INTERPHASE MASS TRANSFER: KINETICS

"Instantaneous" mass transfer

- Interphase mass transfer (sorption/dissolution/volatilization) rate >> than bulk fluid transport rates (advection/dispersion).
- Solute is at equilibrium concentrations in the various phases at a given point in space.
- Known as: LOCAL EQUILIBRIUM ASSUMPTION

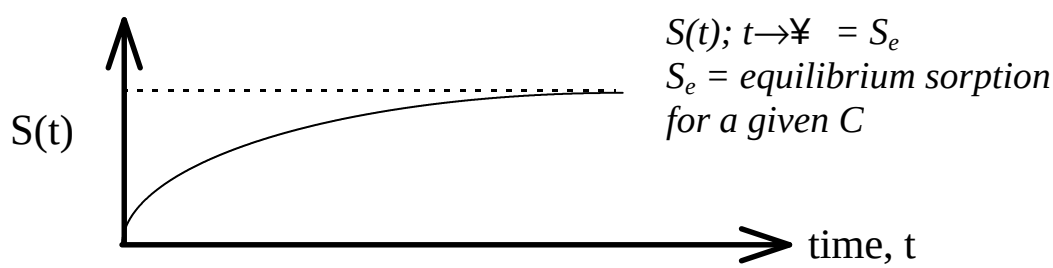
All phases (particularly solid phase) may not be at equilibrium

Causes of nonequilibrium sorption:

- Chemical kinetics
- Diffusion limited mass transfer

Rate-limited mass transfer

- Interphase mass transfer rate is limited by diffusion transport in an immobile phase.
- Scale of diffusion domain << system being modeled (i.e., grain scale or ganglia scale); cannot be modeled as transport.
- Solute concentrations in various phases may not be at equilibrium.



We will discuss rate-limited mass transfer in terms of sorption of nonpolar organic compounds.

Importance: Clean-up time, Exposure time, bioavailability

Cause of Nonequilibrium Sorption: Two Theories

1. Intra-organic matter diffusion (IOMD): (*Brusseau and Rao, Chemosphere, 18:1691-1706, 1989*).

- Soil organic matter is comprised of large humic molecules which form a flexible, porous, polymer-like solid.
- Void spaces in the "humic polymer" are filled with water, and the water is immobile.
- Solutes from the mobile bulk fluid must travel by diffusion along narrow, tortuous paths to interior sorption "sites."

2. Retarded intra-particle diffusion (RIPD): (*Ball and Roberts, ES&T, 25:1237-1249, 1991*).

- Individual soil grains contain micropores (very small cracks and fissures).
- The micropores are filled with immobile water and also contain organic material (humic or kerogen). The organic material is located in patches which may be only one molecule thickness.
- Solute from the bulk fluid must travel by diffusion in the narrow, tortuous micropores to the sorption sites inside the soil particle.

Which theory is correct?

- RIPD developed based on observations of Borden sand, where the intraparticlular volume >> organic matter volume.
- IOMD developed based on observations of several Florida soils, where organic matter volume >> intraparticular volume.
- Both theories are probably correct; however, the dominant process probably depends on the soil type.

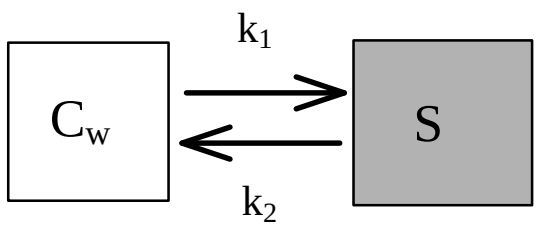
How do we model sorption kinetics?

3 methods:
1. Implicitly, using a effective dispersion term.
2. Explicitly, using first-order kinetics.
3. Explicitly, as Fickian diffusion.

1. Effective Dispersion Methods:

- Rate-limited sorption results in both early arrival (slow sorption means some solute is not sorbed) and long term tailing (slow desorption) relative to LEA.
- Results in more spreading - therefore increase dispersion coefficient.

2. First-Order Kinetics:



- Looks like chemical kinetics model.
- We are modeling diffusion; assumes a linear gradient.

