Mass Transport Processes

Three processes account for the migration of dissolved material in groundwater:

Advection Material is carried by moving water.

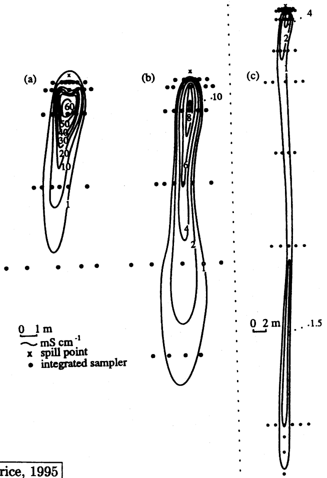
$$v = \frac{-K}{n_e}\frac{dh}{dl}$$

Diffusion Material spreads by Brownian motion.

$$F = -D^o A\frac{dc}{dl}$$

Dispersion Material spreads due to mechanical mixing (velocity variation)

Plume Shape



Hoag and Price, 1995

Fig. 6. Plan views of the plume on (a) 15 July (4 days after the spill), (b) 23 July (Day 14), and (c) 10 August (Day 30). (Note change in scale for (c).) The outer contour represents an EC of 1 mS cm^{-1}.

Diffusion in Porous Media

- diffusion values tabulated in textbooks are open column diffusion rates
- tortuousity τ defined as ratio of the tortuous to straight line path distance
- tortuousity affects the chemical gradient
- tortuousity affects migration distance
- τ^2 needed in the diffusive flux equation

$$\tau = \frac{\Delta x_{winding}}{\Delta x_{straight}}$$

Diffusion in Porous Media

- cross sectional area reduced to only open pores (porosity).

$$F = -n \cdot A \cdot D^o \frac{\partial c}{\partial x}$$

- including toruousity effects:

$$F = -\frac{n \cdot A \cdot D^o}{\tau^2} \frac{\partial c}{\partial x}$$

Tortuousity

- Tortuousity also influences the ability of a saturated porous media to conduct electricity.
- Formation factor (f) of a solution
- Ratio of the electrical resistance (R) of a solution to the resistance of a porous media filled with the same solution.

$$f = \frac{\tau^2}{n} = \frac{R_{porous\ media}}{R_{solution}}$$

Tortuousity and Porosity

- empirical relationship between the tortuousity and porosity

$$\tau^2 = n^{1-x} \quad \text{Archie's Law}$$

$$\tau^2 = 1 - x \cdot ln(n) \quad \text{modified Weissberg equation}$$

$$x = 2 - 3$$

Dispersion

- Mechanically mixed due to variations in the ground-water flow velocity
- Scale dependent
- Large scale (sand lenses, fracture zones) and micro-scale variation (grains) can create mechanical mixing

Dispersion

- Mixing rate of mechanical dispersion increases with increasing velocity
- Rate of mixing is directional
  - higher mixing rates in direction of groundwater flow (longitudinal dispersion, D'_L)
  - slower rates perpendicular to ground-water flow (transverse dispersion, D'_T)
- Dispersivity (α)

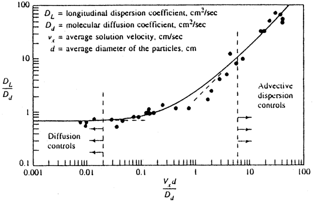
$$D'_L = v\alpha_L \qquad D'_T = v\alpha_T$$

Dispersion

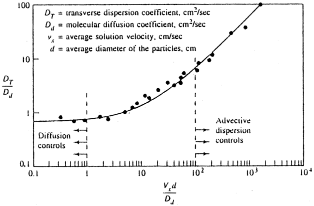
- Diffusion and mechanical dispersion commonly lumped into 'coefficient of hydrodynamic dispersion'

$$D_L = v\alpha_L + D_s^o \qquad D_T = v\alpha_T + D_s^o$$

Peclet Number



(a)



(b)

