III. TRANSPORT PHENOMENA

1. Basic Concepts and Mechanisms

Contaminant Transport

- effect of wastewater discharge to a river on downstream water quality
- effect of an incinerator on downwind air pollutant levels
- overall efficiency of a waste treatment technologies is influenced by the contaminant transport within the control facility
- performance of monitoring and measurement devices depends on the effective transport of contaminants from the sampling point to the detector

Physical Scale of Concern for Contaminant Transport

- Molecular dimension: transport of a contaminant into the pore of an adsorbent
- Global distance: transport of air and waterborne contaminants

Transport phenomena is subdivided into (1) Fluid mechanics, (2) Heat transfer, and (3) Mass transfer

1.1 Contaminant Flux

- "Flux (symbol: J)" is a vector quantity, comprising both a magnitude and a direction

  Direction of a flux vector:

  Magnitude of a flux vector:

1.2 Advection

- Whenever a fluid is in motion, all contaminants in the fluid including both molecules and suspended particles are "advected" along with the fluid.

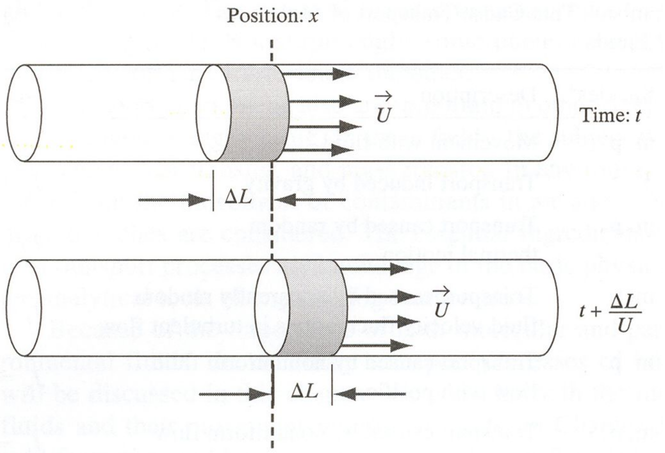


Figure 4.A.2 Advective flux of contaminant through a tube. The two pictures represent the same tube at two points in time, t and $t + \Delta t$, where $\Delta t = \Delta L / U$.

$$J_a = \frac{\text{Mass}}{(\text{Cross Sectional Area})\cdot(\text{Time Interval})} = \frac{C \times \Delta L \times A}{A \times (\Delta L/U)} = C \cdot U$$

$$\vec{J_a}(x, y, z) = C(x, y, z) \times \vec{U}(x, y, z)$$

1.3 Molecular Diffusion (Brownian Motion)

- The botanist Robert Brown, who in 1827 reported observing, through a microscope, the wiggling motion of pollen grains suspended in water. The Brownian motion results from the random collisions of particles suspended in a fluid with surrounding molecules.
- Although the molecular-scale motion seems hopelessly disordered, the macroscopic effects are well understood and predictable. Qualitatively, the random motion of fluid molecules causes a net movement of species from high concentration region to low concentration one.
- The rate of mass movement due to molecular diffusion is greater with larger concentration difference, shorter distance, less molecular size, and higher temperature.
- At high concentrations, diffusion can cause significant net flow of a bulk fluid.

1.3.1 Fick's Law

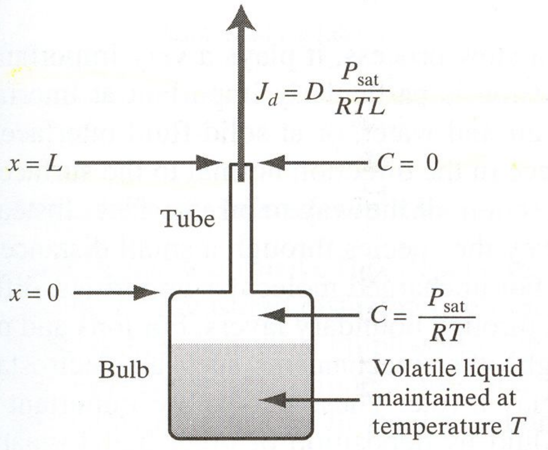


Figure 4.A.3 Apparatus for producing a controlled diffusive flux of a volatile species. P_{sat} is the saturation vapor pressure of the species at temperature T. Provided that the time scale for evaporation and condensation is much more rapid than the time scale for diffusion through the tube, a molar concentration P_{sat}/RT will be attained throughout the bulb. The vapor molecules will diffuse through the tube with a net diffusive flux J_d.

