Technical Note 1.1: Dissolved CO_2 and Units of Measurement

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Introduction

Dissolved carbon dioxide sensors often utilize equilibrator systems with semi-permeable membranes in order to measure CO_2 directly in the gas phase, most commonly using an infrared detector. As a result, these instruments normally report a "gas phase" concentration of CO_2 that is in equilibrium with the surrounding liquid in which the sensor is immersed. The same equilibration dynamics occur at the surface of a body of water in contact with the atmosphere, such that the concentration of CO_2 in the water is in equilibrium with the partial pressure of CO_2 in the atmosphere:

CO_2 (g) <=> CO_2 (aq)

It is important to understand the units of measure to ensure proper measurement and reporting of data. This technical note aims to outline the various units of measure for CO_2 in water, as well as, how to convert between these units to allow the user to correctly measure and report data using dissolved CO_2 sensors, including the CO_2-Pro Series and Mini CO_2 sensors manufactured by Pro-Oceanus Systems.

Gas Phase CO_2

Gaseous Carbon Dioxide, CO_2 (g), is commonly measured in units of ppmv (parts per million by volume). This is the ratio of *x* number of CO_2 molecules per million molecules of total gas. The ppmv of CO_2 in air does not change with pressure. The ppmv CO_2 is also referred to as the mixing ratio, xCO_2.

Figure 1. Dissolved CO_2 sensor with membrane equilibrator.

In natural waters, CO_2 (g) is often reported as a partial pressure, pCO_2, with units of microatmospheres (μatm). Unlike xCO_2, pCO_2 is dependent on the total gas pressure. The two terms are related through pressure by:

$$pCO_2 = xCO_2 \times P$$

where P is the total gas pressure measured in atmospheres and xCO_2 is in ppmv.

A third unit of measure for CO_2 is the fugacity, fCO_2. The fugacity corrects for non-ideal gas behavior of gases and can be estimated from approximate expressions along with temperature and pCO_2. In most cases fCO_2 is within a few μatm of pCO_2.

Figure 2. CO_2-Pro Atmosphere Sensor measures both air and surface water pCO_2 for carbon flux measurements.

The standard units of measurement for CO_2 are normally defined by each application. For example, climate change and ocean acidification scientists use microatmospheres as a standard unit of measure, unlike the aquaculture industry, which uses millligrams per liter in most cases.

CO_2 Solubility

The equilibrated ratio of partial pressure to dissolved concentration is governed by the laws of solubility:

$pCO_2 = K_O [CO_2 (aq)]$

where pCO_2 is the partial pressure of CO_2 in the gas phase, K_O is a solubility coefficient, and CO_2 (aq) is the concentration of CO_2 dissolved in the water.

The solubility of CO_2 in water is a function of both the temperature and the salinity of the water, from Weiss (1974):

$$\ln (Ko) = -60.2409+93.4517(100/T)+23.3585\ln (T/100) + S(0.023517-0.023656(T/100)+0.0047036(T/100)^2)$$

Where the solubility coefficient, K_O has the units of mol kg^{-1} atm^{-1}, temperature, T, is Kelvin, and salinity, S, is in parts per thousand (approximately equal to PSU).

Note that for non-saline waters, the second term of the equation becomes zero, leading to:

$$\ln (K_O) = -60.2409+93.4517(100/T)+23.3585 \ln (T/100)$$

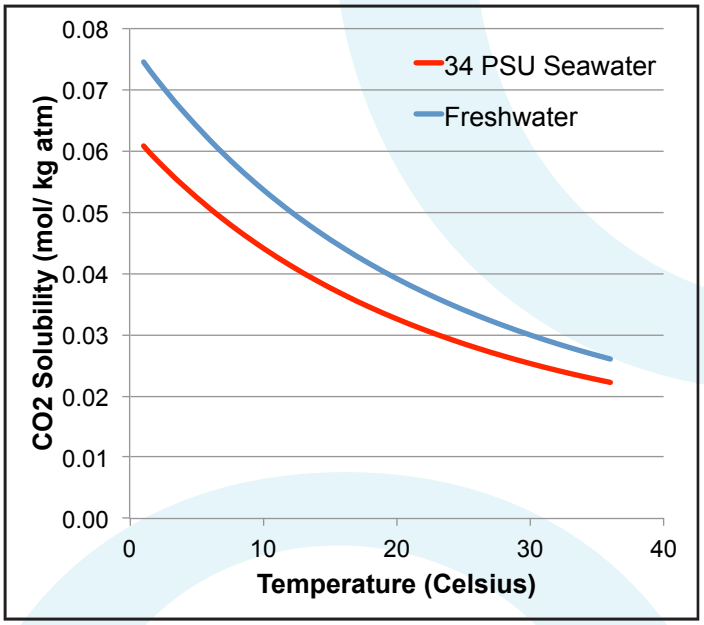

Figure 3. Solubility of CO_2 in freshwater and seawater as a function of temperature.

Figure 3 depicts the solubility of CO_2 in both freshwater and seawater (S=34) as a function of temperature. CO_2 is more soluble in freshwater than seawater, and solubility decreases with increasing temperature.

An excel spreadsheet for conversion calculations can be obtained by contacting Pro-Oceanus Systems at: sales@pro-oceanus.com.

Dissolved CO_2 - Units of Measure

pCO_2 (μatm)	CO_2 (aq) (mg/L)
500	0.9
1000	1.7
1500	2.6
2000	3.4
2500	4.3
3000	5.2
4000	6.9
5000	8.6
7500	12.9
10000	17.2

For applications such as aquaculture, it is common to see units of dissolved CO_2, including mg/L (also referred to as ppmm, parts per million by mass). The use of "ppm" for both gas phase and dissolved phase concentrations of CO_2 in water can lead to confusion and so it must be made clear what units of measure are being used. For example, 1000 ppmv of CO_2 (g) is only be equivalent to 1-3 ppmm of CO_2 (aq).

To the left is a table converting several partial pressures of CO_2 to aqueous phase concentration of mg/L in freshwater at 20°C.

References:

Weiss, RF. 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. Marine Chemistry. 2:203-215. 10.1016/0304-4203(74)90015-2.