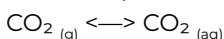


TECHNICAL NOTE 1.1: Dissolved CO₂ and Units of Measurement

INTRODUCTION

Dissolved carbon dioxide sensors often utilize equilibrator systems with semi-permeable membranes in order to measure CO₂ directly in the gas phase, most commonly using an infrared detector. As a result, these instruments normally report a “gas phase” concentration of CO₂ 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 CO₂ in the water is driven toward equilibrium with the partial pressure of CO₂ in the atmosphere:



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 CO₂ in water, as well as, how to convert between these units. This will allow the user to correctly measure and report data using dissolved CO₂ sensors, including the CO₂-Pro Series and Mini CO₂ sensors manufactured by Pro-Oceanus Systems.



Figure 1.
Dissolved CO₂ sensor
with membrane equilibrator.

GAS PHASE CO₂

Gaseous Carbon Dioxide, CO₂ (g), is commonly measured in units of ppmv (parts per million by volume). This is the ratio of the number of CO₂ molecules per million molecules of total gas. The ppmv of CO₂ in air does not change with pressure. The ppmv CO₂ is also referred to as the mixing ratio, xCO₂. Note that xCO₂ refers to dry gas while wCO₂ refers to the total gas including water vapor

In natural waters, CO₂ (g) is often reported as a partial pressure, pCO₂, with units of microatmospheres (µatm). Unlike xCO₂, pCO₂ is

dependent on the total gas pressure. The two terms are related through pressure by:

$$\begin{aligned} p\text{CO}_2 &= x\text{CO}_2 \times P(\text{dry}) \text{ or} \\ p\text{CO}_2 &= w\text{CO}_2 \times P(\text{wet}) \end{aligned}$$

where P is the total gas pressure measured in atmospheres and xCO₂ and wCO₂ are in ppmv.

A third unit of measure for CO₂ is the fugacity, fCO₂. The fugacity corrects for non-ideal gas behavior of gases and can be estimated from approximate expressions along with temperature and pCO₂. In most cases fCO₂ is within a few µatm of pCO₂.

The standard units of measurement for CO₂ 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 typically uses milligrams per liter.



Figure 2. CO₂-Pro Atmosphere Sensor measures both air and surface water pCO₂ for carbon flux measurements.

PRO Dissolved Gas Sensors
OCEANUS

TECHNICAL NOTE 1.1:

Dissolved CO₂ and Units of Measurement

CO₂ SOLUBILITY

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

$$p\text{CO}_2 = KO [\text{CO}_2 (\text{aq})]$$

where $p\text{CO}_2$ is the partial pressure of CO₂ in the gas phase, KO is a solubility coefficient, and CO₂ (aq) is the concentration of CO₂ dissolved in the water.

The solubility of CO₂ in water is a function of both the temperature and the salinity of the water, one relationship 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 (KO) 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

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

Figure 3 depicts the solubility of CO₂ in both freshwater and seawater (S=34) as a function of temperature. CO₂ is more soluble in freshwater than seawater, and solubility decreases with increasing temperature.

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

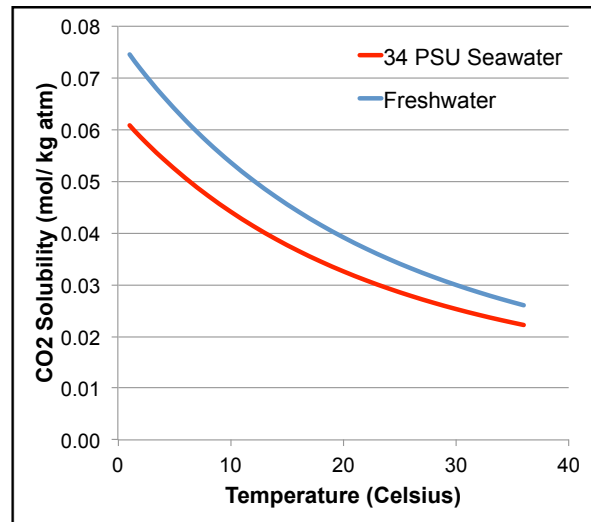


Figure 3. Solubility of CO₂ in freshwater and seawater as a function of temperature.

DISSOLVED CO₂ - UNITS OF MEASURE

For applications such as aquaculture, it is common to see units of dissolved CO₂, including mg/L (also referred to as ppm, parts per million by mass). The use of "ppm" for both gas phase and dissolved phase concentrations of CO₂ 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 CO₂ (g) is only 1-3 ppm of CO₂ (aq).

Conversion of these units depends on temperature and salinity of the water. To the left is a table converting several partial pressures of CO₂ converted to aqueous phase concentration in mg/L for freshwater at 20°C.

pCO ₂ (µatm)	CO ₂ (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

References:
Weiss, R.F. 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.