CARBON DIOXIDE TRANSFER ACROSS THE INTERFACE

1. Rate equation

The physical process of carbon dioxide transfer across a water surface in contact with the atmosphere is described by the simple reaction:

$$CO_2(aq) \leftrightarrow CO_2(g) \qquad (1)$$

This process tends to restore the thermodynamical equilibrium which is reached when the chemical potential (or fugacity) of CO_2 is equal in both phases.

In water, $CO_2(aq)$ is partially hydrated into carbonic acid according to the reaction:

$$CO_2(aq) + H_2O \leftrightarrow H_2CO_3 \qquad (2)$$

the ratio of $CO_2(aq)$ to H_2CO_3 being close to 400:1. For analytical reasons, it is more convenient to consider both the hydrated and non-hydrated forms of CO_2 as a single entity, which is commonly designated by CO_2^*, and equilibrium constants are generally expressed in terms of CO_2^* concentration.

An introduction to the modeling of gas exchange with the atmosphere is given in the section devoted to oxygen transfer across the interface. In particular, like O_2, CO_2 is not a very soluble gas and the resistance to transfer is essentially localized in the water phase. However, the behavior of carbon dioxide differs from that of oxygen because it is involved in an equilibrium reaction with bicarbonate ions. This process can lead, under certain circumstances, to an enhanced diffusivity within the water boundary layer. (For a detailed discussion of diffusion enhancement, refer to the section on ammonia transfer across the interface). It can be shown that the enhancement of CO_2 transfer is generally not important, except in alkaline waters or very quiescent water bodies (Morel and Hering, 1993). It will thus be ignored in the following discussion.

Accordingly, a general expression for the rate of CO_2 transfer across the interface is given by the equation:

$$F_{CO_2} = -v_w^{CO_2}\left(\left[CO_2^*\right] - K_H\, p_{CO_2}\right) \qquad (3)$$

where $v_w^{CO_2}$ is the piston velocity of CO_2 in the water boundary layer, $\left[CO_2^*\right]$ is the bulk water concentration, p_{CO_2} is the partial pressure of CO_2 in the atmosphere and K_H is the Henry's law constant for carbon dioxide. Note that the flux is taken positive when the gas is supplied from the atmosphere to the water. This relation is based on the assumption that the equilibrium between the air and the gas phase is reached instantaneously at the interface. However, it is known that the time to reach equilibrium can be very long in pure water, allowing strong supersaturation of carbon dioxide in the liquid phase. The reaction is also known to be enzymatically mediated. Due to the postulated presence of a large enzyme pool in natural waters, we will consider that the reaction is not kinetically controlled (*i.e.* that the reaction is always at equilibrium at the air/water interface), the exchange process being thus transport limited.

In a 1-D model, the flux must be formulated per unit volume V and Eq.3 must be transformed accordingly. This leads to:

$$[F_{CO_2}]_V = F_{CO_2}\frac{S}{V} = F_{CO_2}\frac{1}{h} \qquad (4)$$

where $[F]_V$ is the flux per unit volume, S [m^2] the surface area of V in contact with the atmosphere and h the water depth [m].

2. Henry's Law constants for carbon dioxide

Henry's Law constant is defined according to :

$$K_H = \frac{\left[CO_2^*\right]}{p_{CO_2}} \qquad (5)$$

where p_{CO_2} is the partial pressure of carbon dioxide in the air [atm], in equilibrium with a concentration $\left[CO_2^*\right]$ [mole.m^{-3}] in the water. The units of K_H are thus mole.m^{-3}.atm^{-1}.

Note that K_H is directly linked to the equilibrium constant K_0 associated to reaction (1):

$$K_0 = \frac{a_{CO_2}}{f_{CO_2}} \qquad (6)$$

in which a_{CO_2} refers to the activity of CO_2 in the water phase and f_{CO_2} to its fugacity in the gas phase. For practical reasons, an "apparent" equilibrium constant $K_0^{'}$ is generally used instead of K_0. It includes the value of the activity coefficient and a correction for fugacity, and is equivalent to the constant K_H defined above.

The value of $K_0^{'}$ is a function of both temperature and salinity. The relation given below is taken from Weiss (1974), adapted in Weiss and Price (1980):

$$\ln\left[K_0^{'}(T,S)\right] = \ln\left[K_0^{'}(T)\right] + f(T).S \qquad (7)$$

where T refers to the absolute temperature [K] and S to the salinity. It includes a function $\ln\left[K_0^{'}(T)\right]$ giving the value of the constant at zero salinity, and a temperature function f(T). These two functions are detailed in the following table.

