Introduction to CO_2 speciation calculations

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Computer programs exist for these calculations

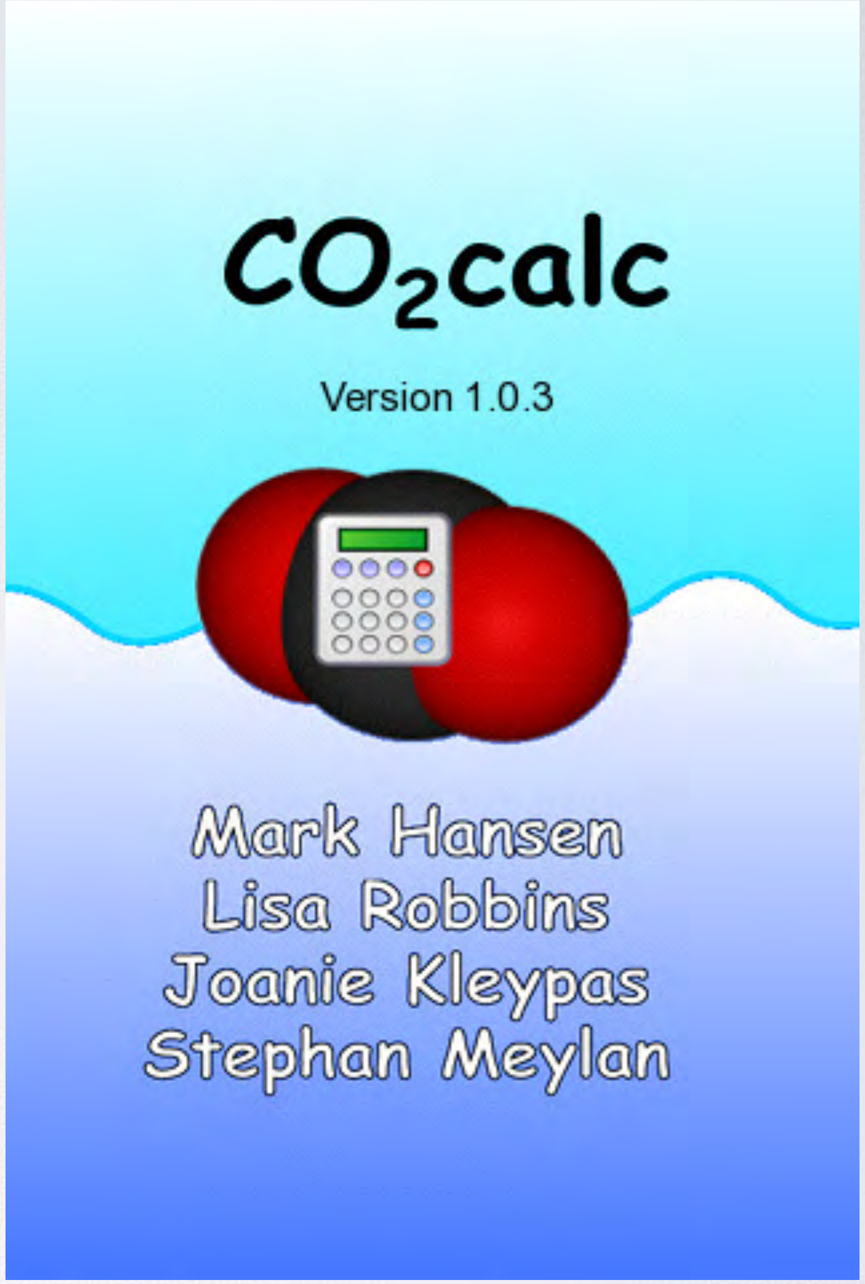
- Provide built in data for the various equilibrium constants which are functions of salinity, temperature, and pressure as well as for total concentrations such as boron that are proportional to salinity.

- Allow some additional acid-base information to be added (*e.g.* total phosphate and/or total silicate concentrations)

- Allow calculation of CO_2 speciation (typically from 2 analytical parameters, salinity & temperature)

Florida Shelf Ecosystems Response to Climate Change Project

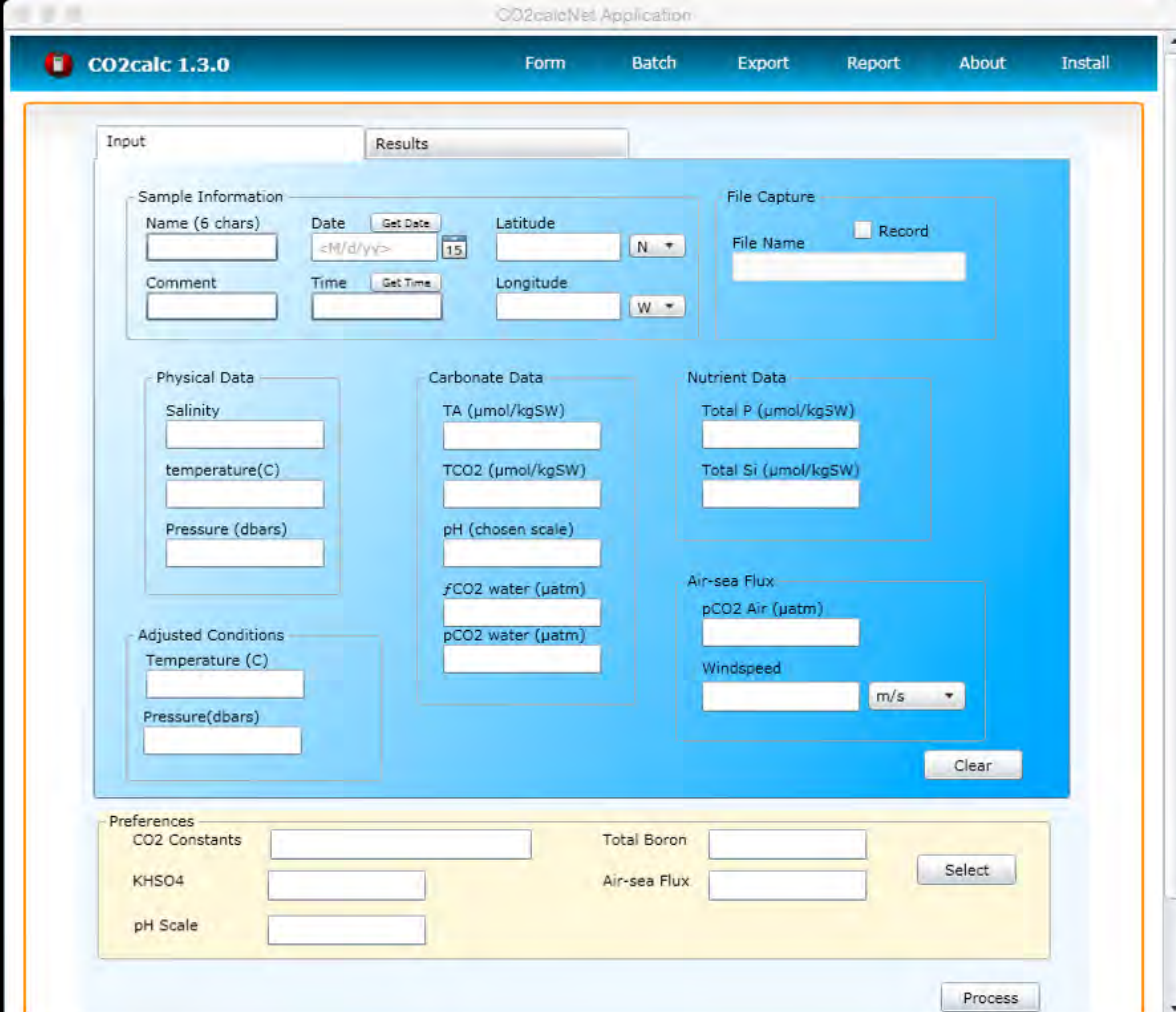
CO2calc: A User-Friendly Seawater Carbon Calculator for Windows, Mac OS X, and iOS (iPhone)



