MASS AND HEAT TRANSFER

GeoEE 500

1. **Mass Transport in Saturated Media**

    1.1. Transport Mechanisms

        1.1.1. Diffusion

        1.1.2. Advection

        1.1.3. Mechanical Dispersion and Taylor Dispersion

        1.1.4. Hydrodynamic Dispersion

2. **Advection-Dispersion Equation**

    2.1. Energy Transport Analog

    2.2. Coupled Environmental Fluid Mechanics Equations

    2.3. Analytical Solutions

        2.3.1. 1-D Step Change in Concentration

        2.3.2. 1-D Continuous Injection

        2.3.3. 1-D Slug Injection

        2.3.4. 3-D Linear Transport – Slug Injection

    2.4. Evaluating Dispersion and Scale Effects

3. **Retardation and Attenuation**

    3.1. Sorption

    3.2. Equilibrium Surface Reactions

    3.3. Concepts of Retardation

        3.3.1. Porous Media

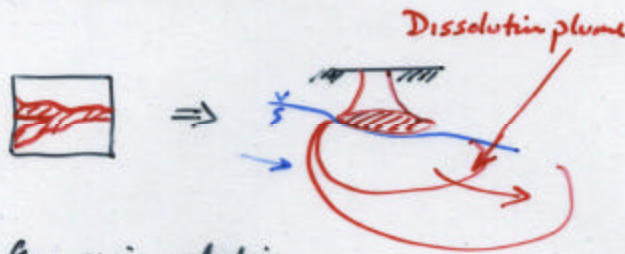   3.3.2. Fractured Media

        3.3.3. Sorbed Mass Evaluation

    3.4. Retardation in Heat Transport

4. **Residence Time Distributions**

        4.1.1. Reactive Transport Behavior

5. MASS TRANSPORT IN SATURATED MEDIA

Context:

Dissolution plume

1. Immiscible flow gives relative
   location and saturation.
   If truly immiscible ⟶ no problem.
   But ⟶ • Slightly soluble
   • Hazardous @ less than solubility
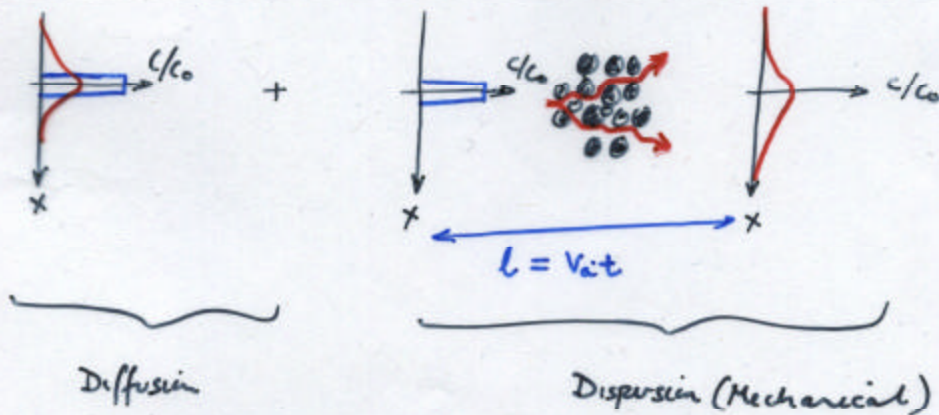
Mass transport accommodates:

     a) Species carried as a dissolved aqueous plume

     b) Same density as water   (ppm or ppb)
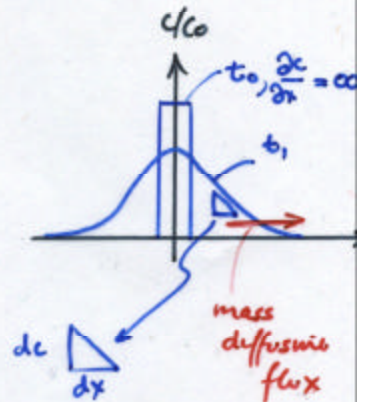   sometimes density important — salt concentrations

