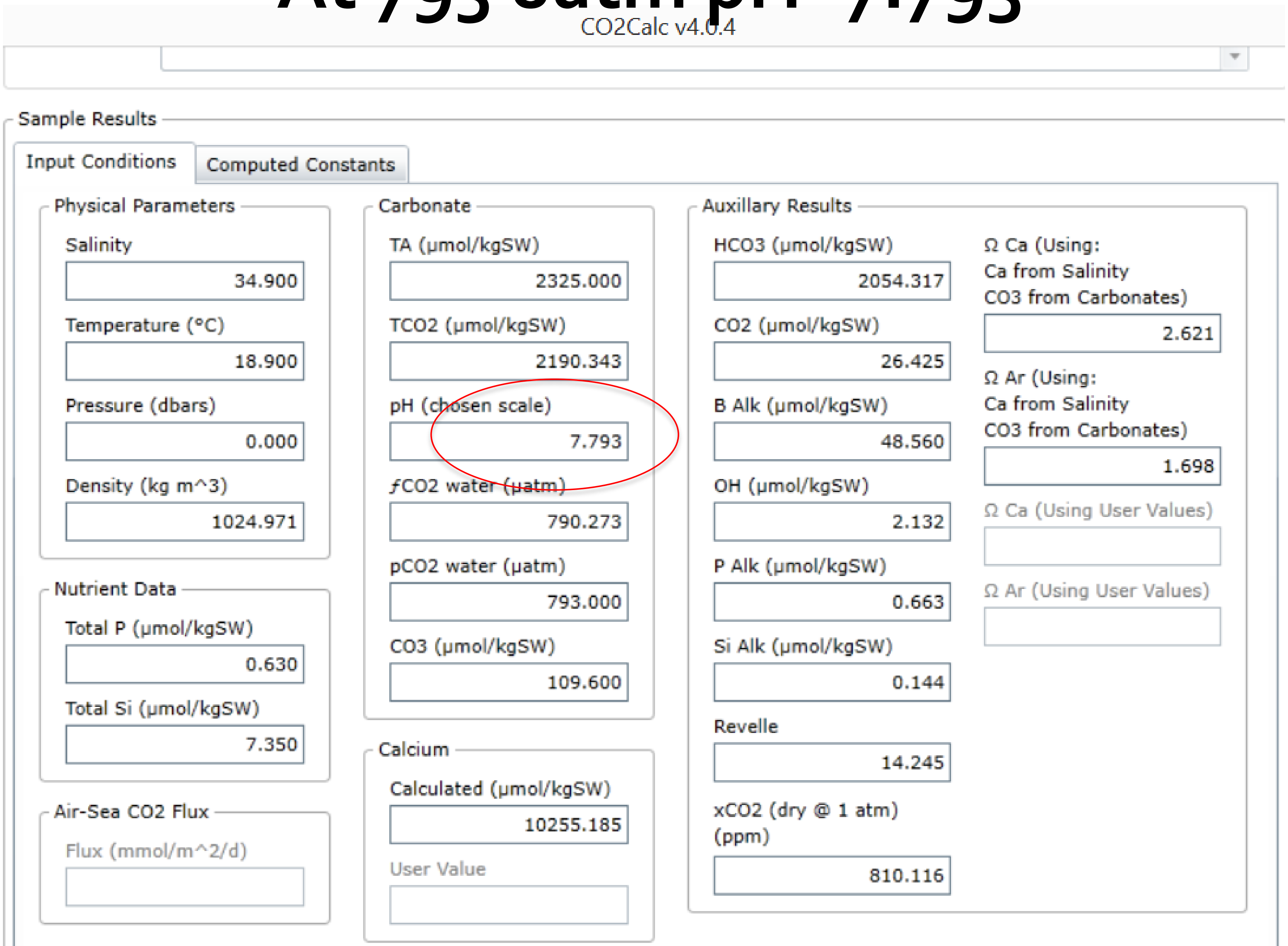
Auxillary Results

HCO3 (µmol/kgSW)	1860.748
CO2 (µmol/kgSW)	12.639
B Alk (µmol/kgSW)	83.246
OH (µmol/kgSW)	4.038
P Alk (µmol/kgSW)	0.701
Si Alk (µmol/kgSW)	0.268
Revelle	10.452
xCO2 (dry @ 1 atm) (ppm)	387.465
Ω Ca (Using: Ca from Salinity CO3 from Carbonates)	4.495
Ω Ar (Using: Ca from Salinity CO3 from Carbonates)	2.913
Ω Ca (Using User Values)	
Ω Ar (Using User Values)	

