

SUPPLEMENT A

Article: “Numerical tools to estimate the flux of a gas across the air-water interface and assess the heterogeneity of its forcing functions.”

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1. air-air concentration conversions

The more accurate definition of *ppm* refers to number of molecules of solute to million molecules of solvent, or number of moles of solute to million moles of solvent. However, when working strictly with gases, a gas concentration in the air is often expressed in *ppm* in a volume context which is also equivalent to its partial pressure. The *ppm* measurements expressed in both contexts are equivalent as the *Avogadro's Law* states that equal volumes of gases, at the same temperature and pressure, contain the same number of molecules. Hence, because in gases equal quantities of solute and solvent occupy equal volumes, expression (A1) is possible:

$$x_{ppm} = x \frac{mol}{10^6 mol} = x \frac{mL}{10^6 mL} = x \frac{mL}{m^3} = x \frac{\mu atm}{atm} \quad (A1)$$

However, it is often wanted to convert the gas concentration into $mol m^{-3}$ or $g m^{-3}$. It is so when it is wanted to estimate the air-water interface gas fluxes, which are usually given in units of $mol m^{-2} day^{-1}$ or $g m^{-2} day^{-1}$. To estimate the gas concentration in $mol m^{-3}$ the volume occupied by the air mixture in the denominator of expression (A1) must be determined exactly. To do that (expression A2) the ideal gas law is used in the

form $V = nRT/P$, where R is the universal gas law constant ($8.314472 \text{ m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1}$), T is the temperature in Kelvin (K), P is air pressure in Pascal (Pa), V is volume (m^3) and n is the amount of molecules (mol). Furthermore, to convert to g m^{-3} the moles of solute must be multiplied by its molecular weight M_S (g mol^{-1}) as in equation (A3).

$$\begin{aligned}
 x \quad \frac{\text{mol}}{10^6 \text{ mol}} &= \\
 \frac{x}{10^6} \quad \frac{\text{mol}}{\text{mol}} &= \quad (A2) \quad \frac{x.P.M_S}{10^6.R.T} = \frac{\text{g}}{\text{m}^3} \quad (A3) \\
 \frac{x.P}{10^6.R.T} \quad \frac{\text{mol}}{\text{m}^3} &
 \end{aligned}$$

2. air-water concentration conversions

CO_2 is representative of a broad class of gases that do not have a liquid state at natural conditions. CO_2 does not have a liquid state at pressures below 5.1 atm passing directly from gas to solid at -78°C at 1 atm . Thus, it is always a gas dissolved in water the reason why its concentration measurements and units may lead to confusion. If it is expressed in ppm in the molar fraction context, in order to convert it to different units the expressions in (A4) must be used, where the development is in the left column, the units are in the right column, M_w is the molecular weight of water and ρ_w is the water density. Alternatively, the concentration of a gas in a mass of water is often given as its equivalent atmospheric partial pressure (or ppm) would both mediums be at equilibrium. Such is the case of the concentration of CO_2 in water measured with the Infra Red Gas Analyser (IRGA) and floating dome technique (Frankignoulle 1988, Frankignoulle et al 2001, Frankignoulle & Borges 2001, Borges et al 2004_{a,b}). These concentrations of CO_2 in water in units of equivalent atmospheric partial pressure (in ppm) in equilibrium are converted into concentration of CO_2 in the water in units of

$mol.m^{-3}$ by taking the steps in expression (A5), where k_{HCP} is the Henry's law constant for the given water temperature and salinity in its C_{liquid}/P_{gas} form in units of $mol.L^{-1}.atm^{-1}$.

$$\begin{aligned}
 x \quad ppm (scalar) &= \frac{mol}{10^6 mol} \\
 \frac{x}{M_w} \quad \frac{mol}{10^6 g} &= \frac{mol}{10^3 Kg} \\
 \frac{x \cdot \rho_w}{M_w} \quad \frac{mol}{10^3 L} &= \frac{mol}{m^3} \\
 \frac{x \cdot \rho_w \cdot M_s}{M_w} \quad \frac{g}{m^3} &= \frac{mg}{L} \\
 x \frac{M_s}{M_w} \quad \frac{g}{10^6 g} &= \frac{mg}{Kg}
 \end{aligned} \tag{A4}$$

$$\begin{aligned}
 x \quad ppm (scalar) \\
 \frac{x}{10^3} \quad \frac{mol}{10^3 mol} \\
 \frac{x \cdot k_{HCP}}{10^3} \quad \frac{mol}{10^3 . atm . L} \\
 \frac{x \cdot k_{HCP} \cdot P}{10^3} \quad \frac{mol . atm}{10^3 . atm . L} = \frac{mol}{m^3}
 \end{aligned} \tag{A5}$$

3. Using the IRGA

To validate the model, CO_2 fluxes across the air-water interface were measured at short time intervals. This was done with the floating dome and IRGA methodology (Frankignoulle 1988). It required a floating dome that isolated a fixed volume of air (V) over an area (A) of the water surface. The CO_2 partial pressure (pCO_2) inside the dome was measured at short time intervals (Δt) using the Infra Red Gas Analyser (IRGA). It evolved asymptotically to equilibrium with the water beneath. The first part of the evolution curve was considered sufficiently approximate to linear and thus its slope was a measure of the CO_2 variation inside the dome in $\Delta ppm / \Delta t$. To convert it to the flux in $mol.m^{-2}.s^{-1}$ the ideal gas law was applied (equation A6) keeping in mind that air temperature is in Kelvin and air pressure is in Pascal. When the evolution curve stabilized the pCO_2 was considered in equilibrium with the water. In practice

convergence to stabilization was so slow that the advective transport could bring a water mass with a different CO₂ concentration beneath the floating dome. Therefore, neither stabilization would occur nor would it be representative of the earlier conditions. To solve this problem a degasification column (also called *equilibrator*) was used allowing a fast and accurate estimate of the water pCO_2 at the time of the CO₂ flux estimate. (Frankignoulle et al 2001). To convert it to the CO₂ on the water in $mol\,m^{-3}$ multiplication by the Henry's law constant is needed in the C_{water}/p_{air} form and for the specified temperature and salinity.

$$\frac{mol}{m^2.s} = \frac{\Delta ppm.P.V}{\Delta t.R.T.A} \quad (A6)$$