The escape rate of a volatile substance from the tube varies (1) in inverse proportion to the tube length, (2) in proportion to the cross-sectional area of the tube, and (3) in proportion to the partial pressure of the substance in the bulb.

$$\frac{\Delta M}{\Delta T} \propto -\frac{A\cdot\Delta C}{\Delta x} \text{ and } J_d \propto -\frac{\Delta C}{\Delta x}$$

$$J_d = -D\cdot\frac{\Delta C}{\Delta x}$$

where D = diffusion coefficient (or diffusivity)

as the distance Δx becomes infinitesimally small,

$$J_d = -D\cdot\frac{dC}{dx} \text{ and}$$

$$\vec{J_d}(x, y, z) = -D\cdot\left(\frac{\partial C}{\partial x}, \frac{\partial C}{\partial y}, \frac{\partial C}{\partial z}\right)$$

1.3.2 Significance of Diffusion

Diffusion is a slow transport process. Albert Einstein showed that characteristic distance a molecule (or a particle) will travel by diffusion in time t is given by

$$x \approx \sqrt{2\cdot D\cdot t}$$

For example, a gas molecule with a diffusivity of 0.1 cm^2/sec is expected to move in 1 second a characteristic distance, $x = \sqrt{2 \times 0.1 cm^2/sec \times 1 sec} = 0.45 cm$

Diffusion is particularly important at interfaces (or boundary layer) because there is no fluid advection at an interface in the direction normal to the surface.

Diffusivity of molecules in air (D_{air})

= 0.05 (Naphthalene) – 0.6 (Helium) cm^2/sec

Diffusivity of molecules in water (D_{water})

= 0.8 (Methanol) x 10^{-5} – 4.5 (Hydrogen) x 10^{-5} cm^2/sec

1.4 Dispersion

Dispersion is caused by nonuniform advection and influenced by diffusion.

1.4.1 Shear-Flow Dispersion

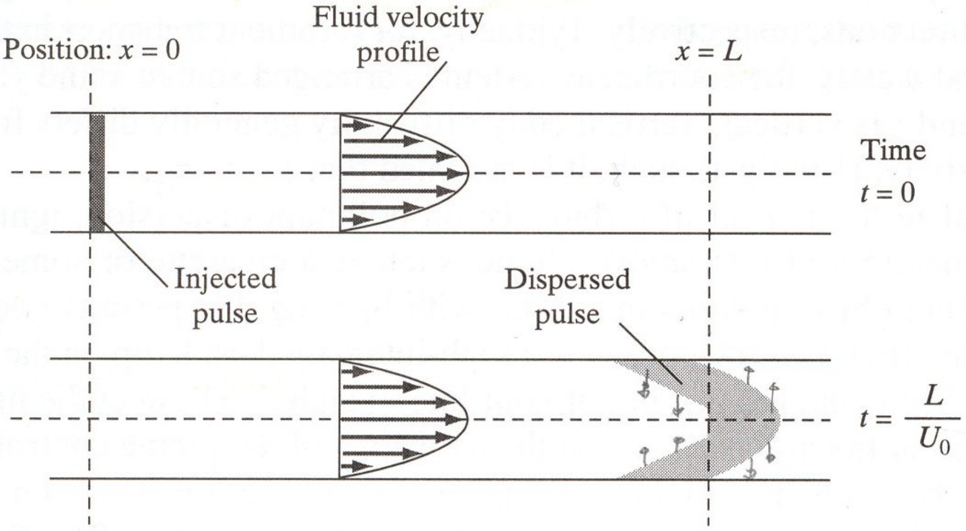


Figure 4.A.6 Schematic of a model problem illustrating the effects of shear-flow dispersion.

The velocity profile of the fluid flow is parabolic because of wall friction. Those molecules that lie close to the centerline of the tube are advected at a higher velocity than those near the wall.

However, the contaminant profile of a pulse input is not a parabolic line but a parabolic range. Contaminant molecules positioned near the leading edge of the pulse and near the center of the tube tend to diffuse toward the walls. Conversely, contaminant molecules located near the tailing edge of the pulse tend to diffuse toward the center.

In this case, the net effect of molecular diffusion is to slow the rate of dispersion.

Under laminar flow condition, the flux due to shear-flow dispersion is described by an equation analogous to Fick's law.

$$J_s = -\varepsilon_s \cdot \frac{dC}{dx}$$

where ε_s = shear-flow dispersivity

1.4.2 Turbulent Diffusion

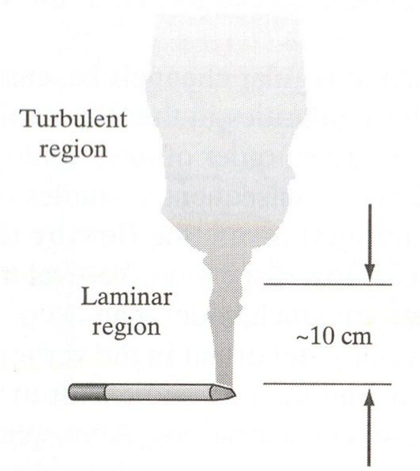


Figure 4.A.7 Schematic representation of time-averaged smoke plume rising from a smoldering cigarette in still air.