$\ln\left[K_0^{'}(T)\right] = a_0 + \frac{a_1}{T} + a_2T^2 + a_3\ln T$	$a_0 = -5.7470126\ 10^{2}$
	$a_1 = 2.154152\ 10^{4}$
	$a_2 = -1.47759\ 10^{-4}$
	$a_3 = 8.9892\ 10^{1}$
$f(T) = b_0 + b_1T + b_2T^2$	$b_0 = 2.9941\ 10^{-2}$
	$b_1 = -2.7455\ 10^{-4}$
	$b_2 = 5.3407\ 10^{-7}$

The value of $K_0^{'}$ obtained by application of this relation is in mole.l^{-1}.atm^{-1}. The result should be multiplied by a factor 10^3 to convert $K_0^{'}$ into mole.m^{-3}.atm^{-1}.

Control values:

at 0°C (273.15 K) , salinity 0:	$\ln(K_0^{'}) = -2.56634$	$pK_0^{'} = -\log(K_0^{'}) = 1.1145$
at 20°C(293.15 K), salinity 35:	$\ln(K_0^{'}) = -3.43085$	$pK_0^{'} = -\log(K_0^{'}) = 1.4900$

3. Piston velocity

The piston velocity of carbon dioxide in the water boundary layer can be estimated from the velocity of a reference gas (*i.e.* oxygen) according to the following relationship:

$$v_w^{CO_2} = v_w^{O_2}\left(\frac{D_w^{CO_2}}{D_w^{O_2}}\right)^{\beta} \tag{8}$$

where $D_w^{CO_2}$ refers to the diffusion coefficient of CO_2 in water and β is close to 0.57 (Holmen and Liss, 1984).

The diffusion coefficient of carbon dioxide is estimated from the diffusion coefficient of oxygen by:

$$D_w^{CO_2} = D_w^{O_2}\left(\frac{\text{mol. weight } O_2}{\text{mol. weight } CO_2}\right)^{0.5} \tag{9}$$

Combining these last two expressions leads to:

$$v_w^{CO_2} = v_w^{O_2}\left(\frac{\text{mol. weight } O_2}{\text{mol. weight } CO_2}\right)^{0.285} = 0.913\ v_w^{O_2} \tag{10}$$

For the complete expression of the piston velocity of oxygen in the water phase as a function of both wind speed and current velocity, the reader is referred to the section on oxygen transfer across the interface.

4. Partial pressure of carbon dioxide in the atmosphere

The present-day CO_2 partial pressure in the atmosphere has been taken equal to 367.10^{-6} atm (Keeling and Whorf, 1999). The corresponding CO_2^* concentration at equilibrium is equal to $1.19\ 10^{-5}$ M (11.9 µM) at 20°C, 35 salinity and $2.82\ 10^{-5}$ M (28.2 µM) at 0°C, salinity 0.

5. Model entries for computing the carbon dioxide transfer across the interface

1. Number of species: **1**
2. Number of kinetic reactions: **1**

3. Number of equilibrium conditions: **0**
4. Variables: $\left[CO_2^*\right]$
5. Reaction:

   R$_1$: $\mathbf{CO_2\,(aq) \leftrightarrow CO_2^*\,(g)}$

6. Rate:

$$\mathbf{F_{CO_2} = -\frac{1}{h} v_w^{CO_2} \left(\left[CO_2^*\right] - K_0' \, p_{CO_2} \right)}$$

$$\mathbf{v_w^{CO_2} = 0.913 v_w^{O_2}}$$

   (refer to O_2 transfer for the expression of $v_w^{O_2}$)

7. Model parameters: K_0' (depends on temperature and salinity); p_{CO_2} (partial pressure of carbon dioxide in air = 367 µatm); h (water depth) is calculated by the hydrodynamic model.

References

Holmen K. and Liss, P., 1984. Models for air-water gas transfer: an experimental investigation. Tellus, 36B, 92-100.

Keeling, C.D. and Whorf, T.P., 1999. Atmospheric CO_2 records from sites in the SIO air sampling network. In Trends: A Compendium of Data on Global Change. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A.

Morel, F.M. and Hering, J.G., 1993. Principles and applications of aquatic chemistry. J. Wiley, New-York, 608 pp.

Weiss, R.F., 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. Mar. Chem., **2**, 203-215.

Weiss, R.F., and Price, B.A., 1980. Nitrous oxide solubility in water and seawater. Mar. Chem., **8**, 347-359.