Transport Mechanisms

1. Advection; $V_a = \ell/t$ $\ell = V_a t$

2. Diffusion + Mechanical dispersion = Hydrodynamic dispersion

$\ell = V_a t$

Diffusion   Dispersion (Mechanical)

5.1 DIFFUSION

- Driven by concentration gradient
- Process of mollecular diffusion (Brownian motion)
- Characteristic for entropy (disorder) to increase
- Stagnant fluid

Fick's first law:

$$F = -D_d \frac{dc}{dx}$$

F = mass of solute per unit area per unit time ($M/L^2 T$)

D_d = diffusion coefficient (L^2/T)

$$(D_d \approx 10^{-9}\ m^2/s \ (range))$$

$\frac{dc}{dx}$ = concentration gradient $((M/L^3)/L)$

Time dependent concentration

$=1$ since not porous medium

$$n \frac{\partial c}{\partial t} = -\left(\frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z} \right)$$

Substituting Fick's first law:

$$\frac{\partial c}{\partial t} = D_d \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right)$$
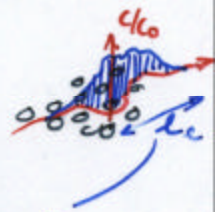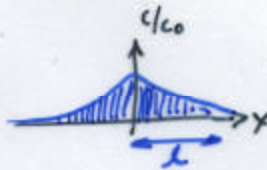
One dimensional equation

$$\frac{\partial c}{\partial t} = D_d \frac{\partial^2 c}{\partial x^2}$$

D_d is the "free" diffusion coefficient (i.e. in a beaker)

In porous medium the "effective" diffusion coefficient is used $D_d \rightarrow D^*$ due to the tortuous flow path

$$D^* = \omega D_d$$

ω is related to tortuosity, $T = l_e/l$

$$T \geq 1$$

Effective length due to tortuous flow path
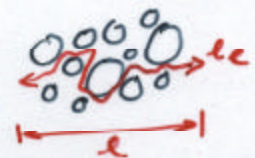
Laboratory studies $\quad 0.01 < \omega \leq 0.5$

but lab studies not very useful.

SOLUTION OF DIFFUSION EQUATION

Solve
$$\frac{\partial c}{\partial t} = D^* \frac{\partial^2 c}{\partial x^2}$$

$c = 0$ $0 > t$ initial condition (no solute)
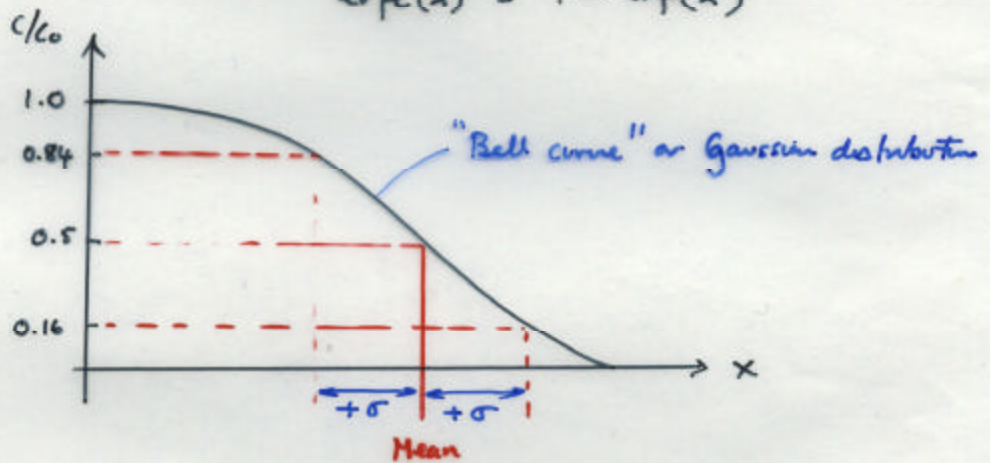
$c = c_0$ $x = 0$ $t \geqslant 0$ step input