The flux due to turbulent dispersion is described by an equation analogous to Fick's law.

$$J_t = -\varepsilon_t \cdot \frac{dC}{dx}$$

$$\vec{J}_t = -\left(\varepsilon_{t,x} \frac{\partial C}{\partial x}, \ \varepsilon_{t,y} \frac{\partial C}{\partial y}, \ \varepsilon_{t,z} \frac{\partial C}{\partial z} \right)$$

where ε_t, $\varepsilon_{t,x}$, $\varepsilon_{t,y}$, $\varepsilon_{t,z}$ = turbulent diffusion coefficients (or eddy diffusivities)

It is often assumed that $\varepsilon_{t,x} = \varepsilon_{t,y}$.

Turbulent diffusivities in rivers are one order magnitude smaller than shear-flow dispersion coefficient. In the atmosphere, turbulent diffusion is especially important in the vertical direction.

2. Particle Motion

- Gravitational settling
- Brown motion (diffusive-type process)

The transport of particles within fluids is very strongly influenced by their size and mass. For larger particles, transport mechanisms depend on mass and predominate over diffusive motion.

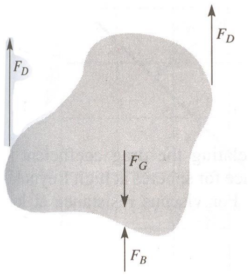
2.1 Drag on Particle

For a settling particle in a fluid, there are three forces acting on the particle. The drag force is the driving force for the acceleration of the particle. If the forces are balanced each other, the settling speed of the particle is constant. The drag force increases as the particle velocity relative to the fluid increases.

$$F_G = \rho_p \cdot g \cdot V_p$$

$$F_B = \rho_f \cdot g \cdot V_p$$

$$F_D = C_D \cdot A_p \cdot \rho_f \cdot \frac{v^2}{2}$$



where F_G = gravitational force;

F_B = buoyancy force;

F_D = drag force;

ρ_p = density of a particle;

ρ_f = density of a fluid;

g = acceleration due to gravity;

V_p = volume of the particle;

C_D = drag coefficient;

A_p = cross sectional area of the particle; and

v = speed of the particle relative to the fluid.

The drag force on a spherical particle (F_D) is computed by the following expression,

$$F_D = C_D \cdot \left(\frac{\pi}{4} \cdot d_p^{\ 2}\right) \cdot \left(\frac{1}{2} \cdot \rho_f \cdot v^2\right)$$

where d_p = particle diameter.

The relationship between drag coefficient and Reynolds number (R) for smooth, spherical, nonaccelerating particles