MBE for soil compartment:

$$\frac{\partial S}{\partial t} = k_1 C_w - k_2 S$$

Change in sorbed phase concentration.

Rate of sorption

Rate of desorption

- Why is there a different rate constant for sorption and desorption? $\rightarrow$ Units problem!

At equilibrium: $\dfrac{\partial S}{\partial t} = 0$; $k_1 C_w = k_2 S = k_2 K_d C_w$

so: $k_1 = K_d k_2$ and: $\boxed{\dfrac{\partial S}{\partial t} = k_2 \left(K_d C_w - S \right)}$

- How does this chemical kinetics model relate to a diffusion model? $\rightarrow$ Linear gradient!

Rewrite the relationship, expressing sorbed concentration on a per volume basis so we can use Fick's Law:

use the identity: $\theta_{om} C_{om} = \rho_B S$

and at equilibrium: $C_w = \dfrac{C_{om}}{K_{om/w}} = \dfrac{S}{K_d}$

we get the new rate equation:

interfacial area

$$\rho_B \frac{\partial S}{\partial t} = \theta_{om} \frac{\partial C_{om}}{\partial t} = a_{om/w} J_{om}^{dif} = -a_{om/w} D_{om} \frac{\partial C_{om}}{\partial x}$$

$$\approx -\left[\xi \frac{\theta_{om}}{\delta} \right] \left[D_{om} \frac{\left(C_{om} - K_{om/w} C_w \right)}{\delta} \right]$$

shape factor

path length

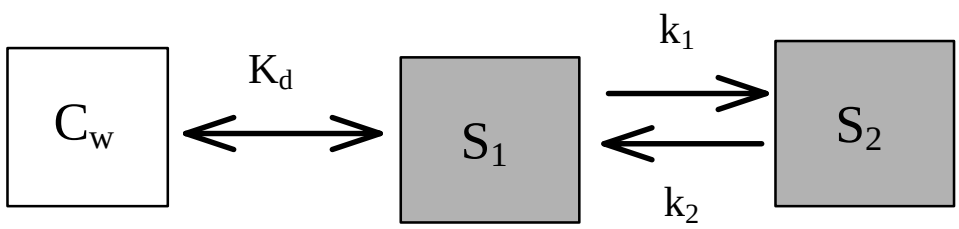
Rewrite linear gradient equation with the original terms:

$$\frac{\partial S}{\partial t} = \left[\frac{\xi D_{om}}{\delta^2}\right]\left(K_d C_w - S\right)$$

k_2 term

For many soils, sorption rate varies with time.

- Initial, fast sorption takes minutes or hours.
- Longer, slow sorption takes days to months.
- Empirical <u>two-site model</u> popular method for this phenomenon.



Sorption is divided into two compartments: $S = S_1 + S_2$

1. Equilibrium sorption between water and first compartment.

$S_1 = F K_d C_w$ (F = mass fraction of instantaneous sites)

2. First-order kinetics between the two soil compartments.

$$\frac{\partial S_2}{\partial t} = k_1 S_1 - k_2 S_2 = k_2\left[(1-F)K_d C_w - S_2\right]$$

Parameter Estimates:
F = 0.5
log k_2 = 0.301 - 0.668 log K_d
(Brusseau and Rao, Chemos., 1989)

Change in slow site concentration with time.

First-order rate constant

Driving force term

3. Diffusion Models:

- Modeling diffusion as a first-order process is makes for simple mathematics but is not an accurate description of the process.
- First-order models tend to have:
  - Velocity-dependent mass transfer rates.
  - Inability to reproduce slow, long-term tailing phenomena.
- If these problems are important, must go to a diffusion model.

Modeling sorption as a diffusion process involves defining a local diffusion domain (e.g., inside organic matter or inside a porous particle). The following parameters must be defined:

- Diffusion coefficient
- Porosity
- Tortuosity
- Sorption equilibrium relationships
- Distribution of sorption sites along a diffusion path length.