$t_0 = 0$
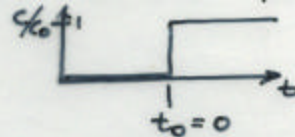
Solution:
$$\frac{c}{c_0}(x,t) = erfc\left(\frac{x}{2\sqrt{D^* t}}\right) = \frac{2}{\sqrt{\pi}} \int_{x}^{\infty} e^{-u^2} du$$

$$erfc(x) = 1 - erf(x)$$

c/c_0

1.0

0.84

0.5

0.16

x

$+\sigma$ $+\sigma$

Mean

"Bell curve" or Gaussian distribution

5.2 ADVECTION   (Convection - movement by "bulk" motion of the fluid (water))

$$V_x^a = - \frac{K_x}{n} \frac{dh}{dx} \quad (1)$$

V_a = average linear advective velocity

n = "effective" porosity

no-dead-end pores.

Advective flux; F_x.

$$F_x = V_x^a \, n \, c \quad (2)$$

volume of water flowing at concentration, C.

Conservation equation!

$$n \frac{\partial c}{\partial t} = -\left(\frac{\partial F_y}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z} \right) \quad (3)$$

Substitute V_x^a from (2) and similar for V_y^a; V_z^a into (3)

$$n \frac{\partial c}{\partial t} = -\left(V_x^a \, n \, \frac{\partial c}{\partial x} + V_y^a \, n \, \frac{\partial c}{\partial y} + V_z^a \, n \, \frac{\partial c}{\partial z} \right) \quad (4)$$

$$V_x^a \, n = V_d$$

Remove, n in (4)

$$\boxed{ \frac{\partial c}{\partial t} = -\left(V_x^a \frac{\partial c}{\partial x} + V_y^a \frac{\partial c}{\partial y} + V_z^a \frac{\partial c}{\partial z} \right) } \quad (5)$$
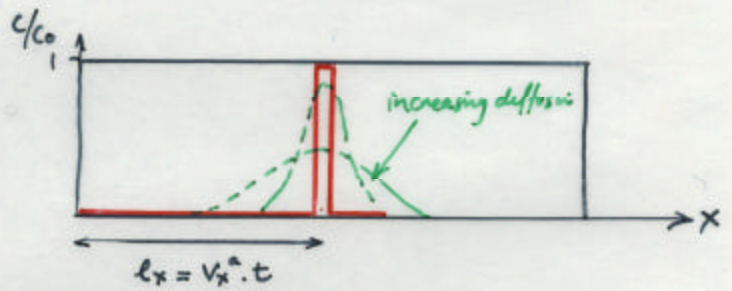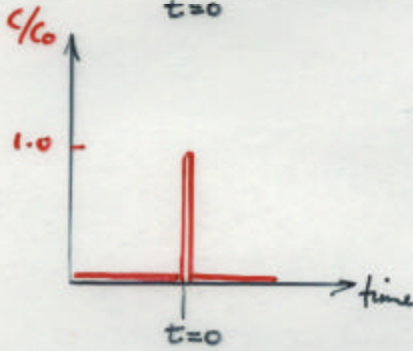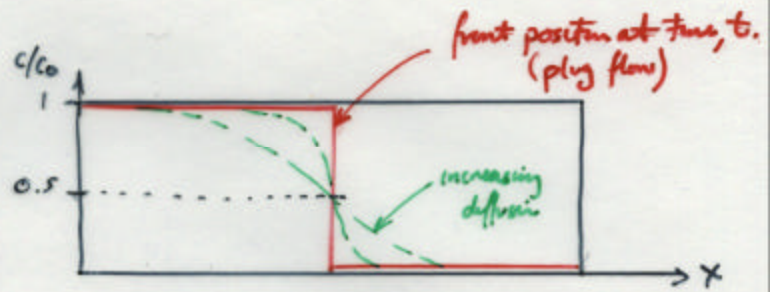
What does this mean, physically?
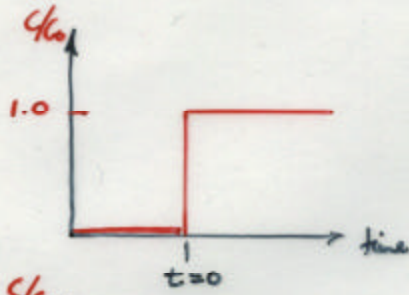
Boundary conditions