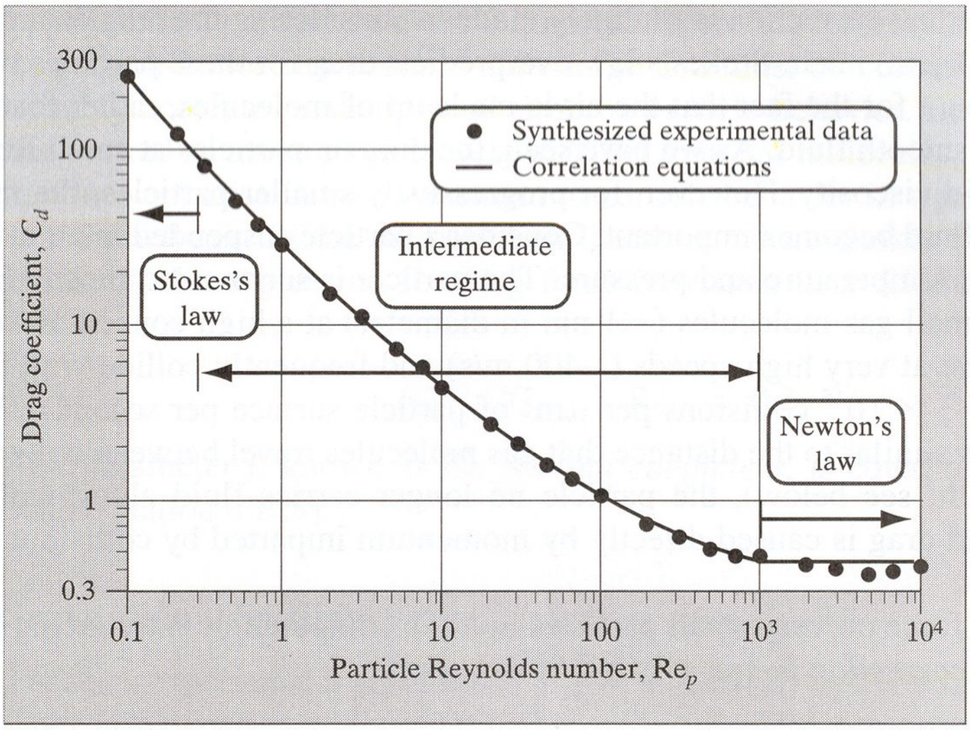


Figure 4.B.1 Drag coefficient as a function of particle Reynolds number for smooth, spherical, nonaccelerating particles in a uniform fluid flow. The experimental data are from Lapple and Shepherd (1940). The correlation equations are described in the text.

$$R = \frac{d_p \cdot v}{\nu} = \frac{d_p \cdot \rho_f \cdot v}{\mu}$$

$$C_D = \frac{24}{R} \ (R < 0.3)$$

$$C_D = \frac{24}{R} \cdot \left(1 + 0.14 \cdot R^{0.7}\right) \ (0.3 < R < 1{,}000)$$

$$C_D = 0.445 \ (1{,}000 < R < 350{,}000)$$

where ν = kinematic viscosity; and

μ = dynamic viscosity

$$F_D = 3 \cdot \pi \cdot \mu \cdot d_p \cdot v \ (R < 0.3)$$

$$F_D = 0.173 \cdot \rho_f \cdot d_p^{\ 2} \cdot v^2 \ (1{,}000 < R < 350{,}000)$$

One important correction is made in considering the drag force on small particle ($d_p < 1\mu m$) in air because the air is made up of molecules rather than a continuously smooth fluid. The drag force on very small particles in air is computed by introducing the Cunningham slip correction factor, C_c,

$$F_D = \frac{1}{C_c} \cdot \left(3 \cdot \pi \cdot \mu \cdot d_p \cdot v\right) = f \cdot v \ (R < 0.3)$$

where f = friction coefficient

C_c decreases as the particle diameter increases, and reach 1 for particles of which diameter is greater than 1μm.

2.2 Gravitational Settling

Terminal Settling Velocity (or Terminal Rising Velocity)

$$F_G = F_B + F_D$$

$$F_G = m \cdot g = \rho_p \cdot \frac{\pi}{6} \cdot d_p^{\ 3} \cdot g$$

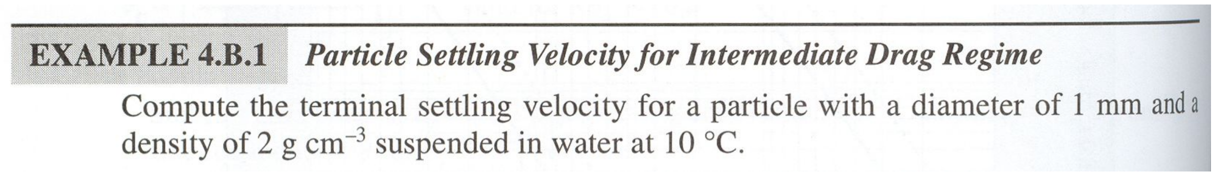
$$F_B = \rho_f \cdot \frac{\pi}{6} \cdot d_p^{\ 3} \cdot g$$

$$F_D = C_D \cdot \left(\frac{\pi}{4} \cdot d_p^{\ 2}\right) \cdot \left(\frac{1}{2} \cdot \rho_f \cdot v^2\right) = C_D \cdot \frac{\pi}{4} \cdot d^2 \cdot \rho_f \cdot \frac{v^2}{2}$$

$$\therefore\ v = \sqrt{\frac{4 \cdot g \cdot d_p}{3 \cdot C_D} \cdot \left(\frac{\rho_p - \rho_f}{\rho_f}\right)}$$

If the density of the settling particle is less than that of the fluid, The terminal rising velocity is,

$$v = \sqrt{\frac{4 \cdot g \cdot d_p}{3 \cdot C_D} \cdot \left(\frac{\rho_f - \rho_p}{\rho_f}\right)}$$



EXAMPLE 4.B.1 *Particle Settling Velocity for Intermediate Drag Regime*

Compute the terminal settling velocity for a particle with a diameter of 1 mm and a density of 2 g cm^{-3} suspended in water at 10 °C.

2.3 Brownian Diffusion

A transport mechanism caused by the random motion of fluid molecules is molecular diffusion. An analogous phenomenon applies to particles suspended in a fluid.