Statistics and Dispersion

- Diffusion and dispersion treated as random processes
- Random mixing produces a normally distributed concentration distribution
- Center of mass (solute front vs. slug) and variance

$$D_L = \frac{\sigma_L^2}{2t}$$

Heterogeneity and Dispersivity

- ‘Random’ mixing is caused by heterogeneity within a porous media
- Link between spatial variability of K with dispersion
- Dispersion proportion to the variance in the $\ln(K)$
- Need lots of K data to estimate α

$$\alpha_L = \frac{\sigma^2_{\ln(K)} \cdot \lambda}{\gamma^2}$$

λ is correlation length (variogram), γ is flow factor (taken as 1.) (Gelhar and Axness, 1983).

correlation length is lag distance where variance is 63% of sill (where variogram levels off).

Estimating D

- K distribution
- Tracer tests
- Model calibration
- Literature values

Advection-Dispersion Equation

- Advection

$$n\frac{\partial C}{\partial t} = -\frac{\partial(q_x C)}{\partial x}$$

- Dispersion

$$n\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)$$

- ADE

$$n\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) - \frac{\partial(q_x C)}{\partial x}$$

Analytic Solutions (error function)

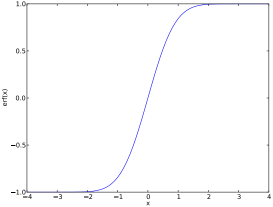
- many closed form solutions to ADE incorporate error function
- erf is integral of exponential function

$$erf(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-(t^2)} dt$$

- $erf(\frac{a}{\sigma\sqrt{2}})$ is the probability that the measurement error (expected value = 0) is between a and -a.

Error function

- S shaped distribution
- erf is 1 at $+\infty$, -1 at $-\infty$, 0 at 0
- $erfc(x) = 1 - erf(x)$ (ranges from 2 to 0)
- $erf(-x) = -erf(x)$
- $erfc(-x) = 1 + erf(x)$



Ogata-Banks Solution

- Semi-infinite, 1-D
- constant V, heavyside step function (fixed C at x=0)
- constant D

$$C = \frac{C_O}{2}\left(erfc\left[\frac{x - vt}{2\sqrt{Dt}}\right] + e^{\frac{vx}{D}} erfc\left[\frac{x + vt}{2\sqrt{Dt}}\right]\right)$$

- second term is important when $\frac{x}{\alpha}$ is large.
- When ratio is 500, a 3% error results when second term ignored

1D Reactive Transport

Some kinetic-based processes can be added to ADE and solved.

- 0th and 1st order decay(production)
- simple sorption

$$C \cdot K_d = \frac{sorbed}{aquifer\ mass} = C^* \frac{n}{\rho_b}$$

- Retardation (solute movement slowed)

$$R = \frac{v}{v_c} = 1 + \frac{\rho_b \cdot K_d}{n}$$

1D Reactive Transport

$$n\frac{\partial C}{\partial t} + \rho\frac{\partial C^*}{\partial t} = \frac{\partial}{\partial x}\left(n \cdot D\frac{\partial C}{\partial x}\right) - \frac{\partial(q_x C)}{\partial x} - n \cdot \lambda \cdot C - \rho \cdot \lambda^* \cdot C^*$$

$$C^* = k_d \cdot C$$

Solution for retardation and decay(1st order)