http://pubs.usgs.gov/of/2010/1280/

Open-File Report 2010–1280

U.S. Department of the Interior
U.S. Geological Survey


CO2calcNet Application
CO2calc 1.3.0
Form
Batch
Export
Report
About
Install
Input
Results
Sample Information
Name (6 chars)
Date
Get Date
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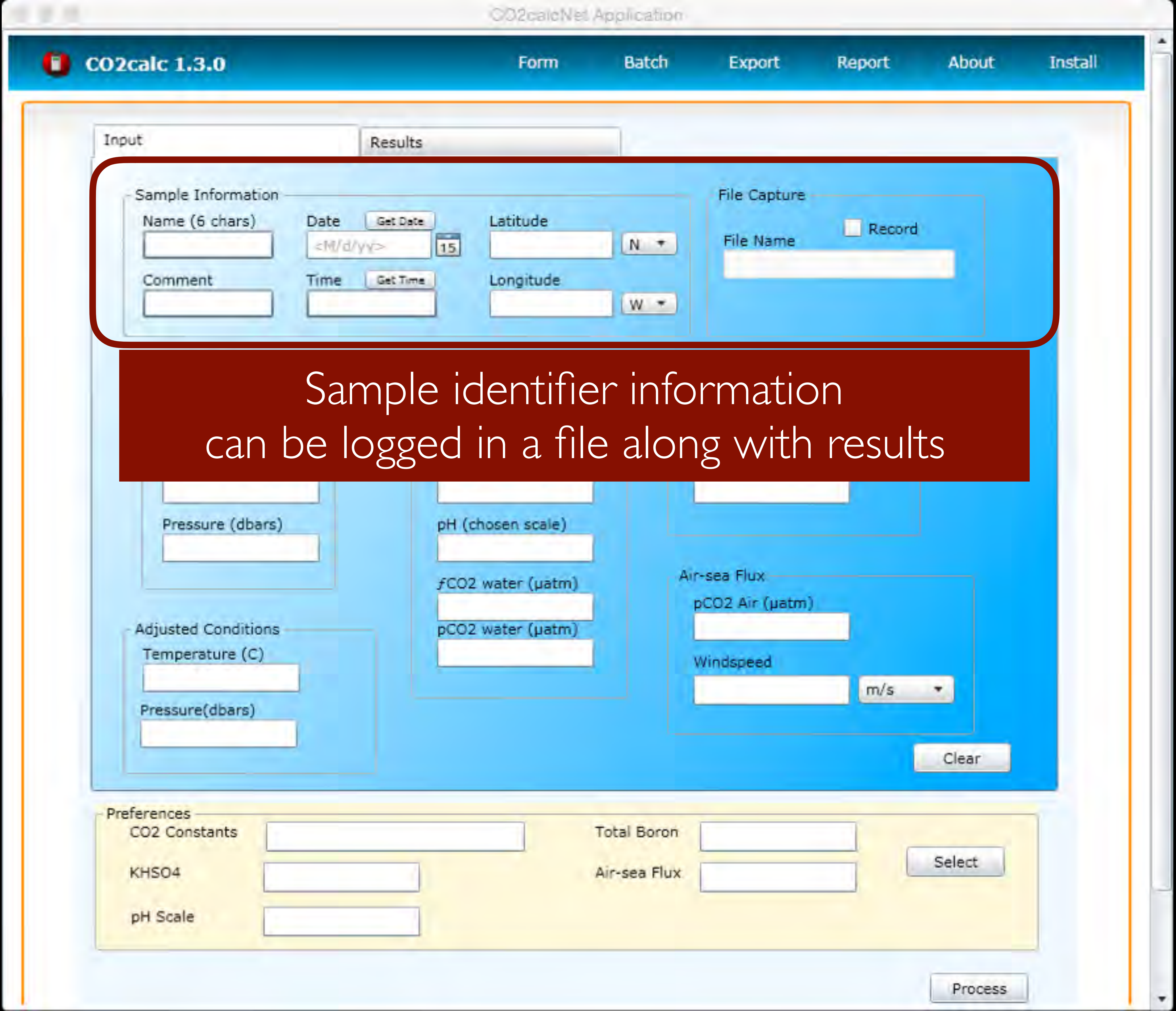
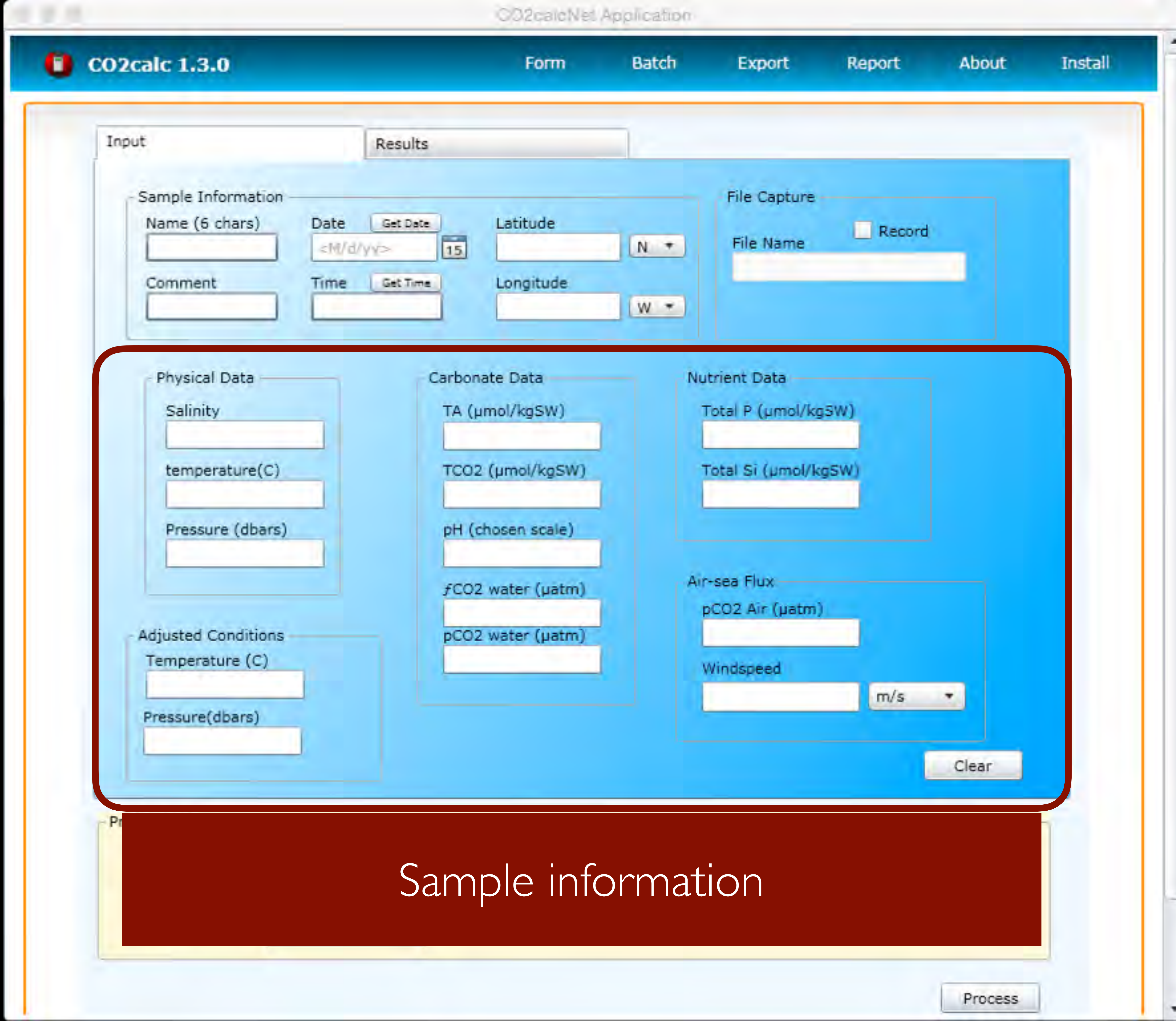
File Capture
Record
File Name
Physical Data
Salinity
temperature(C)
Pressure (dbars)
Carbonate Data
TA (µmol/kgSW)
TCO2 (µmol/kgSW)
pH (chosen scale)
ƒCO2 water (µatm)
pCO2 water (µatm)
Nutrient Data
Total P (µmol/kgSW)
Total Si (µmol/kgSW)
Air-sea Flux
pCO2 Air (µatm)
Windspeed
m/s
Adjusted Conditions
Temperature (C)
Pressure(dbars)
Clear
Preferences
CO2 Constants
Total Boron
KHSO4
Air-sea Flux
Select
pH Scale
Process



Sample identifier information
can be logged in a file along with results

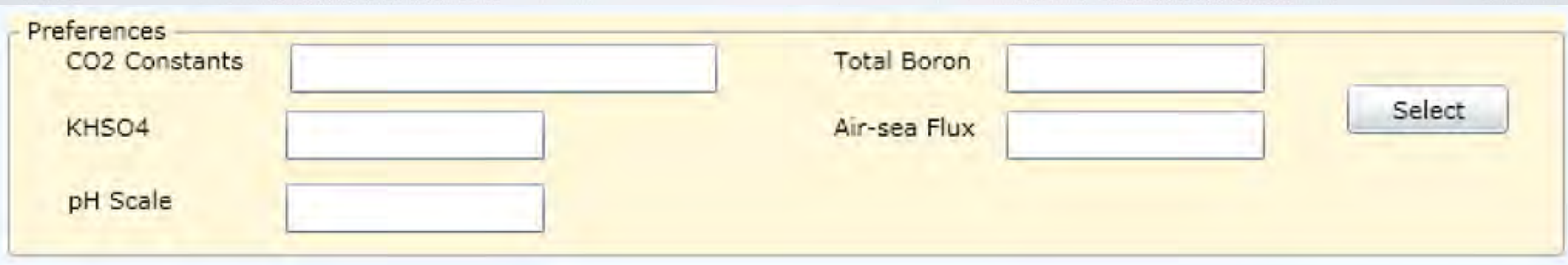


Sample information

Choice of CO_2 constants, etc.

Step 1

Choose the set of equilibrium constants, *etc*. that you wish to use.



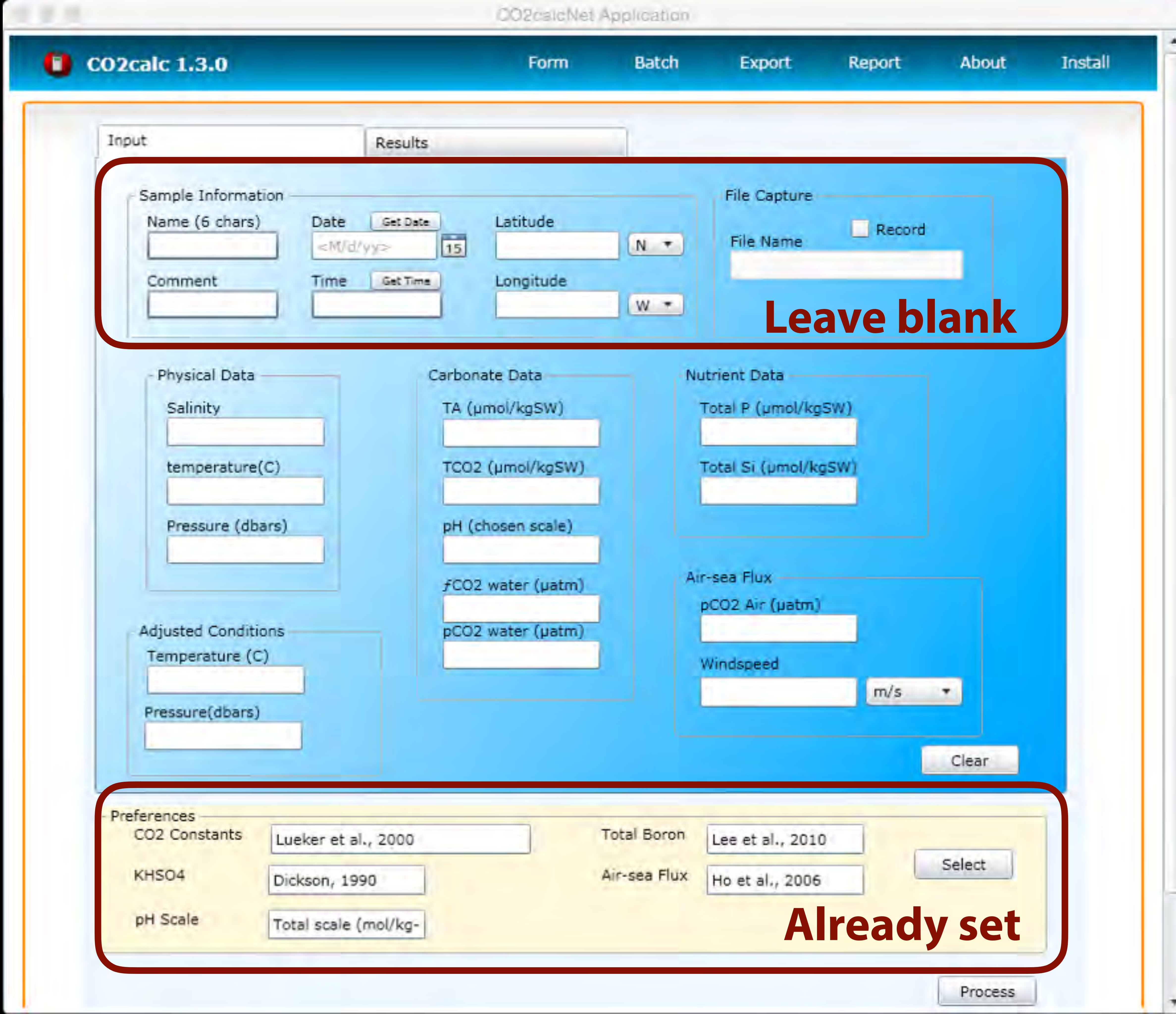
These are the choices I would usually recommend for systems with S > 20; I am sure they could be argued against.

The kinds of chemical questions we need to be able to answer

- How can I estimate the CO_2 composition of a sample of sea water?
- If the CO_2 level in the atmosphere increases by 300 ppm, how much will the pH in the surface ocean change?
- What will be the consequent change in the saturation state of aragonite?
- Will this be the same all over the oceans? Why? (or Why not?)
- How should I modify the CO_2 composition of a sample of sea water to reach a desired target composition?

