Stoke's Law to predict settling of particles (type 1, discrete, non-interacting):

\[ \omega_f = \frac{(2/9) \cdot g \cdot (\rho_s / \rho_f - 1) \cdot \rho^2}{\eta_f} \]

With the sediment and fluid densities, particle size, and kinematic viscosity.

Downward flux due to settling [ML²T⁻¹] is therefore:

\[ J_{\text{Stokes}} = C \cdot \omega_f \]

Corresponding upward flux density:

\[ J_{\text{Fickian}} = D \cdot \frac{dC}{dx} \]

Vertical concentration profile of particles at steady state:

\[ C = C_o \cdot e^{-\omega_f / D \cdot x} \]
Example 2-3

Describe the steady-state distribution of 1 µm clay particles in still water. Assume kinematic viscosity of water at 50°F is 0.013 cm²/sec and a solid density of 2.6 g/cm³. Also calculate the depth when the concentration is halved.

The settling rate for the 1 µm particle is therefore:

\[
\omega_s = \frac{(2/9) \cdot g \cdot (\rho_s - \rho) \cdot r^2}{\eta_v} = \frac{(2/9) \cdot 98 \text{ cm/sec}^2 \cdot ((2.6 \text{ g/cm}^3)/(1 \text{ g/cm}^3) - 1) \cdot (5 \times 10^{-6} \text{ cm}^3)}{0.013 \text{ cm}^2/\text{sec}}
\]

\[
= 6.7 \times 10^{-5} \text{ cm/sec}
\]

Example 2-4

What is the minimum distance the particles will travel before settling to the river bottom? Assume a 2-m river depth and 200 µm particles, 2.6 g/cm³ particle density and 1.3x10⁻² cm²/sec kinematic viscosity.

Settling rate:

\[
\omega_s = \frac{(2/9) \cdot 98 \text{ cm/sec}^2 \cdot ((2.6 \text{ g/cm}^3)/(1 \text{ g/cm}^3) - 1) \cdot (10^{-2} \text{ cm}^3)}{0.013 \text{ cm}^2/\text{sec}}
\]

\[
\omega_s = 2.7 \text{ cm/sec}
\]

The time required to settle 2 m is therefore 75 sec, and the particle will travel:

75 sec \cdot 0.2 \text{ m/sec} = 15 \text{ m}

Sediment accumulations:

The diffusion coefficient for this particle is about 5x10⁻⁹ cm²/sec (from fig 2-11). The first-order decay coefficient for the large particle is therefore:

\[
\omega_j / D = \frac{6.7 \times 10^{-5} \text{ cm/sec}}{5 \times 10^{-9} \text{ cm}^2/\text{sec}} = 1.3 \times 10^4 \text{ /cm}
\]

The distance at which the concentration is halved is:

\[
\frac{1}{2} = e^{-(1.3 \times 10^4 / \text{cm}) \cdot x}
\]

\[
x = 5 \times 10^{-5} \text{ cm} \text{ or } 0.5 \mu \text{m}
\]
Example 2-5

Sediment from a 10 cm depth of a lake has a $^{210}$Pb activity of 2.5 disintegrations per minute (DPM), while surface sediment has a DPM of 4. How rapidly does sediment accumulate in this lake?

Using the basic equation for radioactive decay:

$$t = \frac{-1}{\lambda} \ln \left( \frac{A_0}{A_w} \right) = \frac{-1}{0.03 \text{ year}} \ln \left( \frac{2.5 \text{ DPM}}{4 \text{ DPM}} \right) = 16 \text{ year}$$

$$\frac{10 \text{ cm}}{16 \text{ year}} = 0.6 \text{ cm/ year}$$

Air-Water Exchange

The concentration of a dissolved gas in water at equilibrium with the atmosphere is:

$$C_{\text{equil}} = \frac{C_a}{H}$$

Where $C_a$ is the concentration in air, and $H$ is the Henry’s law constant.

