The Essentials of pH and the Carbon Dioxide System for HAB Researchers

David Turner

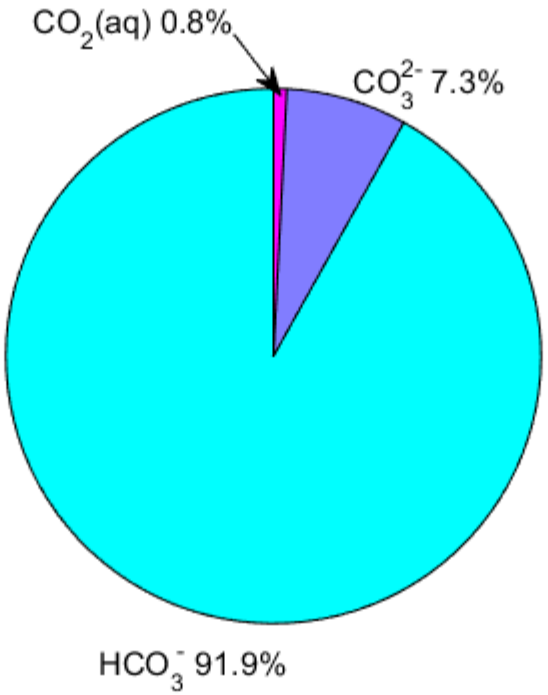
Department of Marine Sciences (from July 2015)

Overview

- Components of the CO_2 system
- pH scales and units
- Measurement techniques
- Calculations

Components of the CO_2 system (salinity = 35, t = 15ºC)

- Carbonic acid H_2CO_3 is only 0.0015% of the total
- The symbol H_2CO_3* is used for the sum of H_2CO_3 and CO_2(aq)



Concentration units

Three concentration scales are in common use in aqueous solution:

molality: moles per kg water

molinity: moles per kg solution

molarity: moles per litre

Marine chemists use moles per kg solution (usually just given as mol kg^{-1}), since this concentration is independent of temperature and pressure.

Conversion to and from moles per litre (mol L^{-1}), molarity, is easily made using density calculated from salinity, temperature and pressure

pH scales

pH scales for seawater are based on the concentration of hydrogen ions*: three different scales can be found in the literature:

”free”: $pH_F = -\log_{10}[H^+]$

”total”: $pH_T = -\log_{10}\{[H^+] + [HSO_4^-]\}$

”seawater”: $pH_{SWS} = -\log_{10}\{[H^+] + [HSO_4^-] + [HF]\}$

The concentrations are always on the mol kg^{-1} scale. Nowadays, almost all measurements are reported on the total scale, pH_T.

* Glass electrodes calibrated with NIST (NBS) buffers are sometimes used. These are not designed for high ionic strength media such as seawater. The resulting pH estimate is an operational quantity whose value depends on the properties of the particular reference electrode used. These pH estimates cannot be used for calculation of other CO_2 system quantities.