A simple example

Surface sea water from the central North Atlantic


CO2calcNet Application
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Latitude
N
Comment
Time
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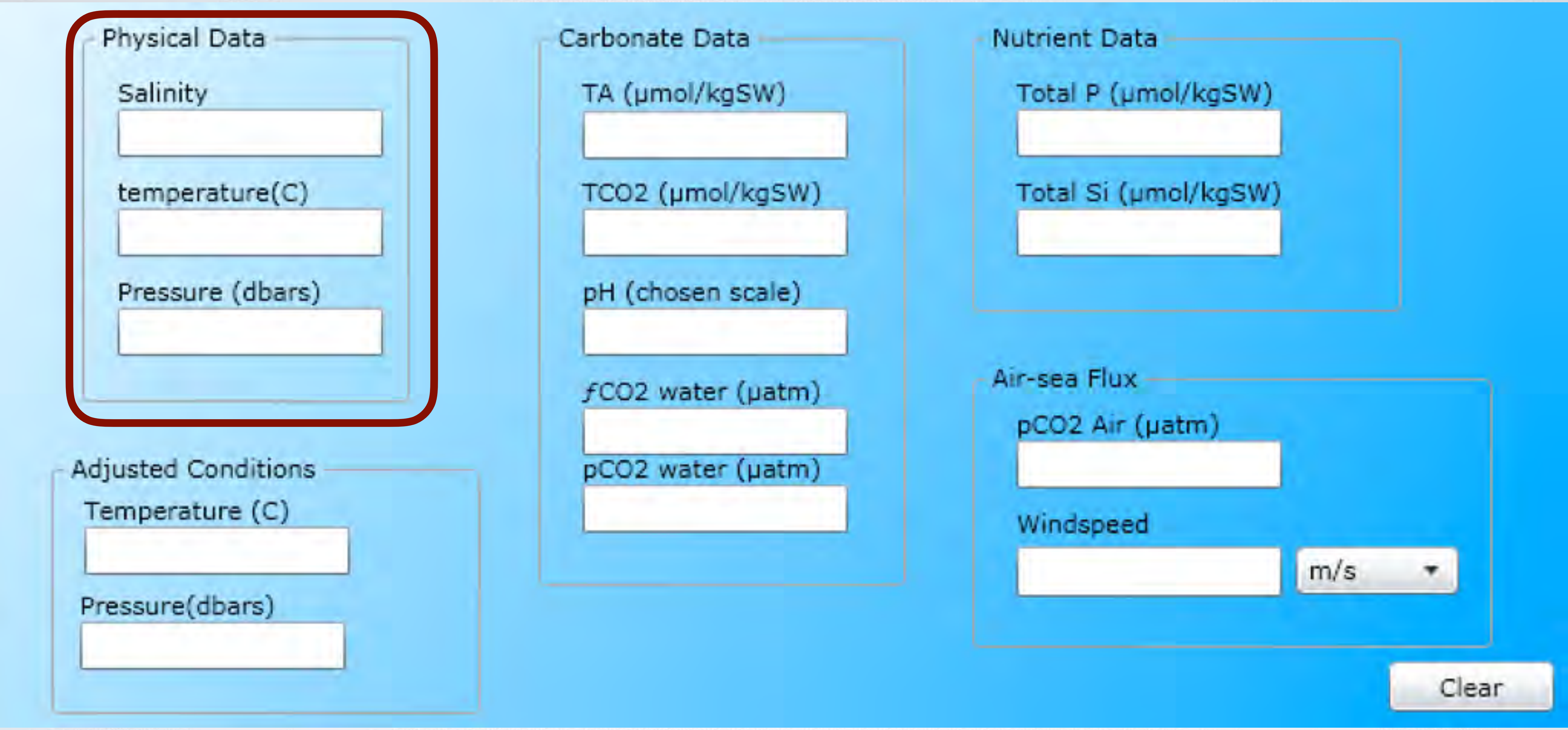
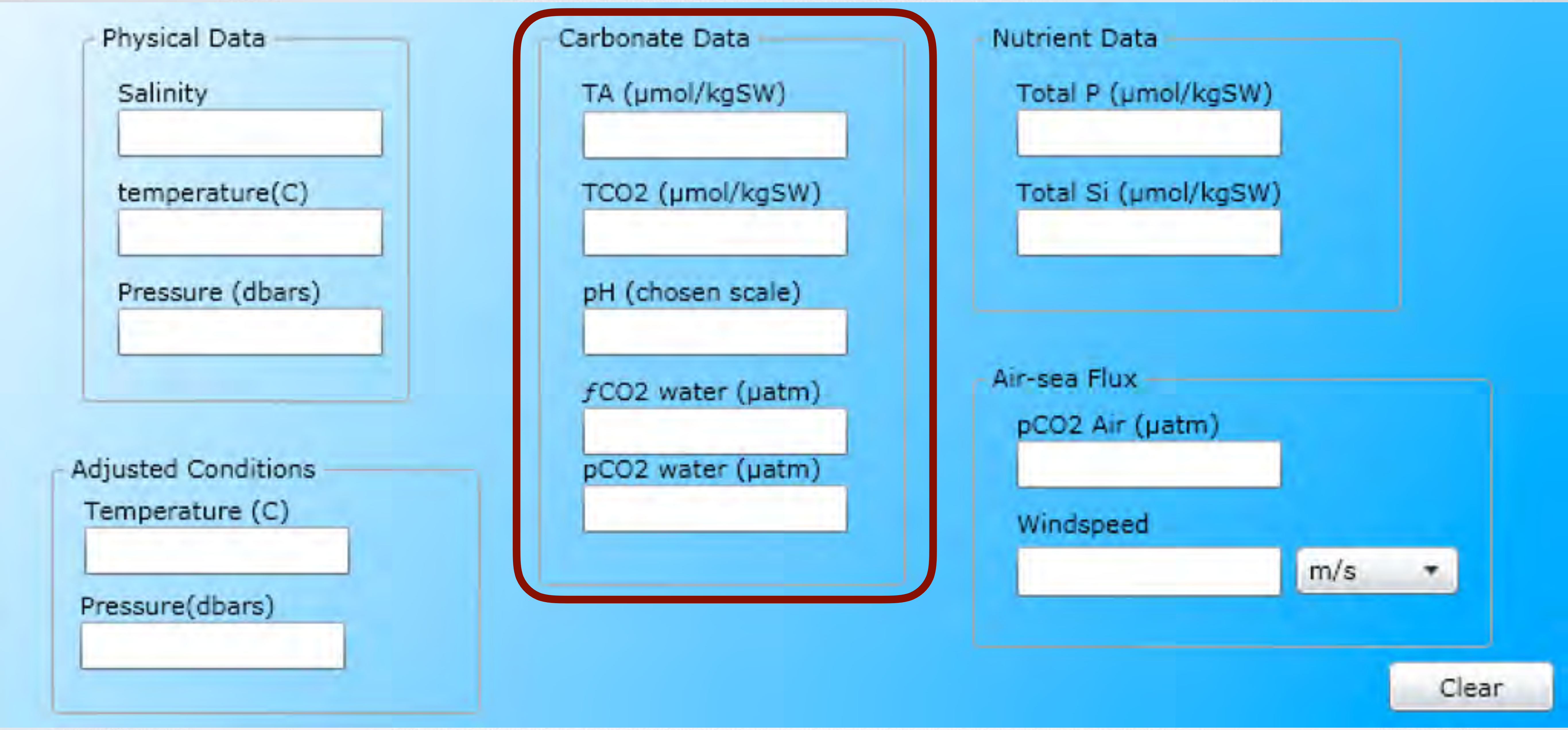
File Capture
Record
File Name
Leave blank
Physical Data
Salinity
temperature(C)
Pressure (dbars)
Carbonate Data
TA (µmol/kgSW)
TCO2 (µmol/kgSW)
pH (chosen scale)
ƒCO2 water (µatm)
pCO2 water (µatm)
Nutrient Data
Total P (µmol/kgSW)
Total Si (µmol/kgSW)
Air-sea Flux
pCO2 Air (µatm)
Windspeed
m/s
Adjusted Conditions
Temperature (C)
Pressure(dbars)
Clear
Preferences
CO2 Constants
Lueker et al., 2000
Total Boron
Lee et al., 2010
KHSO4
Dickson, 1990
Air-sea Flux
Ho et al., 2006
Select
pH Scale
Total scale (mol/kg-
Already set
Process

These are needed because the equilibrium constants are functions of salinity, temperature, and pressure; also total boron is estimated from salinity



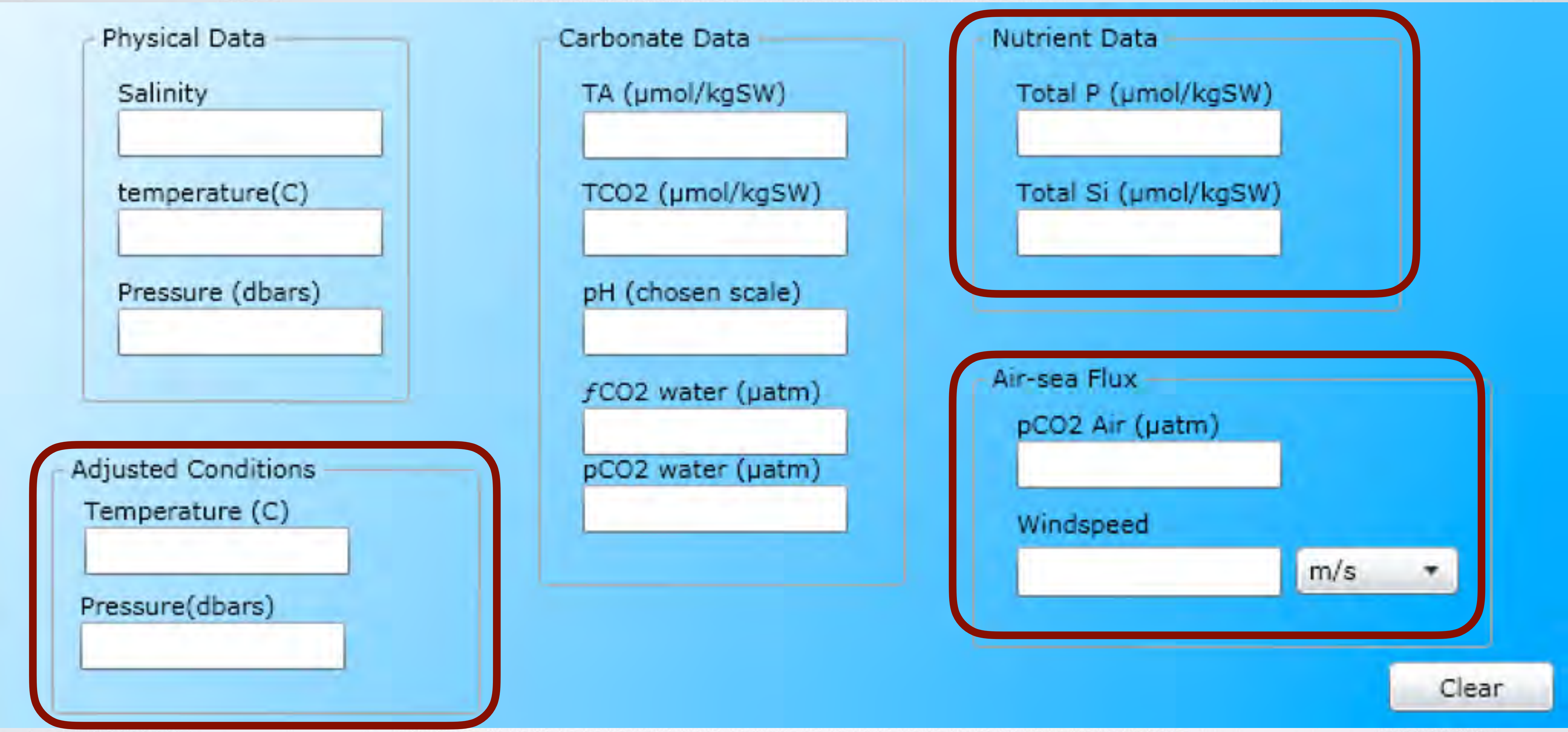
Pressure here is gauge pressure, *i.e.* zero at the sea surface (also 1 dbar $\approx$ pressure exerted by 1 m of seawater)