5.3 MECHANICAL DISPERSION

CAUSES
1. Pore size
2. Path length
3. Taylor dispersion
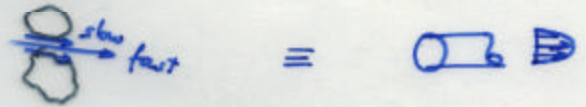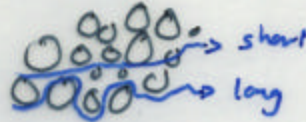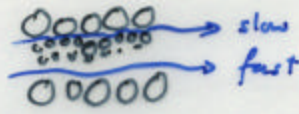
Average behavior ⟶ dispersion coefficients, α

lateral dispersion

longitudinal dispersion
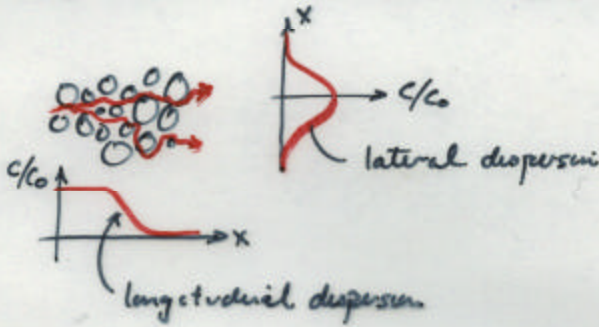
Coefficient of longitudinal dispersion = α_L (L)

Coefficient of transverse (lateral) dispersion = α_T (L)

Units of length, L.

Pre-multiplied by advective velocity to give a dispersion coefficient as $D = \alpha \, v_i$

$$L \, \frac{L}{T} \doteq \frac{L^2}{T}$$

$$D_L = \alpha_L \, v_i$$
$$D_T = \alpha_T \, v_i$$

Concentration distribution at time $t = 0$

$C = C_o$

$C = 0$

Invading liquid, $C = C_o$

$\sim 2r^*|_{x=L}$
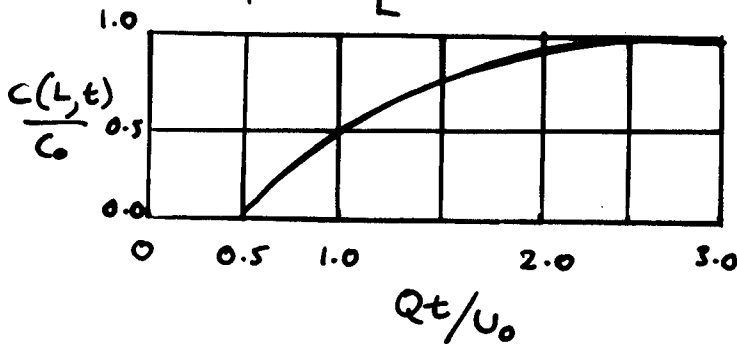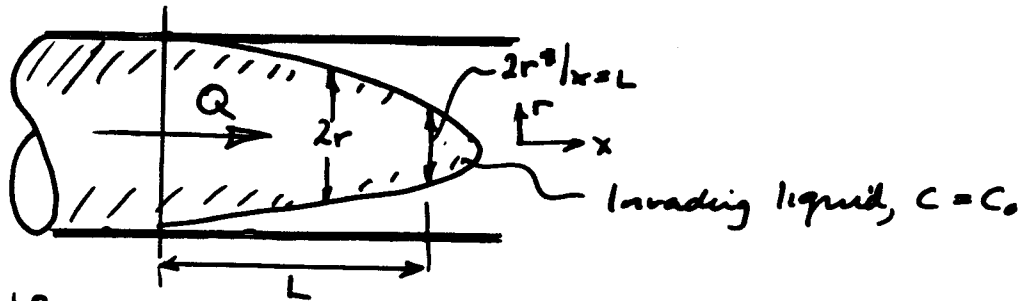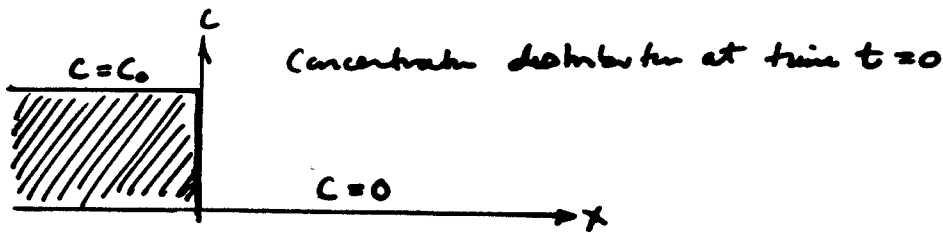
1.   Define average concentration at any cross-section at any time as the ratio of the area occupying the displacing fluid (πr^{*2}) to the total area (πR^2).