The Brownian diffusivity of particles **in air** is determined by an equation known as the Stokes-Einstein relation,

$$D = \frac{k \cdot T}{f}$$

where k = Boltzmann's constant (1.38 x 10^{-16} erg/K);

T = temperature (K); and

f = friction coefficient. $f = \frac{1}{C_c} \cdot \left(3 \cdot \pi \cdot \mu \cdot d_p\right)$

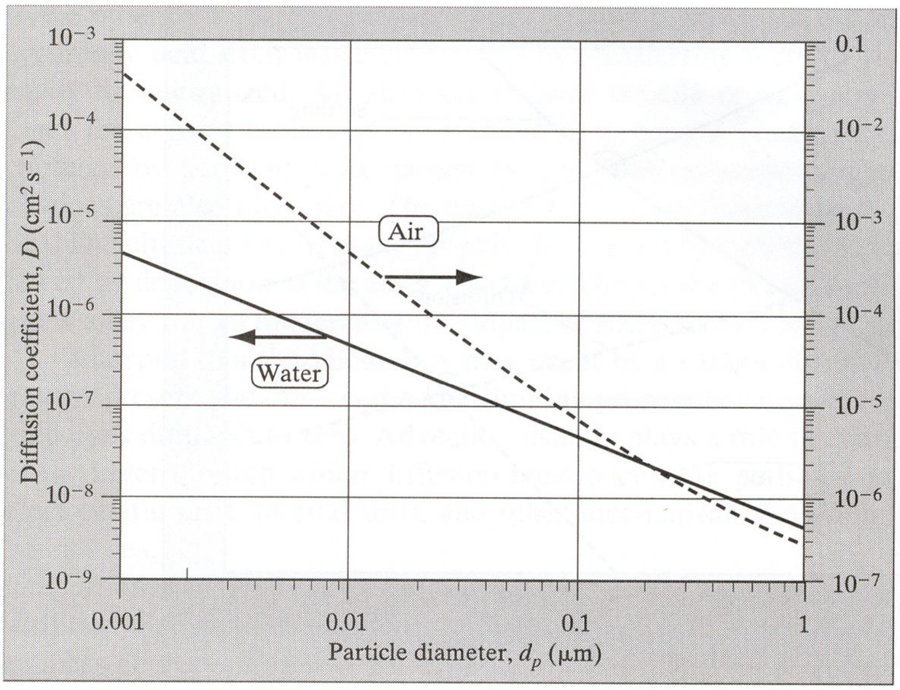


Figure 4.B.6 Brownian diffusivity for particles in air and water; $T = 20$ °C, $P = 1$ atm.

The rate of Brownian diffusion is much slower than the rate of molecular diffusion because particles are much larger and much more massive than molecules.

As the size of the particle that is heavier than a fluid increases, settling is predominant to Brownian diffusion in its transport.

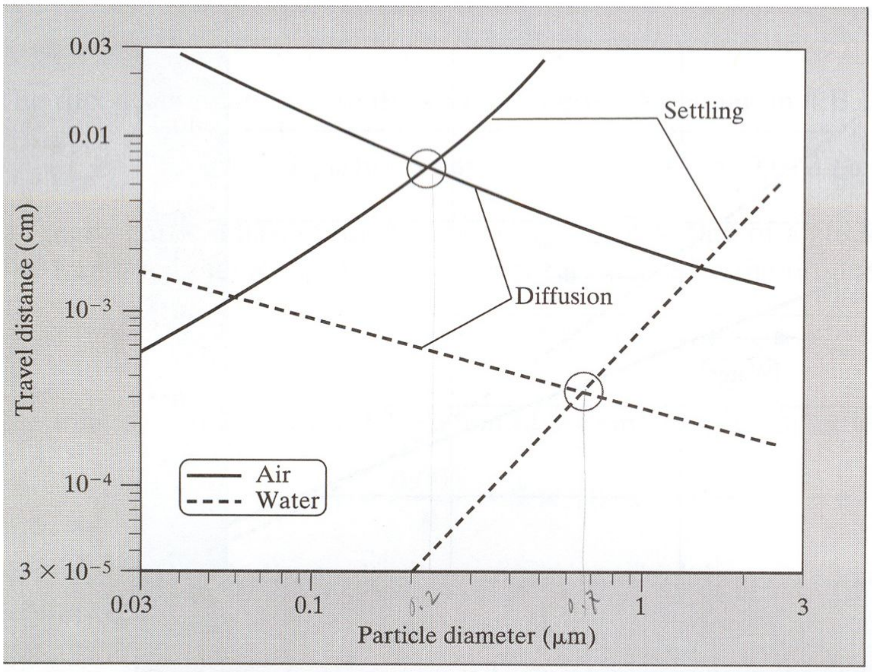


Figure 4.B.7 Distance traveled in 10 s by particles in air or water because of gravitational settling and Brownian diffusion. Particle settling velocities were determined from Stokes's law (Table 4.B.1) with $T = 293$ K and $P = 1$ atm. Diffusion distances were estimated from expression 4.A.7, using the Stokes-Einstein relation to compute diffusivity (equation 4.B.18). Particle density is 2.5 g cm^{-3}.