Remember: only 2 carbonate system measurements are needed to define the chemical state of the system for a particular *S*, *T*, and *p*



If you have more than 2 of these with non-zero values, then the top two are the ones that are used for the calculation

Leaving "Nutrient Data" blank is the same as entering zero total concentrations



Leaving "Adjusted Conditions" blank repeats the values above

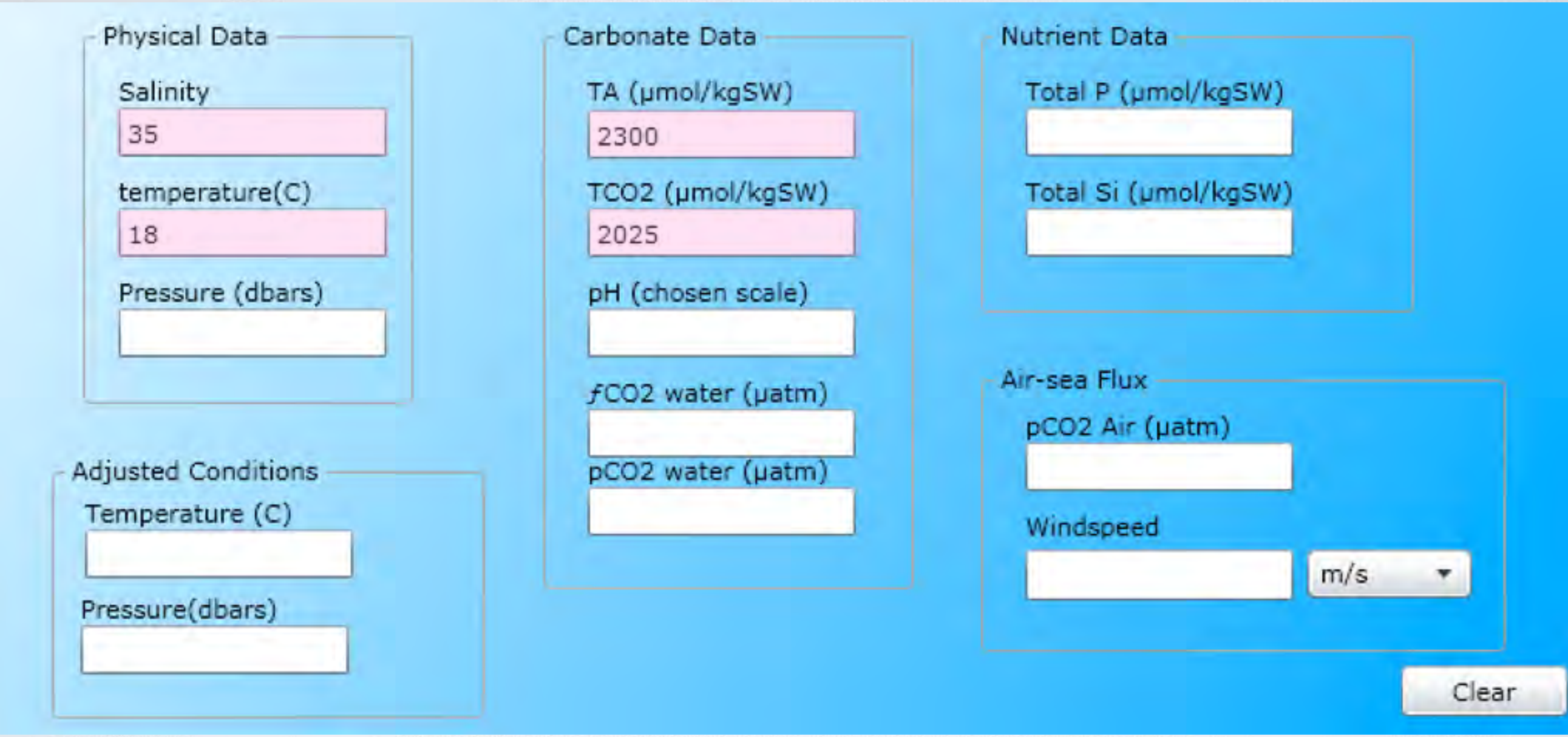
Leaving "Air-sea Flux" blank is OK, but yields a zero result

$S = 35$ **Surface sea water from the central North Atlantic**

$t = 18$ °C

$p = 0$ dbar (sea surface)

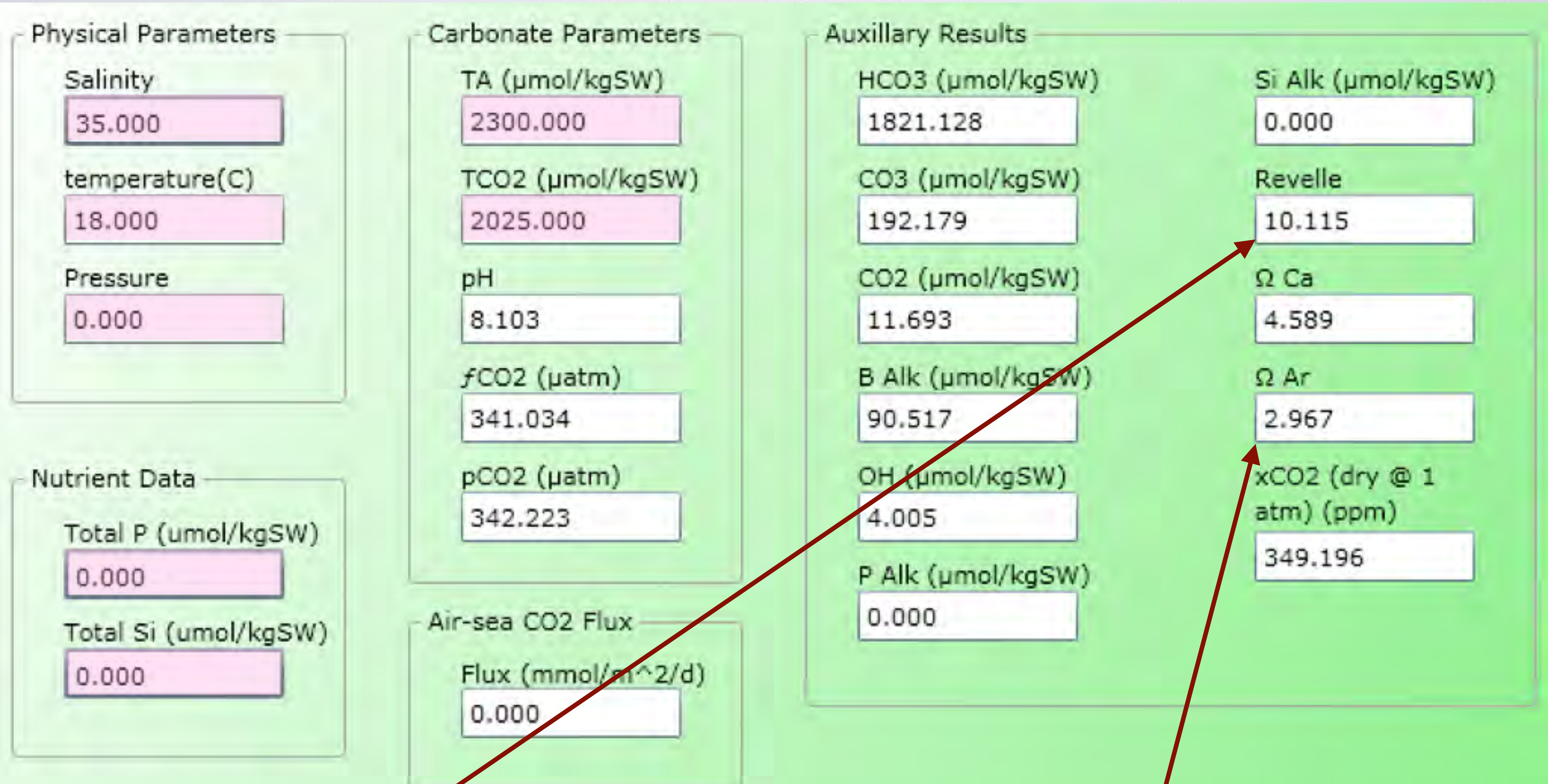
Nutrient concentrations assumed to be negligible



Total Alkalinity = 2300 µmol kg^{-1}

Total Dissolved Inorganic Carbon = 2025 µmol kg^{-1}

The parameters provided originally are repeated here together with a variety of calculated results



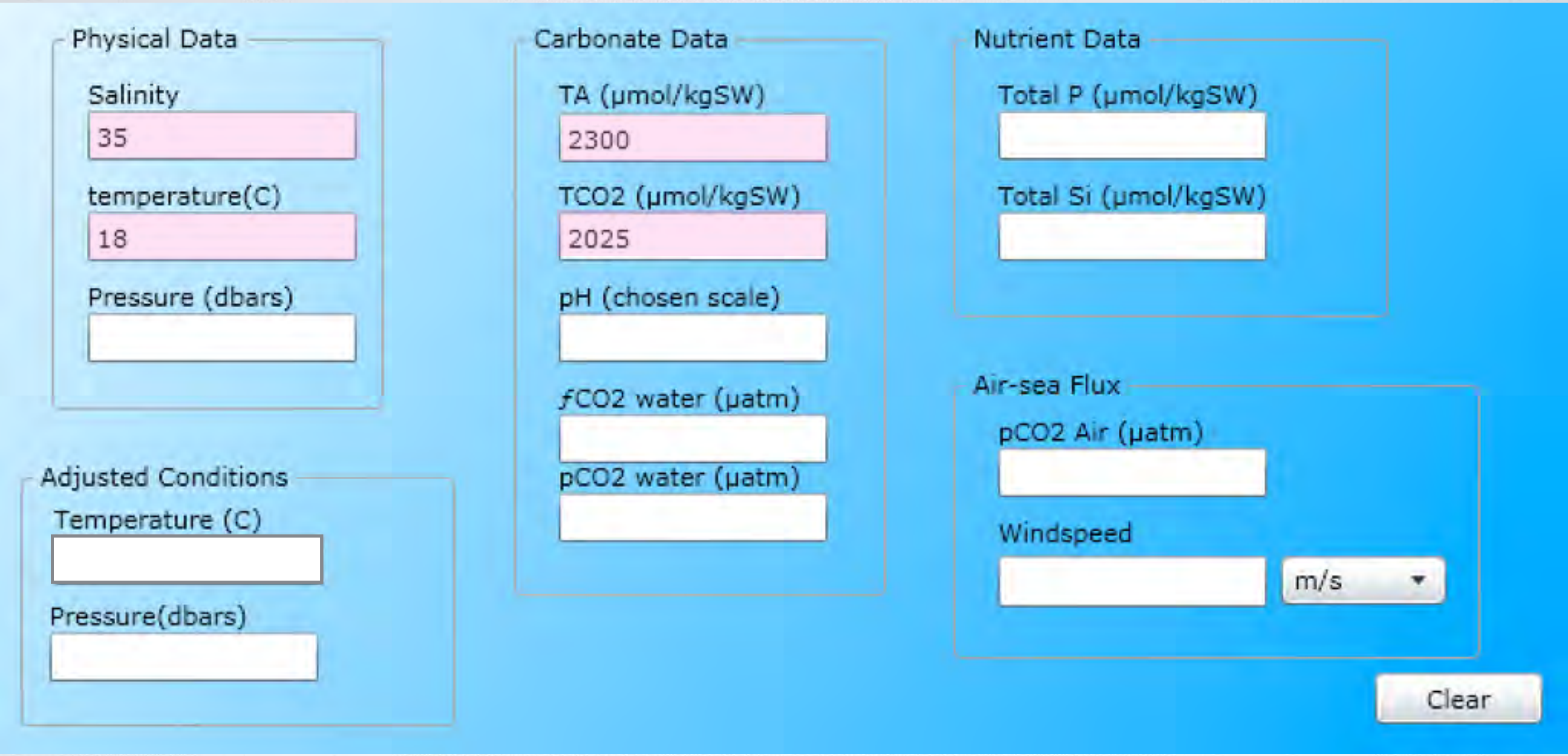
$$R = \frac{\partial \ln[CO_2]}{\partial \ln C_T} = \frac{\partial [CO_2]}{[CO_2]} \Big/ \frac{\partial C_T}{C_T}$$

