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“Introduction to CO2SYS”

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Life prior to CO2SYS

Lewis and Wallace compared some available CO2 programs and calculated the carbonate system using the following input:

TA 2300, CT 2000, T 20C, S 35, Z 0

And the results were:

Program	pCO_2 (μatm)	pH	pH scale	HCO_3^- (μmol/kg)	CO_3^{2-} (μmol/kg)
1	336	8.229	Free	1767	223
2	351	8.088	Seawater	1772	216
3	330	8.247	NBS	1782	208

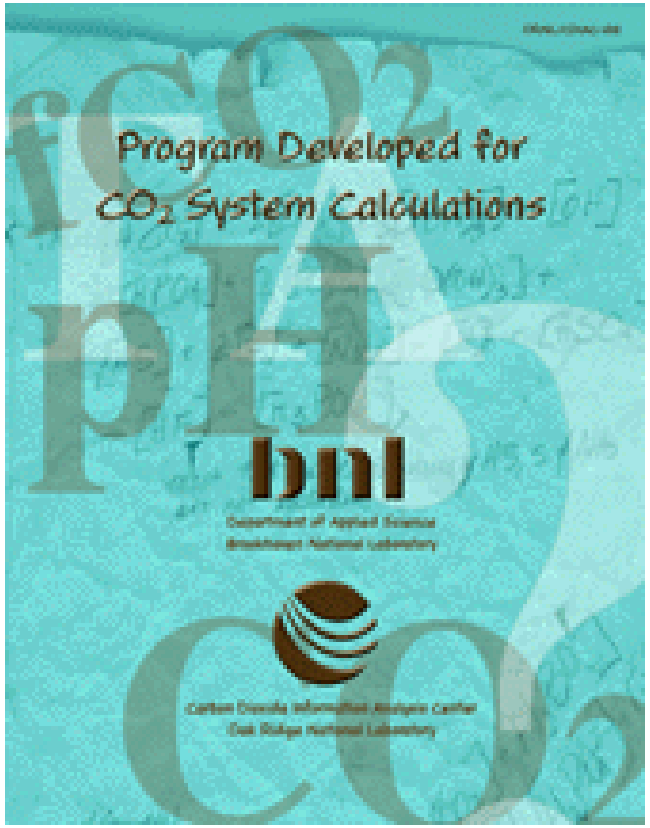
They found that...

Program 1 did not include the contribution of OH to the alkalinity nor the contributions of phosphate and silicate. It used the K1 and K2 values from Goyet and Poisson (1989) and the value of KSO4 from data of Khoo et al. (1977) but refit by other investigators. It didn't include a correction for the non-ideality of CO2, but did include pressure corrections.

Program 2 did not include the contributions of phosphate and silicate, but did include pressure corrections and a correction for the non-ideality of CO2. The values of K1 and K2 were those of Roy et al. (1993), and the value of KSO4 was that of Dickson (1990a).

Program 3 did include the contributions of phosphate and silicate, but had no corrections for the non-ideality of CO2 or for pressure. The values of K1 and K2 used were from Mehrbach et al. (1973).

Each of the programs used a different value for KB, the dissociation constant for boric acid.



http://cdiac.ornl.gov/ftp/co2sys/

Versions of CO2SYS

- CO2SYS running on Windows (E. Lewis and D. Wallace)
- CO2SYS running on Excel (Pierrot, Lewis,and Wallace. 2006.)
- CO2SYS running on Excel (G. Pelletier)
- CO2SYS in MATLAB (van Heuven)

- And note:
- CSYS in MATLAB (R. Zeebe and D. Wolf-Gladrow)

Units and scales in CO2SYS

The units used are μmol.kg-SW for TA and TCO_2

[H+] is in μmol.kg-SW for the free*, total and seawater pH scales and mol.kg-$H_2$0 for the NBS scale

pCO_2 and fCO_2 are in μatm

Total inorganic carbon = TCO_2, CT, C_T, DIC
Total alkalinity = TA, AT, A_T, Alk, Talk

Input

- Salinity
- Phosphate
- Silicate
- Input temperature and pressure
- Output temperature and pressure
- Two known system variables under input conditions (TCO_2, TA, pCO_2 (fCO_2), pH)

The program then calculates the remaining two CO_2 system variables and using TA and TCO_2 to calculate the output conditions

Output

- The four CO_2 system variables
- The speciation of the inorganic carbonic system
- The relative contributions to the total alkalinity
- The sensitivity of the outputs to the precision of the constants
- fCO_2 and pCO_2 in wet (100% saturated air)
- xCO_2 assuming 1 atm atmospheric pressure
- saturation state of seawater for calcite and aragonite
- the revelle factor