Measurable components of the CO_2 system

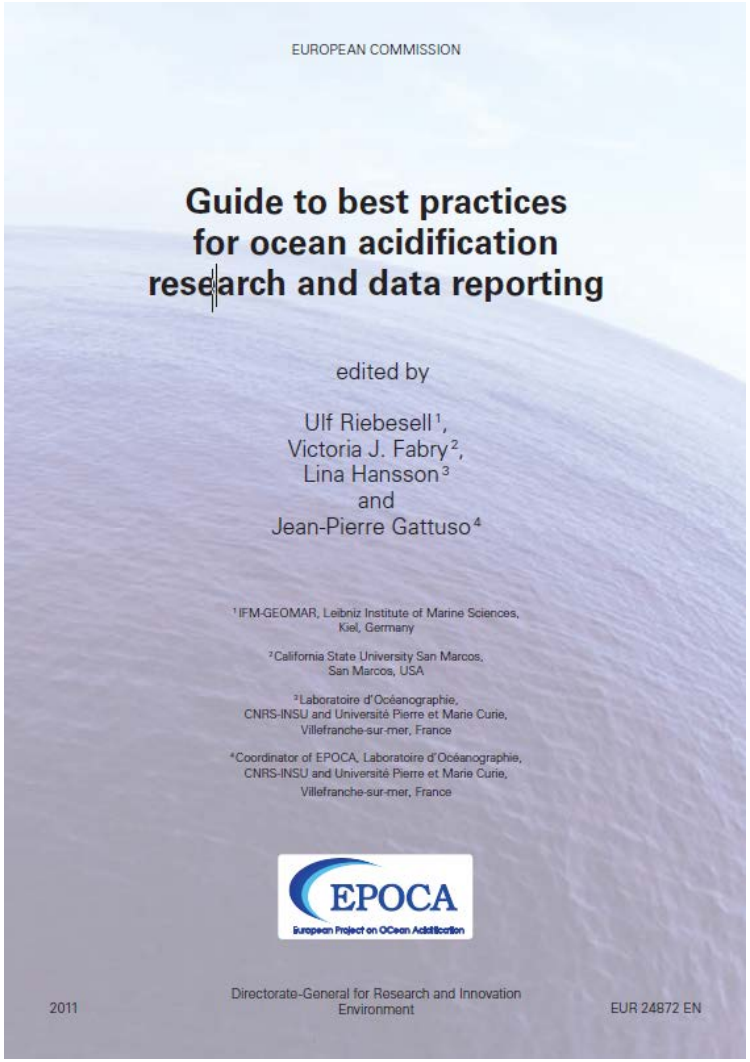
Four quantities can be measured: measurement of any two allows the remaining two, and also individual concentrations such as $[CO_3^{2-}]$ to be calculated.

pH	normally pH_T
pCO_2	partial pressure or fCO_2, fugacity*
C_T	total inorganic carbon, $C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$
A_T	total alkalinity, defined as the quantity of protons required to neutralise all bases with pK > 4,5 minus the concentration of acids with pK < 4,5

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + 2[PO_4^{3-}] + [HPO_4^{2-}] - [HF] - [H^+] - [H_3PO_4]\ldots$$

* The partial pressure is the fraction of atmospheric gases present as CO_2; the fugacity is a quantity representing the free energy of CO_2. The difference is less that 0.5% at 1 atmosphere total pressure, and reflects the non-ideal behaviour of CO_2 gas

Measurement techniques



I recommend that HAB researchers follow the guide to best practice developed for Ocean Acidification studies – there is no advantage to be gained by reinventing the wheel.

This book van be downloaded at epoca-project.eu

ISBN 978-92-79-20650-4
doi 10.2777/66906

Measurement uncertainties, from the OA guide

Table 1.4 Estimated measurement uncertainties for the measurement of parameters of the carbon dioxide system in seawater (for a single measurement on a sample of surface seawater). RM: Reference materials.

Parameter	Reference method	State-of-the-art (using RMs)*	Other techniques (using RMs)	Without using RMs†
Total alkalinity	1.2 µmol kg^{-1}	2-3 µmol kg^{-1}	4-10 µmol kg^{-1}	?
Total dissolved inorganic carbon	1.0 µmol kg^{-1}	2-3 µmol kg^{-1}	4-10 µmol kg^{-1}	?
pH	0.003‡	~0.005‡	0.01-0.03	?
$x'(CO_2)$ / $p(CO_2)$	1.0 µatm	~2 µatm	5-10 µatm	?

*The methods described in Dickson *et al.* (2007), performed by an experienced laboratory with well-trained analysts, and with a good quality assurance program in place.

†If appropriate reference materials are not used, it is usually not practical to assign a measurement uncertainty.

‡These levels of uncertainty in pH require that the apparent dye extinction coefficient ratios be appropriate to the particular lot of dye being used (see discussion in Yao *et al.* (2007)).

State of the art measurement techniques

pH: indicator spectrophotometry (m-cresol purple) or glass electrodes calibrated in certified seawater buffers

pCO_2: equilibration with infrared detection in the gas phase

C_T: acidification and gas stripping followed by coulometric or infrared detection

A_T: open cell titration

Full details are in the ” Guide to Best Practices for Ocean CO_2 Measurements”, available at http://cdiac.ornl.gov/oceans/Handbook_2007.html

In addition, several promising new technologies are also under development (ISFETs for pH, cavity ring-down spectrometry for C_T,..)