3. Mass Transfer at Fluid Boundaries

3.1 Mass-Transfer Coefficient

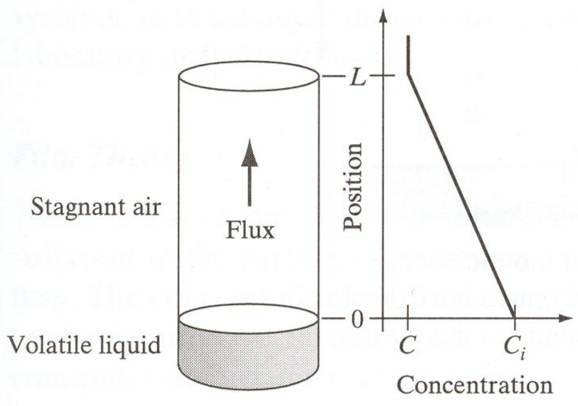


Figure 4.C.1 A simple system in which a mass-transfer coefficient can be directly determined.

$$J_b = k_m \cdot (C - C_i)$$

where J_b = net flux to the boundary (amount of species per area per time);

k_m = mass-transfer coefficient; and

C and C_i = concentration terms.

The diffusive flux through the tube, J_d is given by Fick's law as,

$$J_d = D \cdot \frac{C_i - C}{L}$$

at a steady state, the net transport rate from the air to the liquid is equal to the negative of the diffusive flux and

$$k_m = \frac{D}{L}$$

Discussions on concentrations, i.e., C_i, C

(1) The concentration at the boundary, C_i can be taken to be "0" when a transformation process that is fast and irreversible occurs at the boundary rather than surface-reaction kinetics is the rate-limiting step. In the other hand,

C_i can be determined by assuming local equilibrium at the interface.

(2) When the fluid is well mixed outside of a thin boundary layer, the concentration in bulk fluid, C is easily defined. Only rough approximation of C can be possible for practical environmental engineering problem because C vary strongly with position and time.

3.2 Two Film Model for Transport across the Air-Water Interface

- Two resistance model for interfacial mass transfer

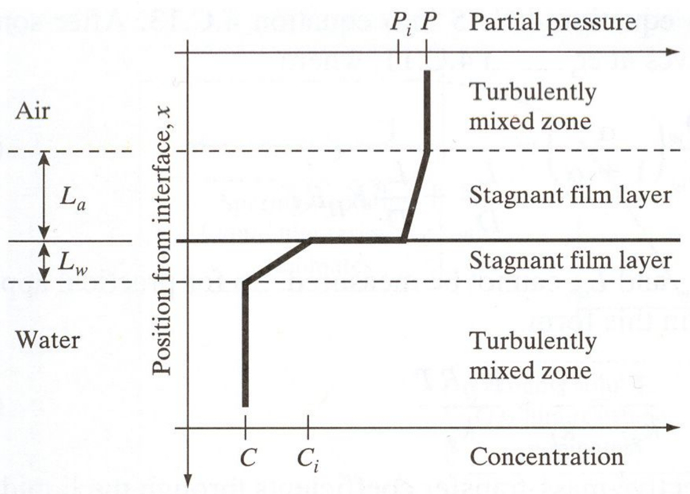


Figure 4.C.6 Schematic of the two-film model for estimating mass transport across an air-water interface.

Applying Fick's law, the gas-side flux (from air to the interface), J_{gl} can be written as

$$J_{gl} = D_a \frac{(P - P_i)/RT}{L_a}$$

where D_a = diffusivity of the species through air;

L_a = thickness of the stagnant film layer in the air

P = partial pressure in the gas phase; and

P_i = partial pressure at the interface.

Likewise, the liquid-side flux (from the interface into the water), J_{gl} is

$$J_{gl} = D_w \frac{(C_i - C)}{L_w}$$

where D_w = diffusivity of the species in water;

L_w = thickness of the stagnant film layer in the water

C = aqueous concentration; and

C_i = aqueous concentration at the interface.