Velocity distribution: $V(r) = 2\bar{V}\left(1 - r^2/R^2\right)$

with $\bar{V} = \dfrac{Q}{A} = \dfrac{Q}{\pi R^2}$

Continuity requires:

$$\pi R^2 \bar{V} \bar{C}(x,t) = C_0 \int_0^{r^*} 2\pi r\, V(r)\, dr \qquad r^*_{(t)} = R\left(1 - \frac{x}{2\bar{V}t}\right)^{1/2}$$

$Q/(\pi R^2)$

Integrate and substitute $Q/(\pi R^2)$ and rearrange

$$\frac{\bar{C}(x,t)}{C_0} = 1 - \frac{x^2}{4\bar{V}^2 t^2} \qquad\qquad\qquad \left.\rule{0pt}{5em}\right\}$$

Or where Qt/U_0 substituted with $U_0 = \pi R^2 L$ $\qquad \dfrac{Qt}{U_0} \geqslant \dfrac{1}{2}$

$$\frac{C(L,t)}{C_0} = 1 - \frac{U_0^2}{4Q^2 t^2}$$

This is the solution for axial convection dominating, i.e. dispersion or diffusion → 0.

Boundary behaviours:

a) $\quad 2L/\bar{V} \ll R^2/4.42 D_L$ — axial convection dominates radial diffusion

b) $\quad 2L/\bar{V} \gg R^2/44.2 D_L$ — radial diffusion dominates.

i.e. $\bar{V}$ is small

$$Re = \frac{\bar{V} R}{D_L} \qquad \text{o small.}$$

where diffusion is significant

Need to solve:
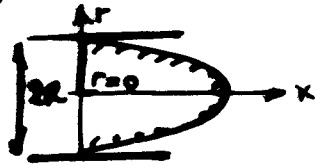
Diffusion equation.

$$\frac{\partial c}{\partial t} = D_d \left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \cancel{\frac{\partial x}{\partial r^2}} \overset{\text{assume small}}{\nearrow} \right) - 2\bar{v}\left(1 - \frac{r^2}{R^2}\right)\frac{\partial c}{\partial x}$$

Boundary conds:
$$\partial c / \partial r = 0 \quad \ominus \quad r = R$$

Initial conds:
$$t = 0 \qquad \begin{array}{l} c = 0 \text{ for } x > 0 \\ c = c_0 \text{ for } x \le 0 \end{array}$$