Calculations between CO_2 system parameters

The most widely used calculation programme is probably CO2SYS, available free from the Carbon Dioxide Information Analysis Center (CDIAC).

The address is http://cdiac.ornl.gov/oceans/co2rprt.html, or just google CO2SYS to find the programme. It is available in both Excel and MATLAB versions

CO2SYS requires that you make several choices. Most of the constant options are provided for backward compatibility with earlier calculations. This is my recommendation!

Set of Constants	$KHSO_4$	pH Scale	$[B]_T$ Value
K1, K2 from Roy, et al., 1993	Dickson	Total scale (mol/kg-SW)	Uppstrom, 1974
K1, K2 from Goyet and Poisson, 1989	Khoo et al	Seawater scale (mol/kg-SW)	Lee et al., 2010
K1, K2 from Hansson, 1973 refit by Dickson and Millero, 1987		Free scale (mol/kg-SW)	
K1, K2 from Mehrbach et al., 1973 refit by Dickson and Millero, 1987		NBS scale (mol/kg-H2O)	
K1, K2 from Hansson and Mehrbach refit by Dickson and Millero, 1987			
GEOSECS constants (NBS scale); K1, K2 from Mehrbach et al., 1973			
Constants from Peng et al. (NBS scale); K1, K2 from Mehrbach et al.			
Salinity = 0 (freshwater); K1, K2 from Millero, 1979			
K1, K2 from Cai and Wang, 1998			
K1, K2 from Lueker et al., 2000			
K1, K2 from Mojica Prieto et al., 2002			
K1, K2 from Millero et al., 2002			
K1, K2 from Millero et al., 2006			
K1, K2 from Millero, 2010			

Which parameters to measure, and which to calculate?

“At this time, I believe that the best combination of parameters for studying the CO2 system in open ocean water is probably total alkalinity and total carbon. It is straightforward to collect and preserve samples for later analysis, the equipment is reasonably readily available, and reference materials are also available to ensure metrological traceability. Also, there will be a close link to the extensive set of open-ocean studies that have been, and will be performed in the future.

Nevertheless, there are occasions when an alkalinity measurement will be difficult to interpret. In that case, I believe that the optimal combination of parameters is pH (measured spectrophotometrically) and total dissolved inorganic carbon (measured using infrared spectroscopy). These two parameters allow a description of the CO2 system alone (without concern as to other co-existing acid-base systems), equipment for making the measurements is available, and reference materials are also available (though pH reference materials are in shorter supply). This pair can also be applied to study normal seawaters and may well be the best all-round choice.”

Quoted from Andrew Dickson in the OA Guide

Alkalinity difficult to interpret?

pH_T	
pCO_2	partial pressure or fCO_2, fugacity
C_T	total inorganic carbon, $C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$
A_T	total alkalinity, defined as the quantity of protons required to neutralise all bases with pK > 4,5 minus the concentration of acids with pK < 4,5

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + 2[PO_4^{3-}] + [HPO_4^{2-}] - [HF] - [H^+] - [H_3PO_4]\ldots$$

Note that pH, pCO_2 and C_T are clearly defined in terms of a small number of chemical species. A_T is, however, open-ended. Recent work in the Baltic Sea has shown that DOC contributes to A_T by 10-12% of DOC on a molar basis. The organic contribution to alkalinity can then be 30 – 40 µmol kg^{-1}, resulting in large errors if the measured A_T is used for calculations in CO2SYS. These observations may well be relevant to HAB studies

Summary

- For accurate pH measurements, use indicator spectrophotometry or glass electrodes calibrated in seawater buffers
- When using two parameters to characterise the CO_2 system, pH and C_T are generally the best choice
- Use CO2SYS for calculations
- C_T and A_T measurements should be calibrated against ”Dickson standards” obtained from Scripps
- Be aware that A_T measurements in high DOC water may include organic alkalinity that is not taken into account in CO2SYS calculations