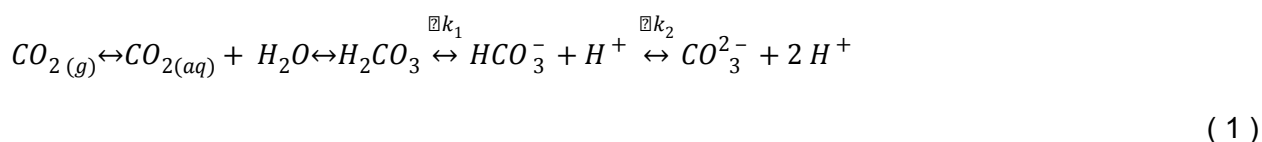**Derivation of Source Function $S(x,t)$:**

The source function $S(x,t)$ quantitatively describes how the microalgae's source of inorganic C, i.e. HCO_3^-, is formed from atmospheric $CO_{2\,(g)}$. In a first step, Henry's law describes a thermodynamic equilibrium between gas and aqueous phase and thus determines the quantity of CO_2 that dissolves into seawater $(CO_{2\,(g)} \rightarrow CO_{2(aq)})$. From $CO_{2(aq)}$, carbonic acid (H_2CO_3) forms which partially dissociates in water resulting in bicarbonate (HCO_3^-) which in turn produces a small quantity of carbonate ions (CO_3^{2-}) (1). As will be discussed in the remainder, the most relevant product formed in this sequence of reactions is HCO_3^-.

$$CO_{2\,(g)} \leftrightarrow CO_{2(aq)} + H_2O \leftrightarrow H_2CO_3 \overset{k_1}{\leftrightarrow} HCO_3^- + H^+ \overset{k_2}{\leftrightarrow} CO_3^{2-} + 2\,H^+$$

(1)

Quantitating the transformation of $CO_{2\,(g)}$ into HCO_3^- requires a detailed analysis. First, the partial pressure of CO_2 in the atmosphere (in atm) needs to be determined:

$$pCO_2 = x\,CO_2 \cdot (P - pH_2O) \cdot 10^{-6}$$

(2)

In (2), $x\,CO_2$ represents is the mole fraction of CO_2 in the atmosphere and P the total atmospheric pressure in atm (used here: 1atm). Since, CO_2 exchange occurs at the air-water interface, saturation vapor pressure of water, pH_2O (atm) needs to be subtracted from the total pressure. Saturation water vapor pressure can be calculated by [1]:

$$\ln\left(pH_2O\right) = 24.4543 - \frac{6745.09}{T} - 4.8489 \cdot \ln\left(\frac{T}{100}\right) - 0.00054 \cdot S$$

(3)

In (3), T represents the temperature of the air-water interface in Kelvin and S denotes the seawater salinity in g/kg. Since, CO_2 is not an ideal gas, its fugacity fCO_2 (in atm) needs to be calculated from its partial pressure and ideal gas constant R [2]:

$$fCO_2 = pCO_2 \cdot \exp\left(P \cdot \frac{B + 2\delta}{R \cdot T}\right)$$

(4)

For calculating fCO_2 (4), B and δ (both in m³·mol⁻¹) are required which denote the virial coefficient and the cross-virial coefficient, respectively [3]:

$$B = \left(-1636.75 + 12.0408 \cdot T - 3.27957 \cdot 10^{-2} \cdot T^2 + 3.16528 \cdot 10^{-5} \cdot T^3\right) \cdot 10^{-6}$$

$$\delta = (57.7 - 0.118 \cdot T) \cdot 10^{-6}$$

After calculating fugacity, the CO_2 concentration (mol/kg) dissolved in seawater can be calculated from $[CO_2] = K_0 \cdot fCO_2$ with K_0 (mol/kg-atm) denoting CO_2 solubility coefficient which has been determined in [3] as:

$$K_0 = 10^{-6} \cdot exp\left\{\frac{9345.17}{T} - 60.2409 + 23.3585 \cdot \ln\left(\frac{T}{100}\right) + S \cdot (0.023\right.$$

Dissolved $CO_{2\,(aq)}$ is in equilibrium with HCO_3^- and CO_3^{2-} according to:

$$CO_{2(aq)} + H_2O \overset{\boxed{?}k_1}{\leftrightarrow} HCO_3^- + H^+$$
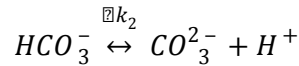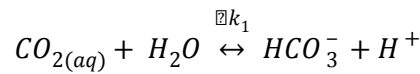
$$HCO_3^- \overset{\boxed{?}k_2}{\leftrightarrow} CO_3^{2-} + H^+$$

The equilibrium constants $k_1 = \dfrac{\left[HCO_3^-\right] \cdot [H^+]}{[CO_2]}$ and $k_2 = \dfrac{\left[CO_3^{2-}\right] \cdot [H^+]}{\left[HCO_3^-\right]}$ are temperature $T\,(= 296K)$ and salinity $S = 35\dfrac{g\ salt}{kg\ seawater}$ dependent functions (in mol/kg) and have been determined in [4] as:

$$\ln(k_1) = 2.83655 - \frac{2307.1266}{T} - 1.5529413 \cdot \ln(T) - \left(0.207608410 + \frac{4.048}{T}\right.$$
$$\ln(1 - 0.001005 \cdot S)$$

$$\ln(k_2) = -9.226508 - \frac{3351.6106}{T} - 0.2005743 \cdot \ln(T) - \left(0.1069018 + \frac{23.97}{T}\right.$$
$$\ln(1 - 0.001005 \cdot S)$$

$[H^+]$ (in mol/kg) can be determined from the pH ($= 8.20;\ buffered$) and density of the seawater solution $\left(= 1.026\dfrac{kg}{L}\right)$. With $[CO_2]$, $[H^+]$, and k_1 known, $\left[HCO_3^-\right]$ (in mol/kg) can be calculated:

$$[HCO_3^-] = \frac{k_1 \cdot [CO_2]}{[H^+]}$$

For completeness purposes, the carbonate ion concentration can be determined, too:

$$[CO_3^{2-}] = \frac{k_2 \cdot [HCO_3^-]}{[H^+]}$$

Finally, gravimetric concentration units (mol/kg) are converted to millimolar (mM) through the density of seawater (kg/L) for this modeling application.

References:

1.   R. F. Weiss and B. A. Price, *Marine Chemistry*, 1980, **8**, 347-359.

2.   A. Kortzinger, L. Mintrop and J. C. Duinker, *Journal of Geophysical Research*, 1998, **103**, 9.

3.   R. F. Weiss, *Marine Chemistry*, 1974, **2**, 203-215.

4.   R. N. Roy, L. N. Roy, K. M. Vogel, C. Porter-Moore, T. Pearson, C. E. Good, F. J. Millero and D. M. Campbell, *Marine Chemistry*, 1993, **44**, 249-267.