$$\Omega(aragonite) = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}(aragonite)}$$

What happens if we warm up that water?

Increase temperature from 18 °C to 25 °C

Can do the calculation twice, changing the temperature from 18 to 25 °C or can take advantage of the "Adjusted Conditions"



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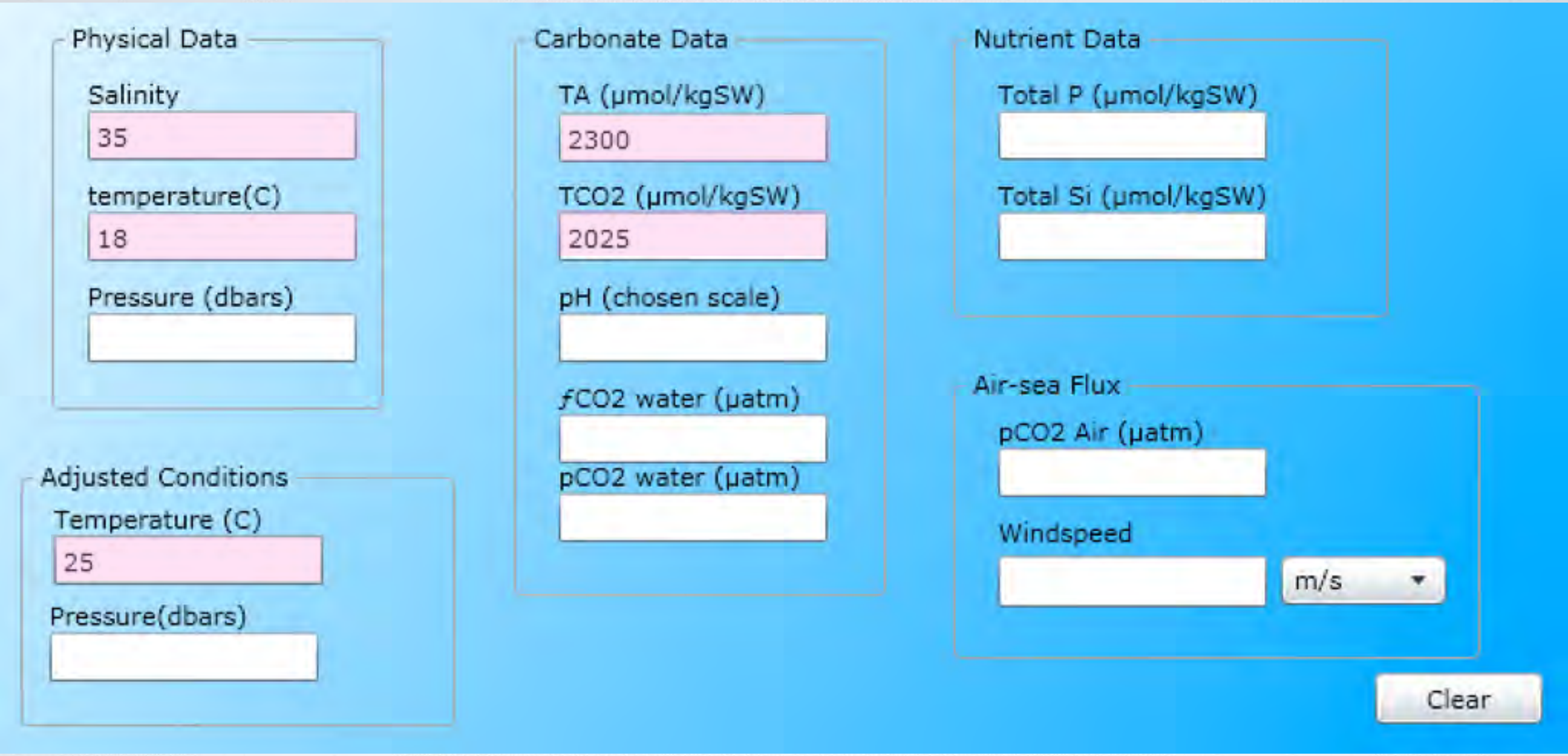


t = 18 °C   The change of temperature is for a closed system.

Results at Input | Results at Adjusted Conditions

Physical Parameters

- Salinity: 35.000
- temperature(C): 18.000
- Pressure: 0.000

Nutrient Data

- Total P (umol/kgSW): 0.000
- Total Si (umol/kgSW): 0.000

Carbonate Parameters

- TA (μmol/kgSW): 2300.000
- TCO2 (μmol/kgSW): 2025.000
- pH: 8.103
- ƒCO2 (μatm): 341.034
- pCO2 (μatm): 342.223

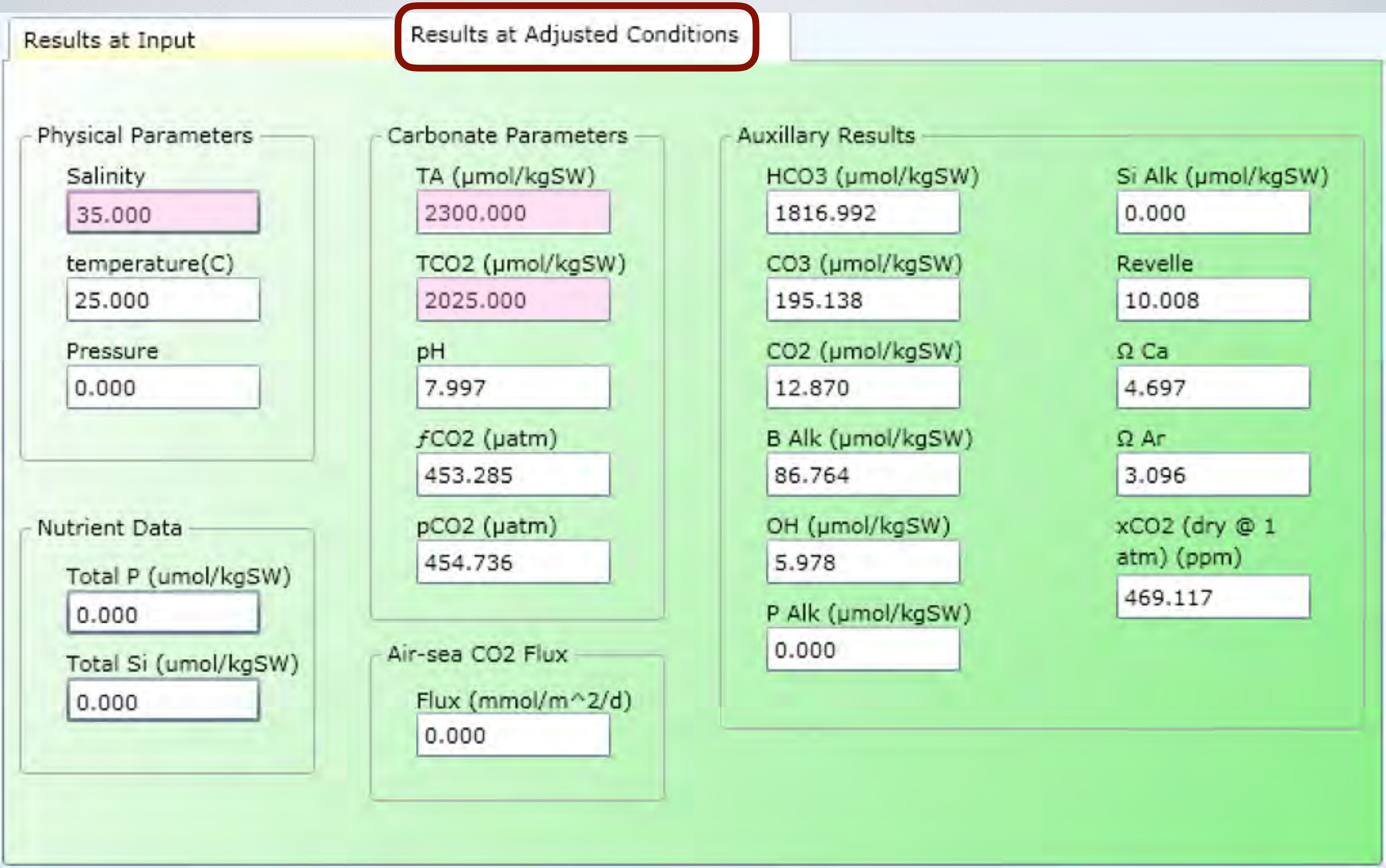
Air-sea CO2 Flux

- Flux (mmol/m^2/d): 0.000

Auxillary Results

- HCO3 (μmol/kgSW): 1821.128
- CO3 (μmol/kgSW): 192.179
- CO2 (μmol/kgSW): 11.693
- B Alk (μmol/kgSW): 90.517
- OH (μmol/kgSW): 4.005
- P Alk (μmol/kgSW): 0.000
- Si Alk (μmol/kgSW): 0.000
- Revelle: 10.115
- Ω Ca: 4.589
- Ω Ar: 2.967
- xCO2 (dry @ 1 atm) (ppm): 349.196

t = 25 °C The change of temperature is for a closed system.