$C_i = K_H \cdot P_i$

Then, we can solve 3 variables, i.e., J_{gl}, C_i, and P_i using the previous 3 equations.

$$C_i = \frac{\alpha \cdot C_s + C}{1 + \alpha}$$

$$\alpha = \frac{D_a \cdot L_w}{D_w \cdot L_a \cdot K_H \cdot R \cdot T}$$

and $C_s = K_H \cdot P$

$$J_{gl} = \frac{D_w}{L_w} \cdot (C_i - C) = \frac{D_w}{L_w} \cdot \frac{\alpha}{1 + \alpha} \cdot (C_s - C) \quad \text{and}$$

$J_{gl} = k_{gl} \cdot (C_s - C)$

Thus,

$$k_{gl} = \frac{D_w}{L_w} \cdot \left(\frac{\alpha}{1 + \alpha} \right) = \frac{1}{\frac{L_w}{D_w} + \frac{L_a}{D_a} \cdot K_H \cdot R \cdot T} \quad \text{and}$$

$$\frac{1}{k_{gl}} = \frac{1}{k_l} + \frac{K_H \cdot R \cdot T}{k_g}$$

where k_l = mass transfer coefficient through the liquid boundary layer ($=D_w/L_w$); and

k_g = mass transfer coefficient through the gas boundary layer ($=D_a/L_a$).

For natural bodies of water, the following expressions can be applied to estimate mass transfer coefficients, k_g and k_l.

$$k_g\ (\mathrm{m/hr}) = \left[\frac{D_a\ (\mathrm{cm^2/sec})}{0.26}\right]^{2/3} \cdot \left(7 \cdot U_{10} + 11\right)$$

for oceans, lakes, and other slowly flowing waters,

$$k_l\ (\mathrm{m/hr}) = \left[\frac{D_w\ (\mathrm{cm^2/sec})}{2.6 \times 10^{-5}}\right]^{0.57} \cdot \left(0.0014 \cdot U_{10}^{\ 2} + 0.014\right)$$

for rivers,

$$k_l\ (\mathrm{m/hr}) = 0.18 \cdot \left[\frac{D_w\ (\mathrm{cm^2/sec})}{2.6 \times 10^{-5}}\right]^{0.57} \cdot \left(\frac{U_w}{d_w}\right)^{1/2}$$

where U_{10} = mean wind speed measured at 10m above the water surface (m/sec)

U_w = mean velocity in the river (m/sec); and

d_w = mean stream depth (m).

4. Transport in Porous Media

Porous materials: solid that contains distributed void space

- Permeable porous materials contain an interconnected network of solids or pores that permits bulk flow of fluid through the material
- Sand filters, column of granular activated carbon, fabric filters, groundwater aquifer, biofilter, etc.

$$n_t = \frac{\text{pore volume}}{\text{total volume}}$$

where n_t = (total) porosity

$$n_t = n_a + n_w$$

where n_a = air-filled porosity; and
n_w = water-filled porosity.

If a particular fluid entirely fills the pores of a porous material, the porous media is “saturated” with the fluid.

Effective porosity:

Solid density vs. Bulk density

$$\rho_b = \rho_s \cdot (1 - n_t)$$

where ρ_b = bulk density [M/L^3]; and
ρ_s = solid density [M/L^3].
ρ_s of sand is typically 2.65 g/cm^3.

4.1 Fluid Flow through Porous Media

Darcy's law (Henri Darcy)

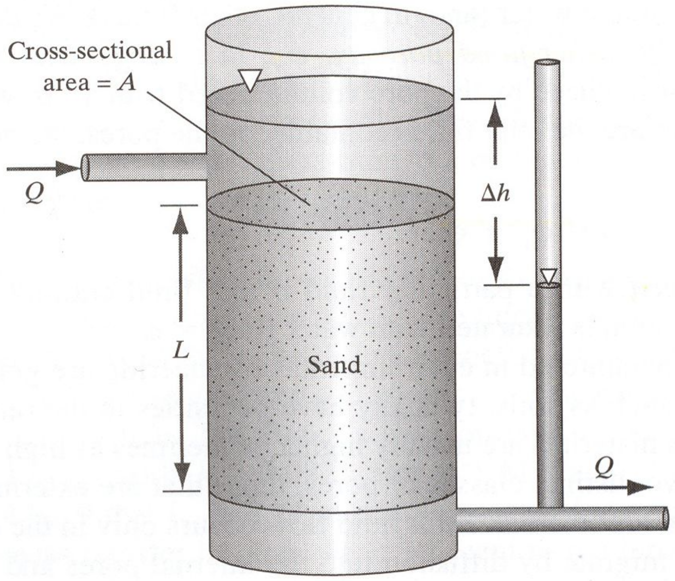


Figure 4.D.1 Apparatus similar to that used by Darcy to study the hydraulics of water flow through sand.

$$Q \propto A \cdot \frac{\Delta h}{L}$$

then $Q = K \cdot i \cdot A$ (Darcy's law)

where K = hydraulic conductivity (or permeability) [L/T]; and

i = hydraulic gradient (=$\frac{\Delta h}{L}$).

