

## Usage notes for JSL code for the CO<sub>2</sub> equilibration calculator script

Usage of this code requires JMP version 14 or higher (not tested on earlier versions). The input data can be an Excel, .CSV or JMP data file containing the following input variables:

- 1) pCO<sub>2</sub> of headspace before equilibration (ppmv). This value is 0 when N<sub>2</sub> or CO<sub>2</sub>-free gas is used as headspace. If ambient air is used, its pCO<sub>2</sub> should be measured or assumed to be close to atmospheric average (currently about 402 ppmv).
- 2) pCO<sub>2</sub> of headspace after equilibration(ppmv).
- 3) Temperature of water during sampling (°C).
- 4) Temperature of vessel during equilibration process (°C).
- 5) Alkalinity (μequiv/L).
- 6) Headspace ratio (Vol<sub>(gas)</sub>:Vol<sub>(water)</sub>).
- 7) Barometric pressure (kPa)

Values for variables 1, 6, 7 and 8 are not required in the data file if they are constant.

Load or import the input data file in JMP. Load and launch the script file. The following dialog box will appear

CO<sub>2</sub> equilibration calculator

Select Columns

- Longitude
- Alkalinity unified
- In situ- ...ture (°C)
- Depth (m)
- pH
- conductivity
- [G] pCO...C (μatm)
- Bottle t...g [G] (°C)
- Salinity
- Bar. Pre... analysis

Required variables

HS pCO<sub>2</sub> before equilibration *required*

HS pCO<sub>2</sub> after equilibration *required*

Water Temperature (C) during sampling *required*

Water Temperature (C) during equil. *required*

Bottle temp. after shaking [G] (°C) *required*

Alkalinity (uequiv/L) *required*

Headspace ratio *required*

Barometric Pressure (kPa) *required*

Salinity (kPa) *required*

☐ Constant HS gas pCO<sub>2</sub> (ppmv) 400

☐ Constant HS ratio (Vgas:Vliquid) 1

☐ Constant Bar. Pres (kPa) 101.325

☐ Constant Salinity (g/kg) 0

Carbonate equilibrium equation set

☒ Freshwater (Millero 1979)

☐ Estuarine (Millero et al. 2010)

☐ Marine (Dickson et al. 2007)

Solution method

☒ Analytical solutions (faster)

☐ Iterative solutions (slower but more stable in extreme situations)

Remove OK

Select or drag the data columns into the appropriate variable selection box. A choice a carbonate equilibrium equation set is given corresponding to various field sample types (freshwater, estuarine or marine). A choice of numerical solution methods is also given. The “Analytical solutions” is nearly instantaneous but can suffer minor imprecisions in extreme situations ( $\text{Alk} > 4000$  ( $\mu\text{equiv/L}$  and  $\text{pCO}_2(\text{after equil.}) < 100$  ppmv) inherent to double precision calculations. The “iterative solutions” is much slower but more stable in such situations. In all cases, results are added as three new columns to the data table (uncorrected  $\text{pCO}_2$ , corrected  $\text{pCO}_2$ , corrected  $[\text{CO}_2]$ ) Partial pressures are in  $\mu\text{atm}$  and concentrations in  $\mu\text{mole/L}$ . The code is available as a JSL script and as a JMP add-in.

#### References:

*Dickson, A. G., Sabine, C. L., and Christian, J. R.* ( 2007): Guide to best practices for ocean  $\text{CO}_2$  measurements, PICES Special Publication 3, 191 pp.

*Millero, F.* (1979). **The thermodynamics of the carbonate system in seawater** *Geochimica et Cosmochimica Acta* 43(10), 1651 1661. [https://dx.doi.org/10.1016/0016-7037\(79\)90184-4](https://dx.doi.org/10.1016/0016-7037(79)90184-4).

*Millero, F.* (2010). **Carbonate constants for estuarine waters** *Marine and Freshwater Research* 61(2), 139. <https://dx.doi.org/10.1071/mf09254>