Results at Input | Results at Adjusted Conditions

Physical Parameters

Salinity	35.000
temperature(C)	25.000
Pressure	0.000

Nutrient Data

Total P (umol/kgSW)	0.000
Total Si (umol/kgSW)	0.000

Carbonate Parameters

TA (μmol/kgSW)	2300.000
TCO2 (μmol/kgSW)	2025.000
pH	7.997
ƒCO2 (μatm)	453.285
pCO2 (μatm)	454.736

Air-sea CO2 Flux

Flux (mmol/m^2/d)	0.000

Auxillary Results

HCO3 (μmol/kgSW)	1816.992
CO3 (μmol/kgSW)	195.138
CO2 (μmol/kgSW)	12.870
B Alk (μmol/kgSW)	86.764
OH (μmol/kgSW)	5.978
P Alk (μmol/kgSW)	0.000
Si Alk (μmol/kgSW)	0.000
Revelle	10.008
Ω Ca	4.697
Ω Ar	3.096
xCO2 (dry @ 1 atm) (ppm)	469.117

What happens to pH or p(CO_2)?

t = 18 °C The change of temperature is for a closed system.

Results at Input | Results at Adjusted Conditions

Physical Parameters

Salinity: 35.000

temperature(C): 18.000

Pressure: 0.000

Nutrient Data

Total P (umol/kgSW): 0.000

Total Si (umol/kgSW): 0.000

Carbonate Parameters

TA (µmol/kgSW): 2300.000

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pH: 8.103

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Flux (mmol/m^2/d): 0.000

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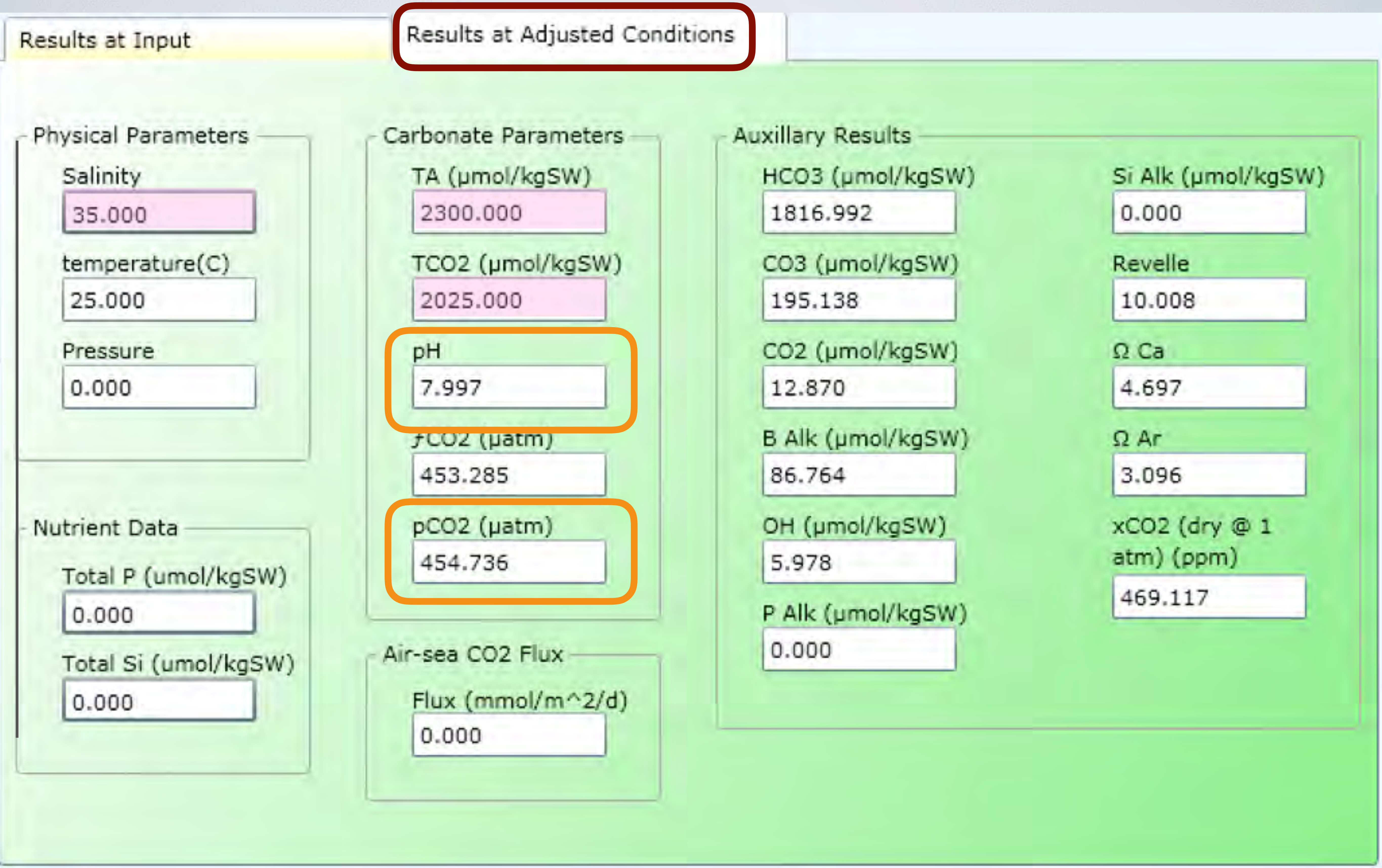
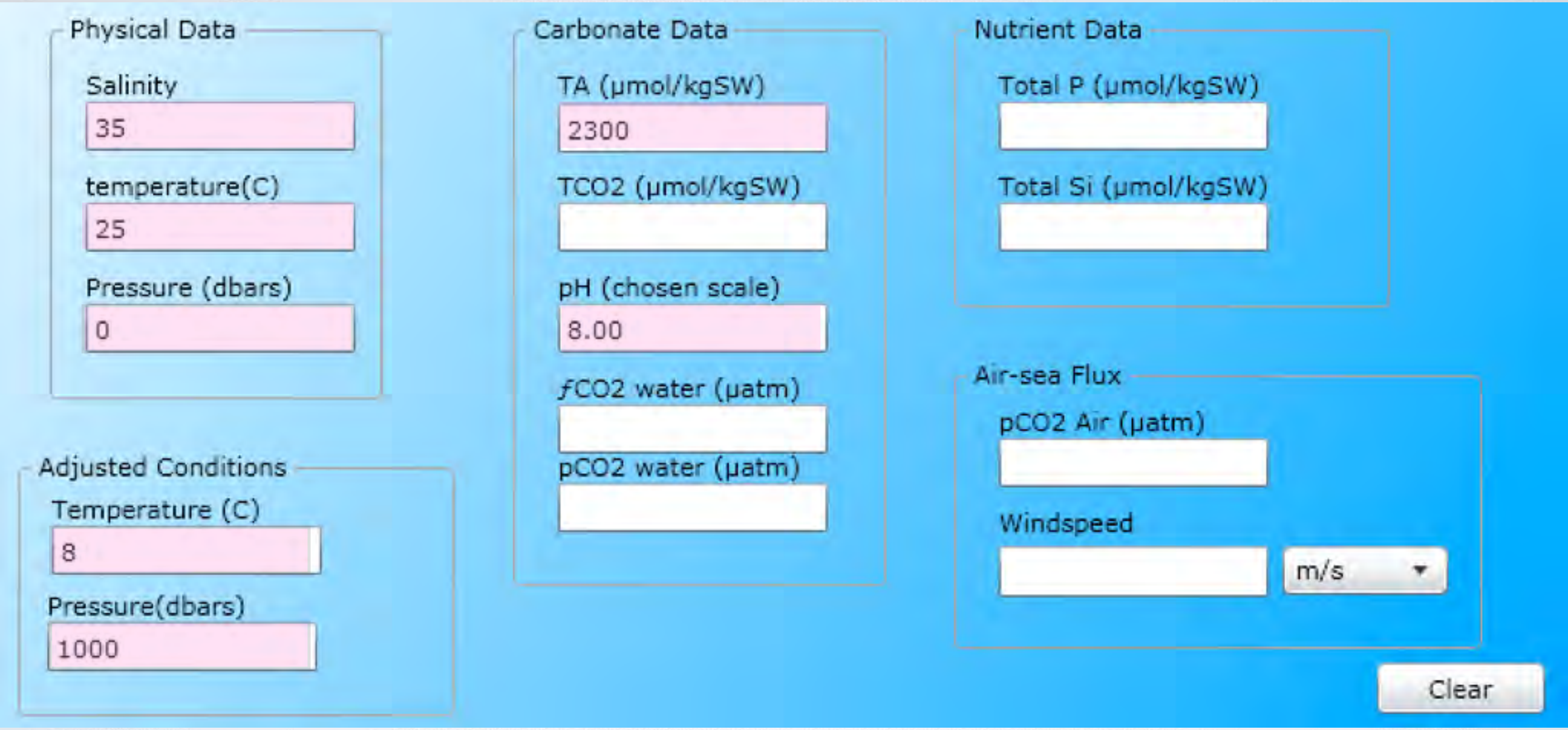


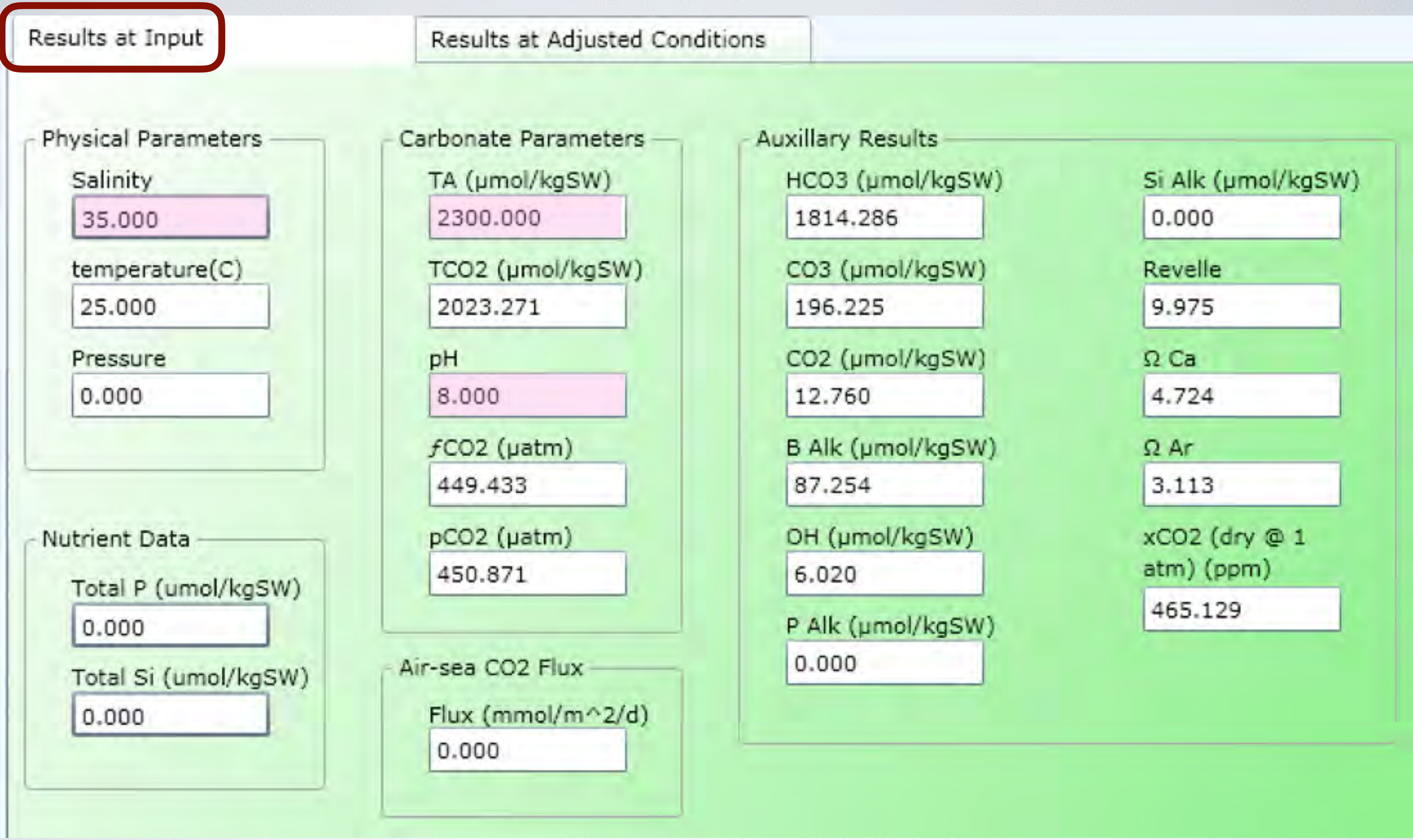
If we measure pH in the laboratory, we can use this approach to convert it to an estimated in situ value

Laboratory measurement of pH at 25 °C ("zero" pressure)



in situ **conditions 8 °C @ 1,000 m depth**

Calculation is for a closed system.



total dissolved inorganic carbon stays constant!