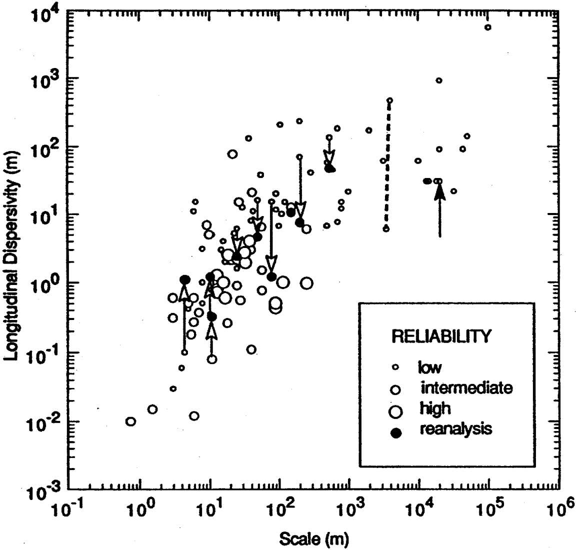
$$U = \sqrt{v^2 + 4\lambda D}$$

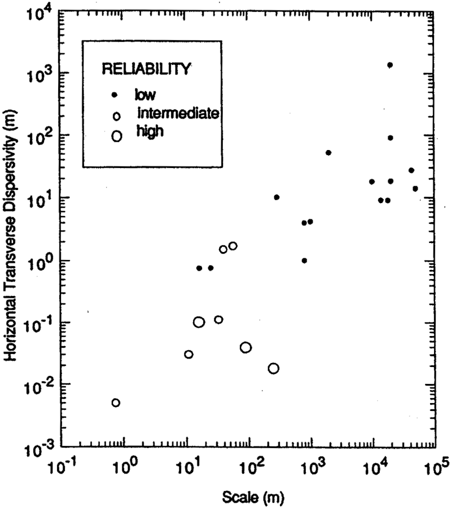
$$C = \frac{C_0}{2}\left(e^{\frac{x(v-U)}{2D}} erfc\left(\frac{xR - Ut}{2\sqrt{DtR}}\right) + e^{\frac{x(v+U)}{2D}} erfc\left(\frac{xR + Ut}{2\sqrt{DtR}}\right)\right)$$

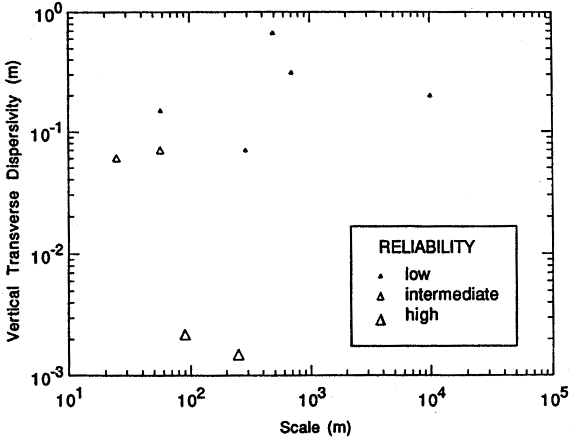
λ is 1st order decay const., v=g.w. velocity (Van Genuchten and Alves, 1982)

Values of Dispersivity

- scale dependent
- controversy over how D scales
- complex model for Dispersion typically reduced:
  - longitudinal
  - transverse horizontal
  - transverse vertical


Longitudinal Dispersivity (m)
Scale (m)
10^4
10^3
10^2
10^1
10^0
10^-1
10^-2
10^-3
10^-1
10^0
10^1
10^2
10^3
10^4
10^5
10^6
RELIABILITY
low
intermediate
high
reanalysis


RELIABILITY
● low
○ intermediate
◯ high
Horizontal Transverse Dispersivity (m)
10^4
10^3
10^2
10^1
10^0
10^-1
10^-2
10^-3
10^-1
10^0
10^1
10^2
10^3
10^4
10^5
Scale (m)


10^0
10^-1
10^-2
10^-3
10^1
10^2
10^3
10^4
10^5
Vertical Transverse Dispersivity (m)
Scale (m)
RELIABILITY
low
intermediate
high

3-D Analytic solutions

- Solutions available in various references
  - Leij et al., 1991. WRR 27:2719-2733
  - Wexler, USGS Tech of Water-Res. Invest. Book 3 CH. B7
- Complex equations, consider numerical solutions
- Some require numerical integration or evaluation of infinite series

3-D Analytic Solution Example (Leij et al, 1991)