Scales and constants 1

K1 and K2 for carbonic acid*

KB for boric acid*

Kw for water

KSO4 for bisulphate ion*

KF for hydrogen fluoride

KP1, KP2, KP3 for phosphoric acid

Ksi for silicic acid

Solubility products Ksp(calcite), Ksp (aragonite) and K0 (CO2 in seawater)

* Requires operator choice

Which pH scale to use

- $a_H = 10^{(-pHNBS)} = f_H * H_{sws}$, and

- $H_{free} = H_{tot} / (1 + TS/K_{SO4}) = H_{sws} / (1 + TS/K_{SO4} + TF/K_F)$

- f_H is the activity coefficient of the hydrogen ion. This value is electrode specific

And which equilibrium constants are the best?

- The important constraint is that the pH and the pKs are on the same scale.
- Not all pKs are determined on the same scale:
  - e.g. Mehrbach – NBS (*only ones made on real seawater*)
  - Goyet – Seawater
  - Mehrbach (reanalysed by Dickson and Millero + Lueker et al.) – total hydrogen ion scale

Which constants to use

- Through comparisons with field data it is presently considered that these are the best:
  - Lueker et al (Mehrbach *et al*. (1973) fitted to total hydrogen ion scale)

NB However, at high latitudes and in deep waters Roy et al. have been shown to be just as good if not better.

However...

DOS VERSION
Roy et al. 1993
Mehrbach 1973 fitted by Dickson and Millero

Excel VERSION14
Roy et al. 1993
Mehrbach 1973 fitted by Dickson and Millero
Cai and Wang (1998) suitable for estuarine waters
Millero at al (2006) suitable for extreme T and S (0-50)

CSYS (Zeebe)
Roy et al. (1993)
Mehrbach et al (1973) as refit by Lueker et al.(2000)

The inclusion of nutrients

8. ALKALINITY

The definition of alkalinity (TA) used in this program for Constant Choices 1 to 5 is the same as that of Dickson (1981):

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

except that the contributions of HS, S, and NH_3 are not included.

We will test the sensitivity to nutrient in(ex)clusion in the practical

Request for future work

- In sea water thermodynamic calculations, pH should always be treated as a measure of hydrogen ion concentration
- Always report the equilibrium constants you use in your calculations
- This enables internal consistency and thus comparison between results
- And allows for reworking of the calculations as our understanding of the carbonic acid and wider CO_2 system evolves

The stoichiometric dissociation constants pK1 and pK2 for carbonic acid have been determined by a number of scientists (Mehrbach et al., 1973; Hansson, 1973; Goyet and Poisson, 1989; Roy et al., 1993). The measurements by Mehrbach et al. (1973) were made on real seawater; while the other studies were made in artificial seawater. The more measurements of Goyet and Poisson (1989) and Roy et al. (1993) were in reasonable agreement and thus were combined by Millero (1995). At room temperatures the values of pK1 and pK2 determined in real seawater are 0.01 and 0.04 respectively, higher than the measurements made in artificial seawater. The examination of the internal consistency of laboratory (Lee et al., 1996; Lueker et al., 2000) and field (Wanninkhof et al., 1999; Lee et al; 2000) measurements of *f*CO2, TCO2 and TALK have indicated that the constants of Mehrbach et al. (1973) are more reliable than those of other scientists. The calculation of *f*CO2 from an input of TALK and TCO2 and calculations of other parameters from an input of *f*CO2 and TALK or TCO2 require reliable values of pK2 pK1 (or K1/K2). Thus, the field measurements suggest that the values pK2 - pK1 from Mehrbach et al. (1973) are more reliable than other laboratory studies. More recently (Millero et al., 2002) the high precision CO2 field measurements made as part of the WOCE and JGOFS programs in the Atlantic, Indian, Southern and Pacific oceans for surface waters (-1.6 to 38oC) yield values of pK2 and pK2 - pK1 in good agreement (within 0.005) with the results of Mehrbach et al. (1973). The calculated deep water measurements of pK1 and pK2 at 4 and 20oC are also in agreement (within 0.01) with all the constants determined in laboratory studies. These studies confirm the earlier internal consistency tests and indicate that the measured values of pK1 and pK2 of Mehrbach et al. (1973) on real seawater are more reliable than the values determined for artificial seawater. It also indicates that the large differences of pK2 - pK1 (0.05 at 20oC) in real and artificial seawater determined by different investigators are mainly due to differences in pK2. The values of pK2 - pK1 determined from the laboratory measurements of Lee et al. (1996) and Lueker et al. (2000) at low *f*CO2 agree with the field-derived data.