Calculation is for a closed system.

total dissolved inorganic carbon stays constant!

Time to try this for yourselves 😢

The kinds of chemical questions we need to be able to answer

- How can I estimate the CO_2 composition of a sample of sea water?
- If the CO_2 level in the atmosphere increases by 300 ppm, how much will the pH in the surface ocean change?
- What will be the consequent change in the saturation state of aragonite?
- Will this be the same all over the oceans? Why? (or Why not?)
- How should I modify the CO_2 composition of a sample of sea water to reach a desired target composition?

If the CO_2 level in the atmosphere increases by 300 ppm, how much will the pH in the surface ocean change?

What will be the consequent change in the saturation state of aragonite?

What information do we need to make this calculation?

1. Estimates of S, t, and P (= 0 at sea surface).

2. $\mathrm{pH} = f(A_T, p(CO_2))$

The simplest assumption (which I recommend here) is to assume that the change in atmospheric $p(CO_2)$ does not affect S, t, & A_T.

A. Can do the calculation for average seawater values.

   $S = 35$; $t = 18$ °C; $A_T = 2300$ µmol kg^{-1}

   Need to assume an initial $p(CO_2)$, *e.g.* 400 µatm

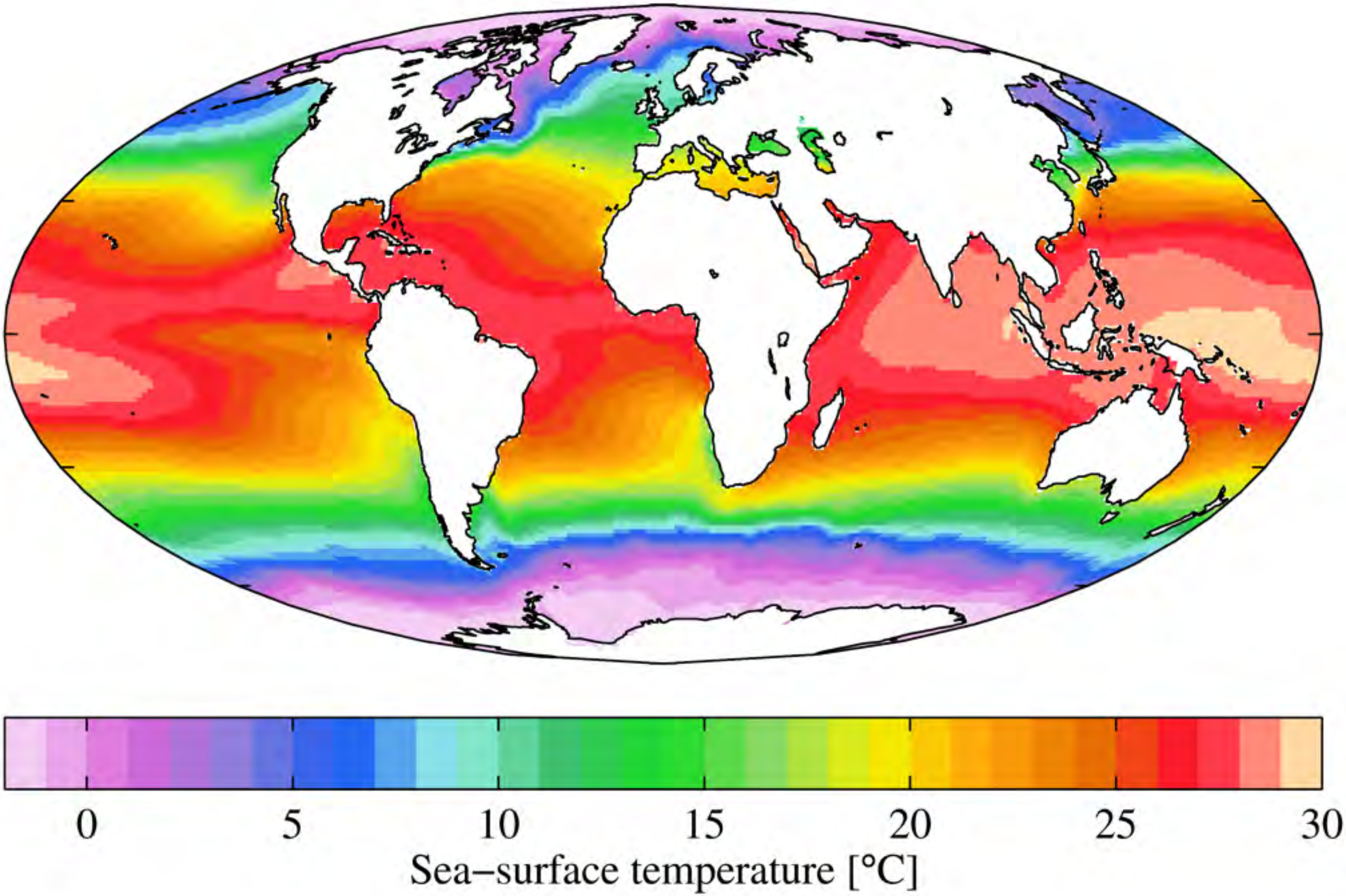
   Repeat calculation for increased $p(CO_2)$, *i.e.* 700 µatm

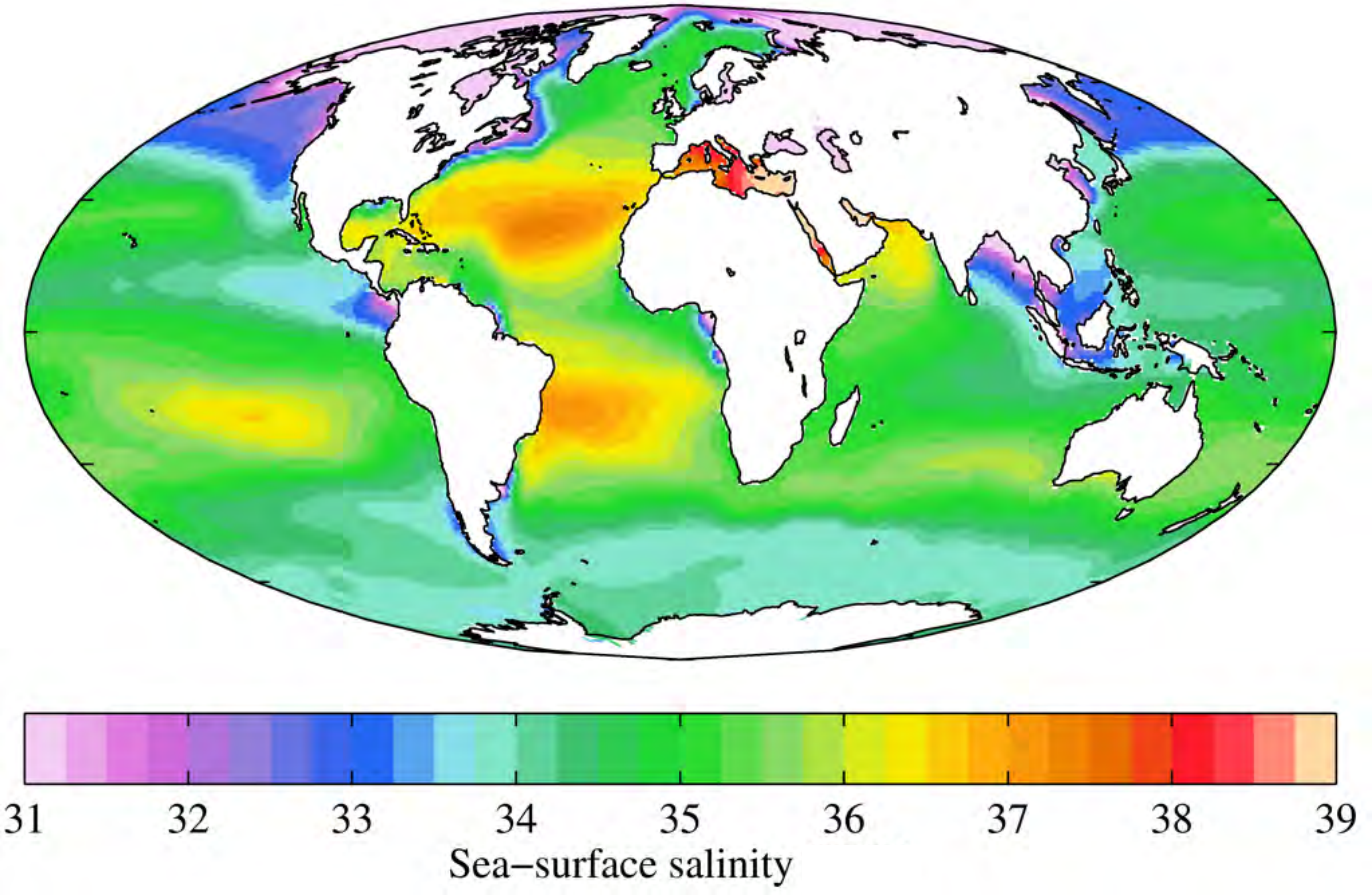
If the CO_2 level in the atmosphere increases by 300 ppm, how much will the pH in the surface ocean change?

What will be the consequent change in the saturation state of aragonite?