The flux density is proportional to the product of the difference between the actual and the equilibrium concentrations:

$$J = -k_w (C_w - \frac{C_a}{H})$$

Thin Film Model:

For water-side control, the flux of the chemical out/in water is:

$$J = \frac{D}{\delta_w} C_w = -k_w C_w$$

Which considers the molecular diffusion coefficient, the film thickness, and the concentration in the water. The thickness cannot be directly measured, but the $k_w$ factor can, and with an estimate of the diffusion coefficient, the film thickness can also be estimated.

The general case (needed when $H$ is on the order of 0.01) and both air and water affect the gas transfer:

$$J = \left[ \frac{1}{\delta_a / D_a + \delta_w / (D_w \cdot H)} \right] C_w - \frac{C_a}{H}$$
Estimation of gas exchange coefficients can be made based on the relative molecular weights of a gas tracer and the gas of interest:

\[
k_A = \frac{D_A}{M_W} = \frac{\sqrt{M_{W_B}}}{\sqrt{M_{W_A}}}
\]

The gas exchange coefficients can also be estimated based on wind speed (measured 10 m above the water). For water side control:

\[k_w (cm/sec) = 4 \times 10^{-4} + 4 \times 10^{-5} \cdot u_{10}^2\]

For air-side control (and cm/hr units for \(k_a\)):

\[k_a (cm/hr) \approx 1100 \cdot u(m/sec)\]

### Example 2-6

The dissolved concentration of trichloroethylene (TCE) \((C_2Cl_3H)\) is 1 \(\mu\)/L. \(H\) is 0.4 and the measured gas exchange rate coefficient for propane \((C_3H_8)\) in water is \(3 \times 10^{-3} \text{ cm/sec}\). What is the flux density for TCE from the lake?

\[\text{MW TCE} = 131 \text{ g/mol and MW propane} = 44 \text{ g/mol. Assuming } C_a \text{ is almost 0. Diffusion through air is not a bottleneck due to Fairly high } H. \text{ Dw for TCE is estimated by the Dw for propane multiplied by the roots of the ratios of the MW:}\]

\[\frac{D_{TCE}}{D_a} = \frac{3 \times 10^{-3} \text{ cm/sec} \cdot \sqrt{44}}{\sqrt{131}} = 1.7 \times 10^{-3} \text{ cm/sec}\]

\[J = -\frac{D_{TCE}}{D_a} C_a = -k_a C_w\]

\[J_{TCE} = \left(1.7 \times 10^{-3} \text{ cm/sec}\right) \left(\frac{1 \mu g}{liter} \cdot \frac{1 \text{ liter}}{1000 \text{ cm}^3}\right) = 1.7 \times 10^{-6} \frac{\mu g}{cm^2 \cdot \text{sec}}\]

### Volatilization from Pure Phase Liquids

The concentration at the base of a stagnant air layer, just above the surface of a NAPL, is determined by:

\[C_a = \frac{P}{RT} (MW)\]

Where \(P\) is the vapor pressure of the chemical, \(R\) is the universal gas constant, \(T\) is the absolute temperature, and \(MW\) is the molecular weight of the chemical (g/mol).

The volatilization rate from the NAPL surface is:

\[J = -\frac{D_a}{\delta_a} \cdot C_a\]

### Example 2-6

Benzene is spilled in a lake from an overturned tanker truck. The 10m high wind speed is 3 m/sec. What is the flux density from the slick?

The concentration of benzene at the air-NAPL interface is:

\[C_a = \frac{P}{RT} (MW) = \frac{(0.12\text{ atm})(0.082 \text{ atm liter mol}^{-1} \text{ mol}^{-1} \text{ K}^{-1})(293\text{K})}{(78 \text{ g/mol})} = 0.4 \text{ g/liter}\]

The flux density is therefore:

\[J = \left(\frac{3300\text{ cm}}{hr}\right) \left(\frac{0.4 \text{ g}}{liter}\right) \left(\frac{1 \text{ liter}}{1000 \text{ cm}^3}\right) = \frac{1.3 \text{ g}}{cm^2 \cdot hr} \Rightarrow 360 \mu g/cm^2 \cdot \text{sec}\]