- Solutions subdivided based on boundary (Type 1 or 3) and initial solute distribution (surface rectangle, cylinder, etc.)
- for type 1 boundary with rectangular source at inflow:

$$C(x,y,z,t) = \frac{C_0}{4}\int_0^t \frac{x}{\tau}\Lambda_1(\tau)\Gamma_2(\tau)d\tau + \frac{\lambda}{2\cdot R}\int_0^t \Lambda_2(\tau)d\tau$$

$$\Lambda_1 = \sqrt{\frac{R}{4\pi D_x\tau}}\exp\left(\frac{-k\tau}{R} - \frac{(Rx - v\tau)^2}{4RD_x\tau}\right)$$

$$\Lambda_2 = \exp\left(\frac{-k\tau}{R}\right)\left[erfc\left(\frac{v\tau - Rx}{\sqrt{4RD_x\tau}}\right) - \exp\left(\frac{vx}{D_x}\right) erfc\left(\frac{v\tau + Rx}{\sqrt{4RD_x\tau}}\right)\right]$$

$$\Gamma_2 = \left[erfc\left(\frac{y-a}{\sqrt{\frac{4RD_y\tau}{R}}}\right) - erfc\left(\frac{y+a}{\sqrt{\frac{4RD_y\tau}{R}}}\right)\right]\left[erfc\left(\frac{z-b}{\sqrt{\frac{4RD_z\tau}{R}}}\right) - erfc\left(\frac{z+b}{\sqrt{\frac{4RD_z\tau}{R}}}\right)\right]$$

R=retardation, k=1st order decay const., λ=0th order decay const., a and b are half lengths of the rectangular source.

3-D Analytic Solution Example Cont.

- Need to numerically integrate equations (or use available software: 3dADE)
- Many scripting or computational platforms have numerical integration capabilities.
- See script solving previous equation.

Contaminant Transport-Types

- miscible
- immiscible (oil & water, air & water, solvent, air, & water)
  - LNAPL (hydrocarbons)
  - DNALP (solvents, chlorinated hydrocarbons)
- Made up of multiple compounds with varying properties (BTEX, PCB's)
- Sources of NAPL's
  - degreasers (dry cleaning, metal fabrication)
  - fuel stations
  - plastics production
  - paint

Regulation

- RCRA
  - called the Cradle to Grave act because it tracks waste from its birth to its final disposal
  - passed in 1976 and later amended and re-authorized in 1986.
  - regulates both hazardous and solid waste
- CERCLA
  - also called Superfund
  - deals with the release of hazardous products and uncontained waste sites (i.e. waste sites with no identified responsible party).
  - CERCLA identifies responsible parties through legal action and provides money for these sites to be remediated

Love Canal

- CERCLA (1980) due in part to the impact of Love Canal. Waste disposal site near Buffalo, New York.
- History
    - William Love created 6 by 3000 ft canal for transportation/power gen. (1892)
    - land sold through public auction (1920), used for waste disposal
    - land was purchased by Niagara Falls Board of Education for $1 (1953)
    - elementary school was constructed adjacent near old Love Canal

Love Canal

- 1976, residents noted plants dying, bicycle tires and shoes disintegrating, dogs developing sores that would not heal.
- Strange liquid seeping into basements and surface. A swimming pool foundation failed and was found floating in liquid chemicals (Keller, 1992).
- These results and health problems prompted an investigation.
- Repeated investigations/problems identified/no action
- Media attention by local newspaper and grassroots action (about 1978)
  - closure of school
  - NY State Health Commissioner declares State of Emergency
  - Carter signs CERCLA (1980)

NAPL Migration

- wetting and non-wetting fluids
- water usually wetting fluid, strongest attraction to solids
- contact angle (Θ)is a measure of wettability
- controlled by interfacial energy between solid and fluids (eg oil and waer)
- one fluid must push other fluid out of way to move
  - driven by pore pressure difference between fluids
  - curvature of invading fluid small enough to allow movement