The value of "$K \cdot i$" has the identical dimension to "velocity". However, it does not represent the velocity of water through sand pores. We call it "Darcy velocity".

Hydraulic conductivity vs. Intrinsic permeability

$$K = \frac{k \cdot \rho_w \cdot g}{\mu_w}$$

where k = intrinsic permeability [L^2];

ρ_w = density of water [M/L^3];

g = gravitational acceleration [L/T^2]; and

μ_w = dynamic viscosity of water [M/L,T}.

1 darcy = 0.987×10^{-12} m^2

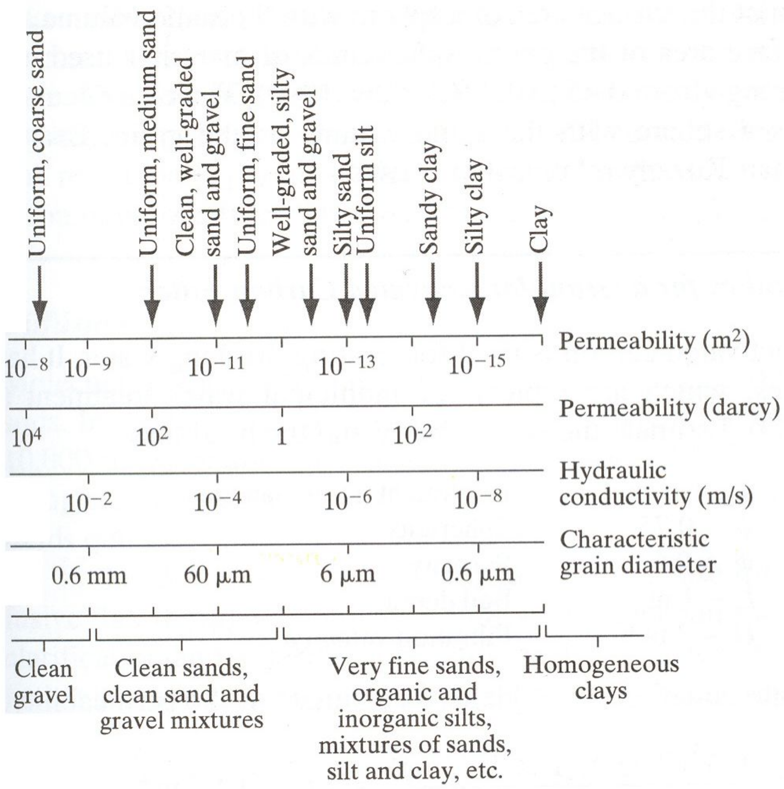


Figure 4.D.2 Permeability and hydraulic conductivity scales, indicating representative values for soils and gravel (Terzaghi and Peck, 1967; Tuma and Abdel-Hady, 1973). Characteristic grain diameters are computed from the Carman-Kozeny equation (4.D.8), assuming $\phi = 0.5$.

Carman-Kozeny equation: k estimation for grains

$$k = \frac{n_t^3 \cdot d_g^2}{180 \cdot \left(1 - n_t^2\right)}$$

where d_g = grain diameter

4.2 Contaminant Transport in Porous Media

Advection, Diffusion, and Dispersion, Chemical or Biological reactions, Sorption, Ion exchange, …

Hydrodynamic dispersion = Molecular diffusion + Mechanical dispersion

Molecular diffusion is characteristics of a compound and porous medium.

Mechanical dispersion is function of velocity.

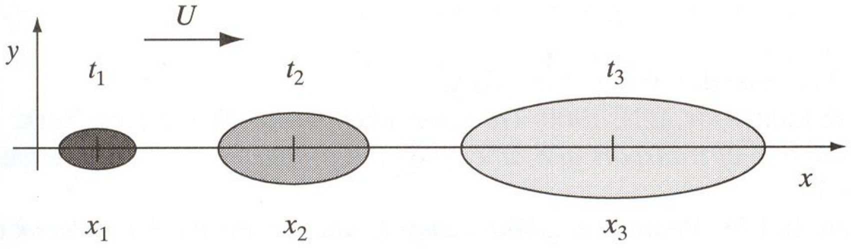


Figure 4.D.4 Transport and dispersion of a fixed quantity of a nonreactive groundwater contaminant. The figure schematically shows the areal extent of contamination at three instants in time, with $t_3 > t_2 > t_1$. The center of mass of contamination is advected in the x-direction at a rate given by the mean velocity, U. Hydrodynamic dispersion causes the contamination to spread more rapidly in the direction of flow than in the transverse direction.