These parameters are difficult to obtain independently. Assumptions have to be made, primarily about the diffusion domain geometry.
Common assumptions:

- Tortuosity ≈ 0.1
- Geometry = uniform (film or coating of organic matter)
  spherical (RIPD into average grain size)

Most common sorption diffusion model = diffusion into a porous sphere *(Goltz and Roberts, J. Contam. Hydrol., 1:77-93, 1986)*:

System GE:

$$R_m \theta_m \frac{\partial C_m}{\partial t} + \theta_{im} R_{im} \frac{\partial \overline{C}_{im}}{\partial t} = -q_m \frac{\partial C_m}{\partial x} + D_m \theta_m \frac{\partial^2 C_{im}}{\partial x^2}$$

Solute in mobile zone

Solute in immobile zone (intragrain porosity)

Grain-Scale GE:

$$R_{im} \frac{\partial C_{im}}{\partial t} = \frac{D_e}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial C_{im}}{\partial r} \right)$$

BC1: $C_{im}(x, a, t) = C_m(x, t)$

BC2: $\left.\frac{\partial C_{im}}{\partial r}\right|_{r=0} = 0$

a = *average grain radius*

$$\overline{C}_{im}(x, t) = \frac{3}{a^3} \int_0^a r^2 C_{im}(x, r, t) dr$$

Diffusion Models:

- Are mathematically rigorous.
- Allow non-linear concentration gradients = more accurate description of process than first-order models.

APPLY INTERPHASE MASS TRANSFER TO MBE:

1. Combine interphase mass transfer with MBE
   - equilibrium: one variable/one equation
   - mass transfer: two variables/two equations
2. Explore use of dimensionless parameters.

Assume: 1-D Advective-Dispersive Groundwater Transport
Incompressible fluid (water), nondeformable media
Homogeneous, steady-state flow field (D, θ_w constant)
Linear isotherms.

[1] 4 phases (water, NAPL, air, solid), equilibrium conditions:

$$\theta_w \frac{\partial C_w}{\partial t} + \theta_a \frac{\partial C_a}{\partial t} + \theta_N \frac{\partial C_N}{\partial t} + \rho_B \frac{\partial S}{\partial t} = -\vec{q}_w \bullet \vec{\nabla} C_w + \theta_w \vec{D}_w \bullet \vec{\nabla} C_w + \theta_a \vec{D}_a \bullet \vec{\nabla} C_a$$

Insert: $C_a = HC_w$ $\quad C_N = K_{N/w} C_w$ $\quad S = K_d C_w$

$$\left(\theta_w + \theta_a H + \theta_N K_{N/w} + \rho_B K_d\right) \frac{\partial C_w}{\partial t} = -\vec{q}_w \bullet \vec{\nabla} C_w + \left(\theta_w \vec{D}_w + \theta_a H \vec{D}_a\right) \bullet \vec{\nabla} C_w$$

One Equation, One unknown (C_w)

Define R: Retardation Factor $R = \dfrac{\Sigma A_i}{A_w}$

ΣA_i: *Mass of solute in all phases at equilibrium*

A_w: *Mass of solute in water phase*

In this case: $$R = \frac{\theta_w + \theta_a H + \theta_N K_{N/w} + \rho_B K_d}{\theta_w}$$

Insert R, divide by θ_w:

$$R\frac{\partial C_w}{\partial t} = -\vec{v}_w \bullet \vec{\nabla} C_w + \left(\vec{D}_w + \frac{\theta_a H}{\theta_w}\vec{D}_a\right) \bullet \vec{\nabla} C_w$$

[2] <u>2 Phases (water, solid), equilibrium conditions</u>:

$$\theta_w \frac{\partial C_w}{\partial t} + \rho_B \frac{\partial S}{\partial t} = -q_w \frac{\partial C_w}{\partial x} + D_w \theta_w \frac{\partial^2 C_w}{\partial x^2} \qquad \text{and} \quad S = K_d C_w$$

$$\left(\theta_w + \rho_B K_d\right)\frac{\partial C_w}{\partial t} = -q_w \frac{\partial C_w}{\partial x} + D_w \theta_w \frac{\partial^2 C_w}{\partial x^2}$$