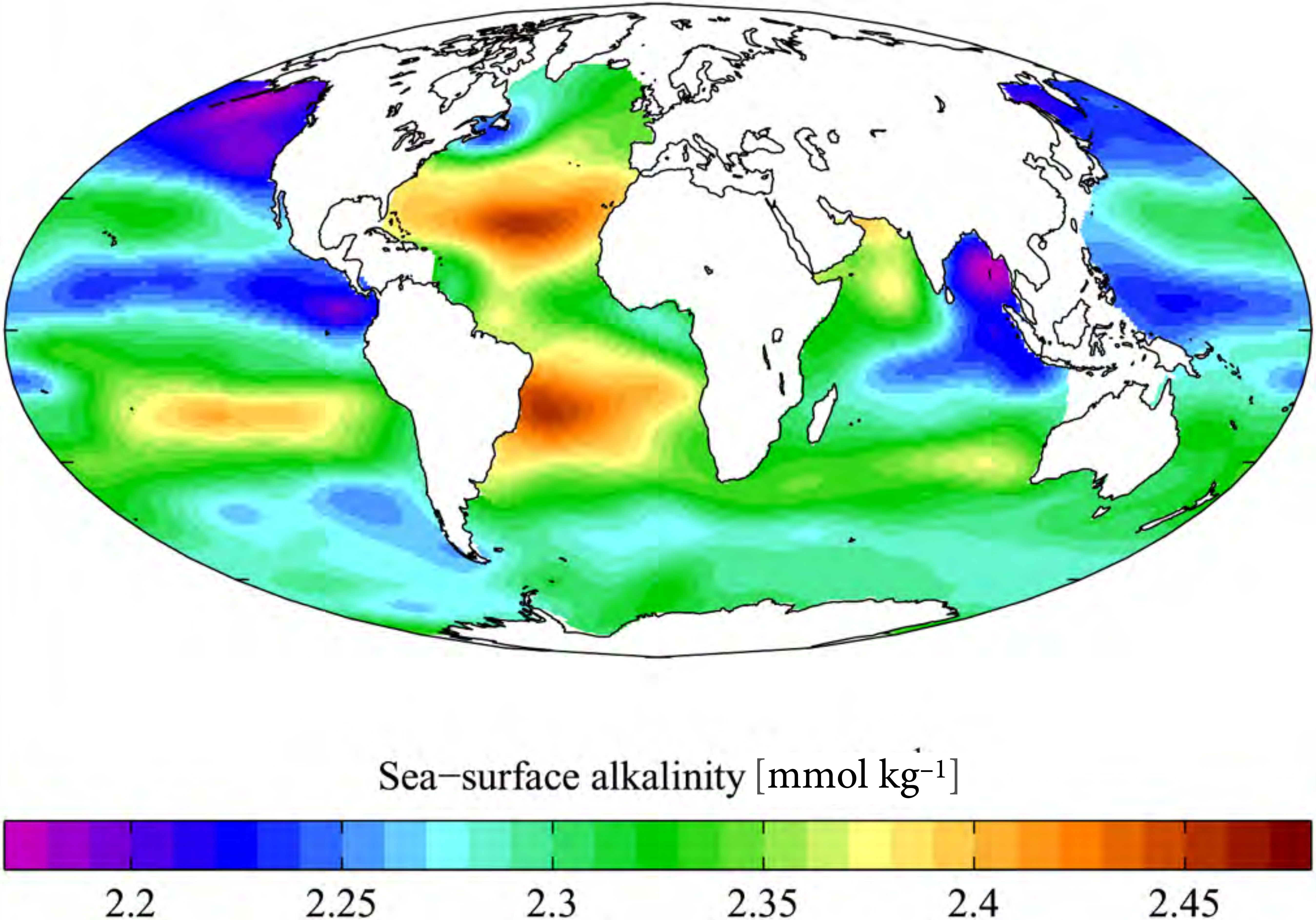
Will this be the same all over the oceans?

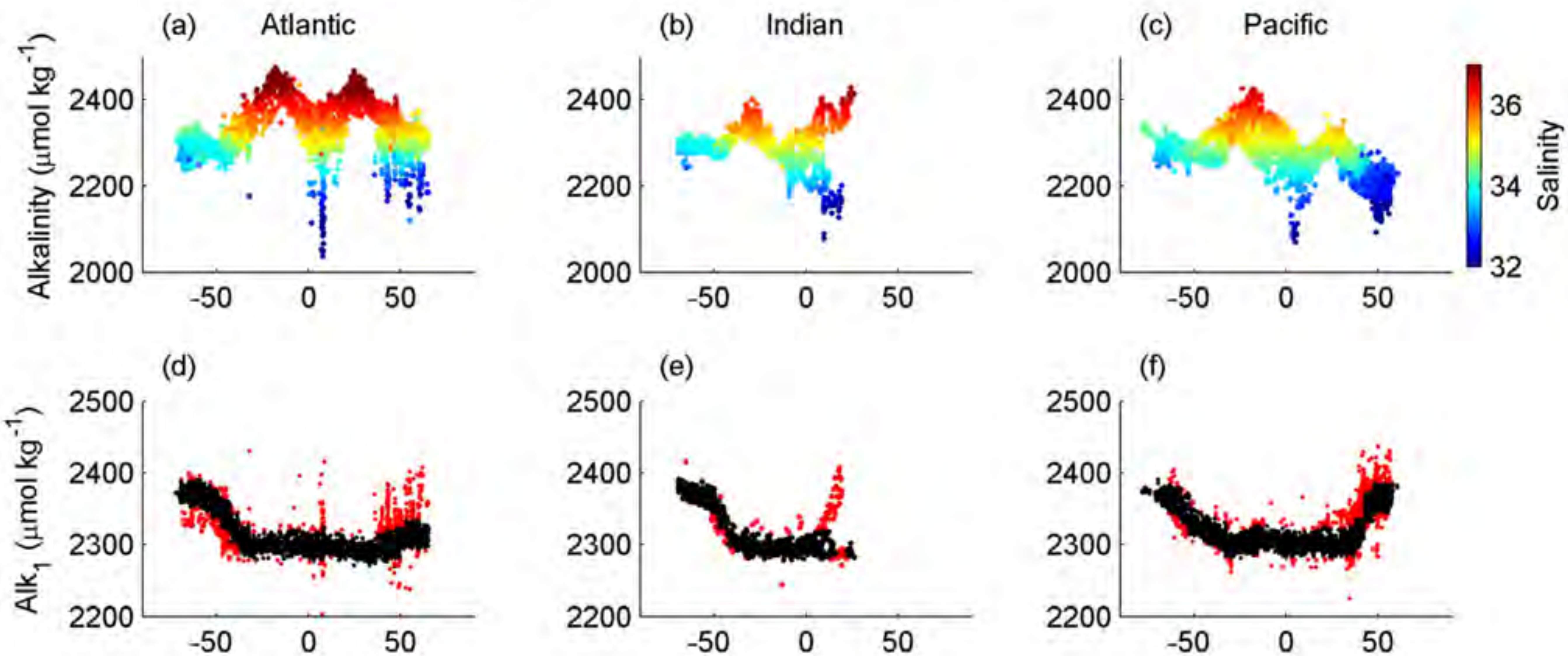
1. Need estimates of range of S, t, and A_T.
2. Repeat a few calculations to get an estimate of the likely variability in the pH change and in the the aragonite saturation state change


0
5
10
15
20
25
30
Sea−surface temperature [°C]



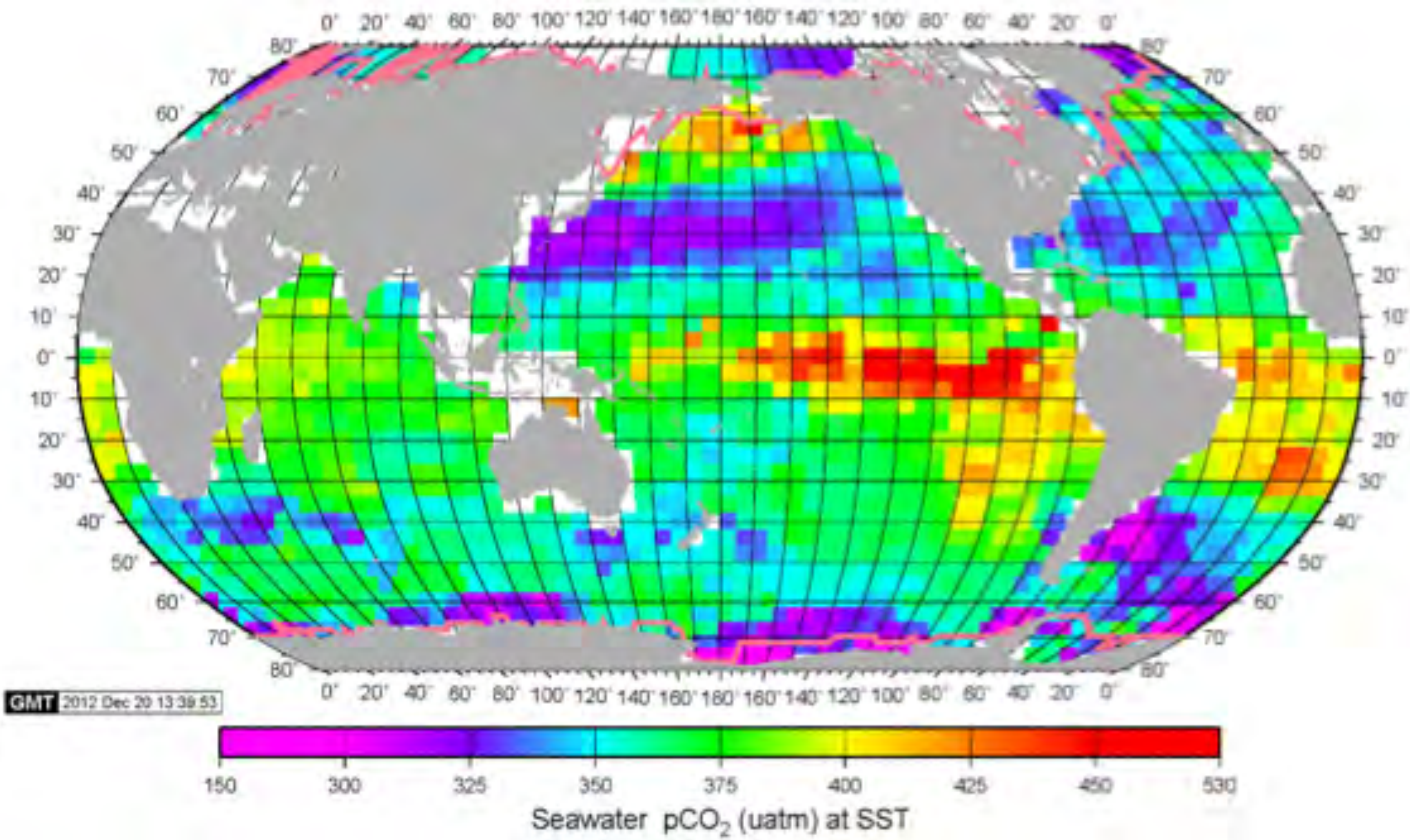
31
32
33
34
35
36
37
38
39
Sea−surface salinity


Sea−surface alkalinity [mmol kg^{-1}]
2.2
2.25
2.3
2.35
2.4
2.45



$$Alk_1 = \frac{Alk_m}{S} \times 35.$$

Reference year 2005



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- How should I modify the CO_2 composition of a sample of sea water to reach a desired target composition?

How should I modify the CO_2 composition of a sample of sea water to reach a desired target composition?

Need to know the initial composition of your water

Need to define the target (pH, $p(CO_2)$, $\Omega(arag)$)

Need to decide what form of modification is simpler
(or more relevant)

Often it is most straightforward to keep A_T approximately constant, and to change the C_T by addition/removal of CO_2.

It is also simpler to monitor pH: rather than $p(CO_2)$ or $\Omega(arag)$