Result

$$\frac{c}{c_0} = \frac{1}{2}\left[1 \pm erf\left(\frac{(x - \bar{v}t)}{2\sqrt{D't}}\right)\right] \begin{cases} + \text{ for } x - \bar{v}t < 0 \\ - \text{ for } x - \bar{v}t > 0 \end{cases}$$

$$D' = \left(\frac{R^2}{48 D_d}\right)\bar{V}^2 \qquad\qquad erf(z) = \frac{2}{\pi}\int_0^t e^{-\alpha^2} d\alpha$$
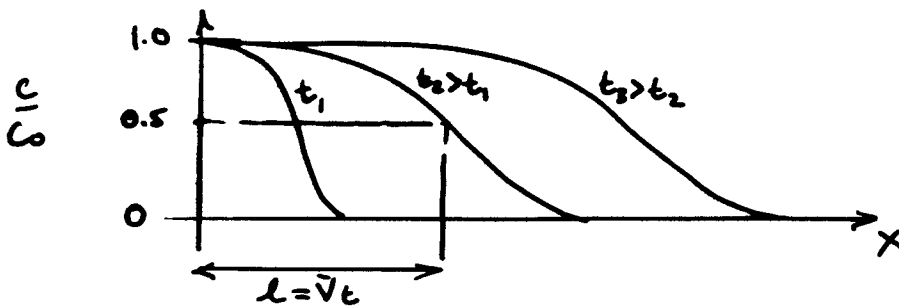
5.4 HYDRODYNAMIC DISPERSION

Hydrodynamic dispersion = Diffusion + Mechanical dispersion $\quad (L^2/T)$

$$D_L = \alpha_L v_i^a + D^*$$
$$D_T = \alpha_T v_i^a + D^*$$

Relative dominance of diffusion depends on:

1) Clays, $\quad v \to 0 \quad \therefore \quad$ diffusion dominant
   (also retardation)

2) Sands, gravels, fractured rock. $\quad v \to$ high
   $\therefore$ mechanical dispersion dominant

Measure in situ for best results.
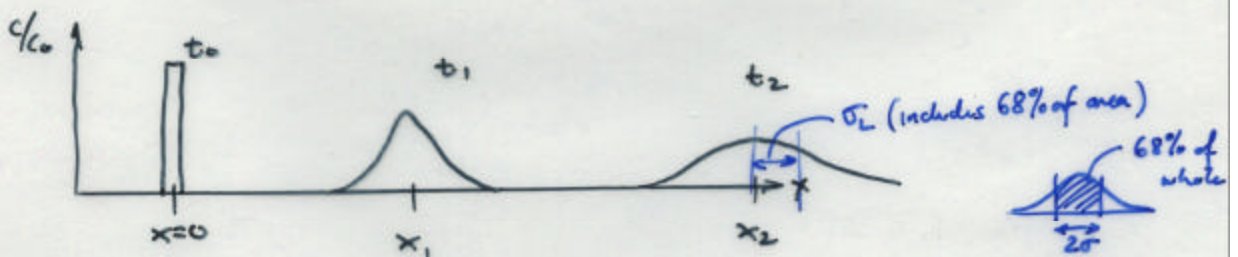
$$D_L = \frac{\sigma_L^2}{2t} \quad ; \quad D_T = \frac{\sigma_T^2}{2t}$$

$\sigma =$ standard deviation

$\sigma^2 =$ variance

$$D_L = \alpha_L V + D_d^*$$

- D_L = longitudinal dispersion coefficient, cm²/sec
- D_d = molecular diffusion coefficient, cm²/sec
- v_s = average solution velocity, cm/sec
- d = average diameter of the particles, cm

Advective dispersion controls

Diffusion controls

(a)

$$D_T = \alpha_T V + D_d^*$$

- D_T = transverse dispersion coefficient, cm²/sec
- D_d = molecular diffusion coefficient, cm²/sec
- v_s = average solution velocity, cm/sec
- d = average diameter of the particles, cm

Advective dispersion controls

Diffusion controls

(b)

FIGURE 2.7 Graph of dimensionless dispersion coefficients versus Peclet number, $P = v_s d/D_e$ (a) D_L/D_e versus P and (b) D_t/D_e versus P. Source: T. K. Perkins and O. C. Johnson, *Society of Petroleum Engineers Journal*, 3 (1963):70–84. Copyright 1963, Society of Petroleum Engineers.