NOW 793 µatm (2100)



At 793 uatm pH=7.793



TCO_2 increased
TA constant

Summary: Bubbling of CO_2 gas

Technique: Bubble different CO_2 gas mixtures in seawater

(1) air and CO_2

(2) CO_2-free air and CO_2

(3) CO_2-free air, air and CO_2

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(1) pH-stat or pCO_2-stat

(2) bubbling with premixed gases (purchased or made with mass flow controllers or gas mixing pumps)

In both cases, TCO_2 increased and TA remained same

Advantages: TA assumed constant (or measured)

Disadvantages: Requires daily calibration; Can cause coagulation of organic matter, or unwanted turbulence; changes in alkalinity because of precipitation or dissolution of caco3 not accounted for

seacarb: pgas

TCO2 increased
TA constant

Bubbling of CO2 gas

Example: **Estimate the volume of CO2 gas needed to adjust pCO2 from 384 to 793 µatm**

@STP:

L of $CO2_{(g)}$ = ΔTCO2 (mol kg^{-1} SW) * Mol. Wt. CO2 / density of $CO2_{(g)}$

L of $CO2_{(g)}$ = (0.000129 mol kg^{-1} SW * 44.01 g CO2 mol^{-1})/1.808 g L^{-1}

= 0.00314 L kg^{-1} SW

= 3.14 mL kg^{-1} SW

In reality, this calculation is not very useful.
The best way to determine volume of gas needed is to experiment with it!

TCO_2 increased
TA constant

Adding high-CO_2 water

Technique: Mixing of two water masses

(T=18.9°C; S=34.9; TA=2325 µmol kg^{-1})

Water mass #1: $pCO_2=10^6$ µatm (CO_2-saturated)

Water mass #2: pCO_2=384 µatm

Desired water mass pCO_2: pCO_2=793 µatm

Q: What proportions of water masses #1 and #2 should be mixed to achieve the desired concentration?

TCO2 increased
TA constant

Adding high-CO_2 water

Technique: Mixing of two water masses

(T=18.9°C; S=34.9; TA=2325 µmol kg^{-1})

Water mass #1: $pCO_2=10^6$ µatm -> TCO_2 = 35666 µmol kg^{-1}

Water mass #2: pCO_2=384 µatm -> TCO_2 = 2063 µmol kg^{-1}

Desired mass: pCO_2=793 µatm -> TCO_2 = 2190 µmol kg^{-1}

TCO_2 increased
TA constant

Adding high-CO_2 water

Technique: Mixing of two water masses

(T=18.9°C; S=34.9; TA=2325 µmol kg^{-1})

Water mass #1: $pCO_2=10^6$ µatm -> TCO_2 = 35666 µmol kg^{-1}

Water mass #2: pCO_2=384 µatm -> TCO_2 = 2063 µmol kg^{-1}

Desired mass: pCO_2=793 µatm -> TCO_2 = 2190 µmol kg^{-1}

Basic Mixing Equation:

$$Conc_1 \times Vol_1 + Conc_2 \times (Vol_2 - Vol_1) = Conc_3 \times (Vol_2)$$

$$35666\ \mu mol\ kg^{-1} \times (V_1) + 2063\ \mu mol\ kg^{-1} \times (1-V_1) = 2190\ \mu mol\ kg^{-1} \times (1)$$

Vol_1 = 0.00378 kg of high pCO_2 seawater

$1-V_1$ = 0.99622 kg of normal pCO_2 seawater

TCO2 increased
TA constant

Summary:Adding high-CO_2 water

Technique: Mixing of two water masses

1. Water with normal values (e.g. pCO_2=373 µatm)
2. Water that has been saturated with CO_2 ($pCO_2=10^6$ µatm)

Advantages:

- Natural simulation of future conditions
- No effect on TA

Disadvantages:

- High pCO_2 waters can easily lose CO_2 due to gas exchange

Seacarb function: pmix

TCO2 changed
TA changed

Adding CO_3^{2-} and/or HCO_3^- (no acid addition)

Technique: Add CO_3 and/or HCO_3 to obtain desired TCO2 level

1. Closed system:

   TA increases by: $2x\Delta[CO_3^{2-}]$ and $1x\Delta[HCO_3^-]$

   DIC increases by: $1x\Delta[CO_3^{2-}]$ and $1x\Delta[HCO_3^-]$

2. Open system: DIC equilibrates due to air-sea gas exchange

Advantages:

- Can be used to examine physiological responses to different components of the carbonate chemistry

Disadvantages:

- Both TCO2 and TA changes and not realistic of year 2100

- **seacarb function:** pTA

TCO2 increased
TA constant

Adding CO_3^{2-} and/or HCO_3^- + acid

Technique:

1. Add CO3 and/or HCO3 to obtain desired TCO2 level
2. Add acid to lower TA to desired target level

Example:

1. **Add 15.3×10^{-6} mol kg^{-1} of Na_2CO_3**
   Add 111.2×10^{-6} mol kg^{-1} of $NaHCO_3$

Note that this elevates DIC by 126.5 umol
But also elevates TA by 141.8 umol

Remember: DIC increases by:1x$\Delta[CO3^{2-}]$ and 1x$\Delta[HCO3^-]$
TA increases by: 2x$\Delta[CO3^{2-}]$ and 1x$\Delta[HCO3^-]$

2. **Both DIC and TA increased, so reduce TA to initial value by adding 14.18 ml of 0.01N HCl to restore TA to initial value**

Adding CO_3^{2-} and/or HCO_3^- + acid

	$pCO_{2\,sw}$ (μatm)	pH_T (–)	$[H^+]$ (a)	TA (b)	DIC (b)	$[CO_2]$ (b)	$[HCO_3^-]$ (b)	$[CO_3^{2-}]$ (b)	Ω_c (–)	Ω_a (–)
Year 2007	384	8.065	8.6	2325	2065	12.8	1865	187	4.5	2.9
Year 2100	793	7.793	16.1	2325	2191	26.4	2055	110	2.6	1.7
Addition of:										
CO_3^{2-} and HCO_3^-; closed sys.	400	8.073	8.4	2467	2191	13.3	1977	201	4.8	3.1
followed by acid addition; closed sys.	793	7.793	16.1	2325	2191	26.4	2055	110	2.6	1.7

TCO_2 constant
TA increased

Adding strong acids, bases

Technique: Add strong acids to decrease TA - OR –
Add strong bases to increase TA

1. In a closed system, DIC remains unchanged
2. In an open system, DIC will change due to air-sea gas exchange

Example:

1. ***How much acid do you need to change the alkalinity to cause a pCO_2 change from 394 to 793 uatm?***
   Answer 140.8 umol kg^{-1}
2. **Add 14.08 ml of 0.01N HCl to 1 kg seawater**

seacarb function: ppH

Addition of strong acid

	pCO_{2sw} (μatm)	pH_T (–)	$[H^+]$ (a)	TA (b)	DIC (b)	$[CO_2]$ (b)	$[HCO_3^-]$ (b)	$[CO_3^{2-}]$ (b)	Ω_c (–)	Ω_a (–)
Year 2007	384	8.065	8.6	2325	2065	12.8	1865	187	4.5	2.9
Year 2100	793	7.793	16.1	2325	2191	26.4	2055	110	2.6	1.7
Acid addition; closed sys.	793	7.768	17.1	2184	2065	26.4	1940	98	2.3	1.5
Acid addition; open sys.	384	8.042	9.1	2184	194	12.8	1767	167	4	2.6

TCO_2 constant
TA increased

Adding strong acids, bases to bring pCO_2 to target

Technique: Add strong acids to decrease TA - OR –

Add strong bases to increase TA

1. In a closed system, DIC remains unchanged
2. In an open system, DIC will change due to air-sea gas exchange

Advantages:

Relatively easy to do

Can be used in flow-through systems

Disadvantages:

Not a realistic representation of the CO_2 chemistry but depends on your question

Manipulation of [Ca^{2+}]

Technique: Add or reduce the [Ca2+] levels

Causes changes in the $CaCO_3$ saturation states

Advantages:

Can be used to examine the role of Ca2+ in saturation state and it's effects on organisms

seacarb function: pCa

Summary of Methods

Approach	Target values reached?	Ease of use	Relative cost
Acid addition	No (only pCO2)	***	*
Acid addition and restoration of TA	Yes	*	*
Gas bubbling	Yes	***	***
Mixing with high-CO_2 seawater	Yes	**	*
Addition of HCO_3^- and/or CO_3^{2-}	No	**	*
Calcium manipulation	No (only Ω)	*	*

LAST THOUGHTS

- ✓ **Understand how your choice of approach affects carbonate chemistry**
- ✓ **The more information you have for planning, the better**
- ✓ **Choose reasonable target conditions**
- ✓ **Know your chemistry…don't rely on CO2calc (or any other program) to know it for you…this is a VERY common mistake**
- ✓ **Biological effects on the chemistry must be considered in experimental design**
- ✓ **Monitor closely - before, during, and after chemical manipulations and throughout experiments**