Definition of R depends on phases

$$R = 1 + \frac{\rho_B K_d}{\theta_w}$$

R for two phases.

$$R\frac{\partial C_w}{\partial t} = -v_w \frac{\partial C_w}{\partial x} + D_w \frac{\partial^2 C_w}{\partial x^2}$$

3. <u>2 Phases, nonequilibrium sorption (1st order kinetics):</u>

$$\theta_w \frac{\partial C_w}{\partial t} + \rho_B \frac{\partial S}{\partial t} = -q_w \frac{\partial C_w}{\partial x} + D_w \theta_w \frac{\partial^2 C_w}{\partial x^2}$$

Water phase MBE

$$\frac{\partial S}{\partial t} = k_2\left(K_d C_w - S\right)$$

Solid phase MBE

<u>Two equations, two unknowns (C_w, S)</u>

DIMENSIONLESS ANALYSIS:

- How do parameters in MBE equation effect solute transport?
- Many parameters work in combination with other parameters.
- Introduce DIMENSIONLESS parameters.
  - Reduce all scenarios to a common scale for comparison.
  - Reduce the number of parameters for sensitivity analysis.

Start with case 2: Advection/dispersion/equilibrium sorption:

Define terms:

$$X = \frac{x}{L}$$

normalized distance

$$p = \frac{v_w t}{L}$$

pore volumes

$$C^* = \frac{C_w}{C_{max}}$$

normalized concentration

$$R = 1 + \frac{\rho_B K_d}{\theta_w}$$

Retardation factor

$$Pe = \frac{v_w L}{D_w}$$

Peclet number = time for dispersion / time for advection

Start with MBE:

$$R\frac{\partial C_w}{\partial t} = -v_w \frac{\partial C_w}{\partial x} + D_w \frac{\partial^2 C_w}{\partial x^2}$$

Insert dimensionless numbers:

$$\frac{R C_{max} v_w}{L}\frac{\partial C^*}{\partial p} = -\frac{C_{max} v_w}{L}\frac{\partial C^*}{\partial X} + \frac{C_{max} v_w L}{Pe\, L^2}\frac{\partial^2 C^*}{\partial X^2}$$

Dividing by $\frac{C_{max} v_w}{L}$:

$$\boxed{R\frac{\partial C^*}{\partial p} = -\frac{\partial C^*}{\partial X} + \frac{1}{Pe}\frac{\partial^2 C^*}{\partial X^2}}$$

2 major parameters: R, Pe

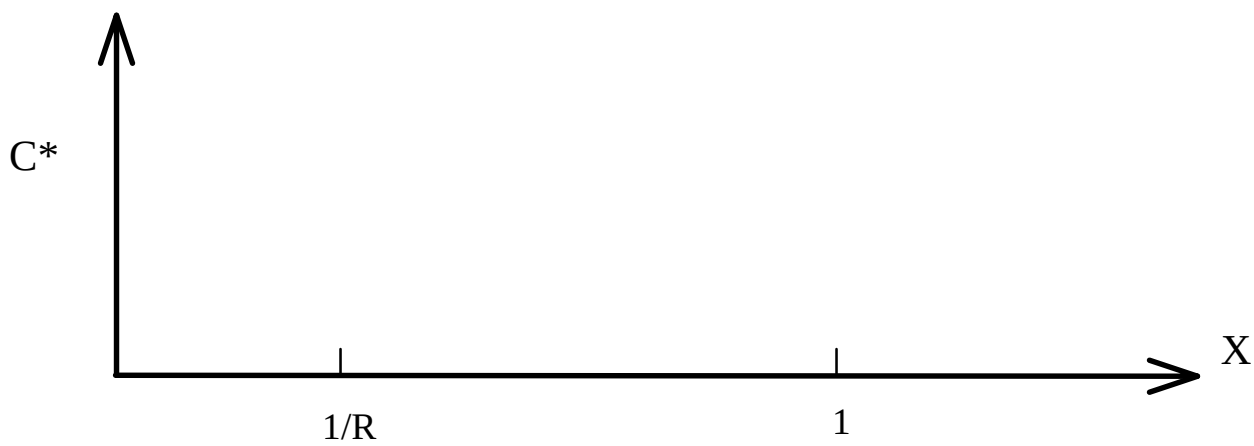
How do R and Pe affect solute transport:

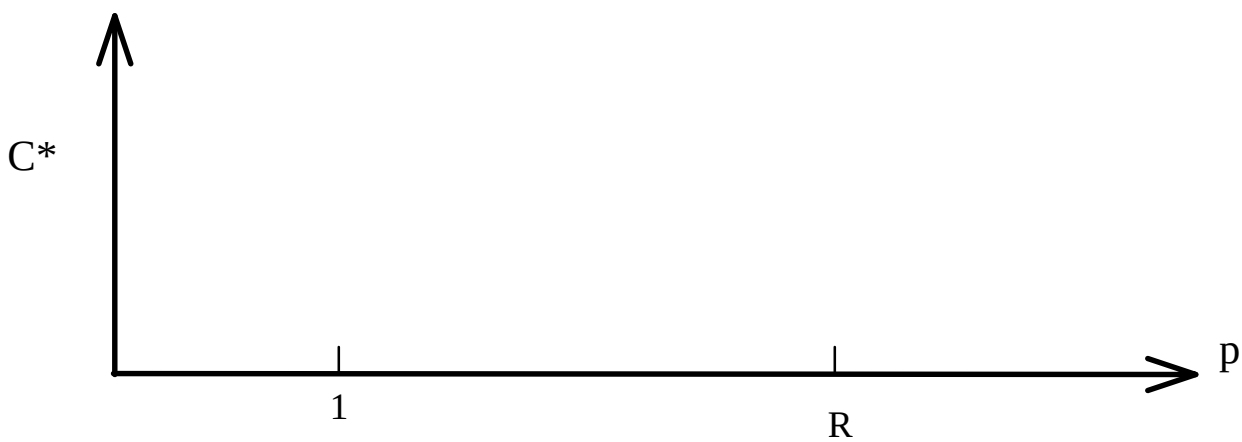
Retardation Factor, R:

- Possible values: $1 \leq R \leq \infty$
- Average rate of solute migration = v_w/R
  - As R increases, its migration rate decreases.
  - |As R increases, proportion of mass in aqueous phase decreases.

Peclet Number, Pe:

- Possible values: $0 \leq Pe \leq \infty$
  - $Pe = \infty$, no dispersion = plug flow
  - Pe decreases, dispersion increases, more spreading.





Damkohler Number: Dimensionless mass transfer rate.

$$Da = \frac{\text{time for advective transport}}{\text{time for mass transfer}}$$

$$Da = \frac{(R-1)k_2 L}{v_w}$$

Damkohler number for one-site model

$$Da = \frac{(1-F)(R-1)k_2 L}{v_w}$$

Damkohler number for two-site model

Da > 1: Advective transport takes longer than mass transfer.
Da < 1: Advective transport is faster than mass transfer.
Da ≥ 100: Local equilibrium can be assumed.
Mass tranfer is much faster than advection.

Write Case 3 in dimensionless terms:

Also need normalized sorbed concentration: $S^* = \frac{S}{K_d C_{max}}$

$$\theta_w \frac{\partial C_w}{\partial t} + \rho_B \frac{\partial S}{\partial t} = -q_w \frac{\partial C_w}{\partial x} + D_w \theta_w \frac{\partial^2 C_w}{\partial x^2}$$

$$\frac{\partial S}{\partial t} = k_2 \left(K_d C_w - S\right)$$

Reduced number of parameters from 8 (q_w, r_b, q_w, D_w, x, t, k_2, K_d) to only 5 (R, Pe, Da, X, p)

$$\frac{\partial C^*}{\partial p} + (R-1)\frac{\partial S^*}{\partial p} = -\frac{\partial C^*}{\partial X} + \frac{1}{Pe}\frac{\partial^2 C^*}{\partial X^2}$$

$$(R-1)\frac{\partial S^*}{\partial p} = Da\left(C^* - S^*\right)$$