$$P_E = \frac{V^* L}{D_L}$$

- Fixed-step function
- Continuous injection
- Approximate solution

$$t_R = U = \text{pore volumes}$$
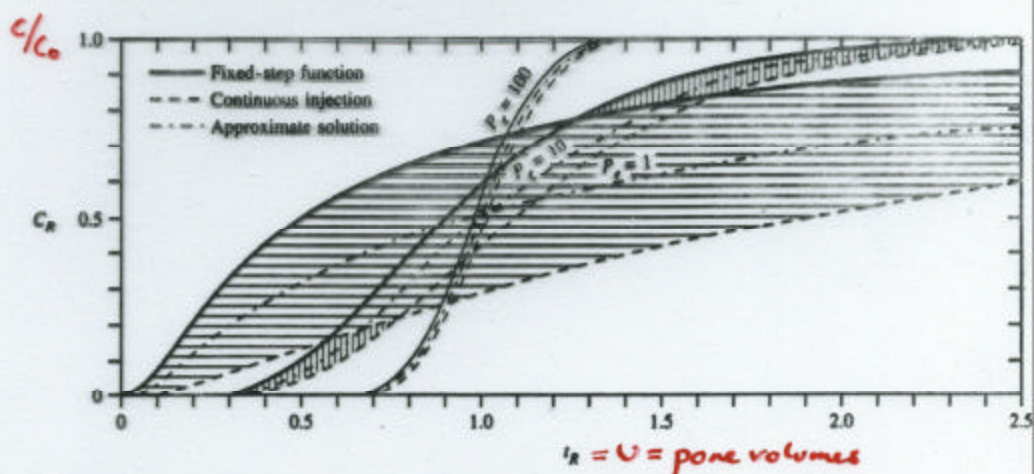
FIGURE 2.9 Dimensionless-type curves for the continuous injection of a tracer into a one-dimensional flow field. Source: J. P. Sauty, *Water Resources Research* 16, no. 1 (1980):145–58. Copyright by the American Geophysical Union.
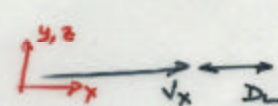
5.5 ADVECTION-DISPERSION EQUATION

Summing the diffusive and advective components:

$$n \frac{\partial c}{\partial t} = n \left\{ \frac{\partial}{\partial x} D_x \frac{\partial c}{\partial x} + \frac{\partial}{\partial y} D_y \frac{\partial c}{\partial y} + \frac{\partial}{\partial z} D_z \frac{\partial c}{\partial z} \right\}$$

$$- \left\{ \frac{\partial}{\partial x} (v_x^d \, c) + \frac{\partial}{\partial y} (v_y^d c) + \frac{\partial}{\partial z} (v_z^d c) \right\}$$

Reduces to:

1-D case!

$$D_L \frac{\partial^2 c}{\partial x^2} - \frac{v_x^d}{n} \frac{\partial c}{\partial x} = \frac{\partial c}{\partial t}$$

v_x^a

2-D case!

$$D_L \frac{\partial^2 c}{\partial x^2} + D_T \frac{\partial^2 c}{\partial y^2} - \frac{v_x^d}{n} \frac{\partial c}{\partial x} = \frac{\partial c}{\partial t}$$

v_x^a

Usual assumptions:

- Homogeneous medium
- Constant value of D_L, D_T } analytical solutions

- Heterogeneous
- Velocity dependent D_L, D_T } numerical solutions.

ENERGY CONSERVATION EQUATIONS

$D^* = $ thermal conductivity

$q_D^x = $ Darcy flux in x-direction

CONSERVATION OF ENERGY

$$\frac{\partial(\rho c T)}{\partial t} = -\frac{\partial}{\partial x}\left(q_{Thermal}^x\right) \quad (1)$$

Energy accumulation $=$ Balance (In $-$ Out)
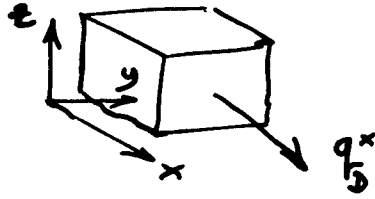
Diffusive flux $-$ Fourier's Law

$$q_{T\,diffusive}^x = -D^* \frac{dT}{dx} \quad (2)$$

Advective flux.

$$q_{T advective}^x = \rho c \, q_D^x T \quad (3)$$

Substituting (2) and (3) into (1) gives $\left(\text{noting that } \frac{\partial(\rho c)}{\partial t} = 0\right)$ sometimes

$$\rho c \frac{\partial T}{\partial t} = D^* \frac{\partial^2 T}{\partial x^2} - \rho c \, q_D^x \frac{\partial T}{\partial x} \quad \left(\text{for 1-D problems}\right)$$

ADVECTIVE HEAT TRANSPORT (ADVECTIVE + CONDUCTIVE) – In a porous medium.

Assume: – Thermal equilibrium of fluid and porous medium
$$T_R = T_F \quad \therefore \text{ only one variable}$$

– This assumption is not necessary (convenient)

$$D^* \frac{\partial^2 T}{\partial x^2} - \rho_f c_f q_D \frac{\partial T}{\partial x} = (\overline{\rho c}) \frac{\partial T}{\partial t}$$

$$\rho_f c_f n + (1-n) \rho_r c_r$$

Darcy flux, $q_D = -\frac{k}{\mu} \frac{\partial p}{\partial x}$

Aggregate thermal diffusivity, $D^* = D_r(1-n) + D_f(n)$

conductivity

$$\text{Thermal diffusivity} = \frac{D}{\rho c}$$

Solid — Fluid

Fluid $\quad \uparrow n$

$1 \quad$ Solid $\quad (1-n)$

porosity, n
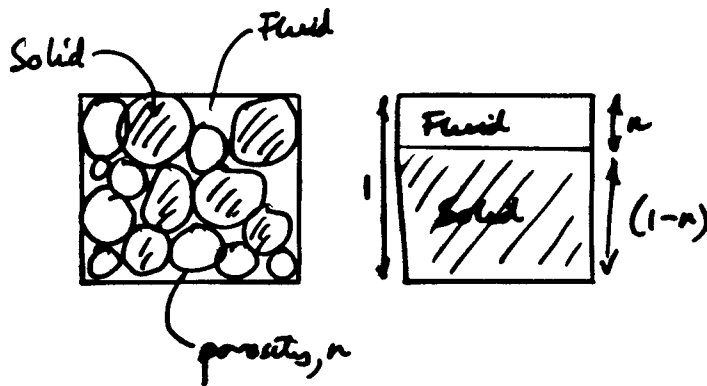
General form for solution:

$$\frac{D^*}{\overline{\rho c}} \frac{\partial^2 T}{\partial x^2} - \frac{\rho_f c_f q_D}{\overline{\rho c}} \frac{\partial T}{\partial x} = \frac{\partial T}{\partial t}$$

TRANSPORT EQUATIONS

Two modes of transport: Diffusion: $q_i^d = -D_{ij} \dfrac{\partial c}{\partial x_j}$ (1)

flow, V
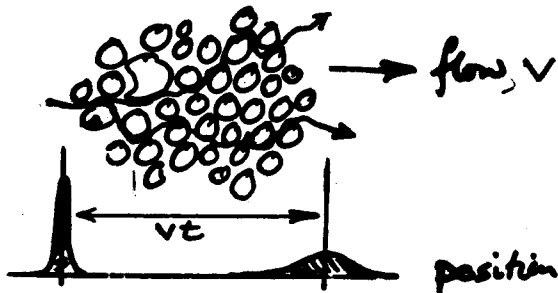
Fick's law and hydrodynamic dispersion.

vt

position

c = mass per unit volume

increasing dispersion
(similar to a diffusive process)
(but as a result of flow tortuosity and not diffusion gradient $\partial c/\partial x$)

Advection: $q_i^a = v_i c$ $v_i = \dfrac{V_{darcy}}{n}$

---

continuity: $\dfrac{\partial q_i}{\partial x_i} = \dfrac{\partial c}{\partial t}$ (3)

substituting (1) and (2) into (3) gives (where $q_i = q_i^d + q_i^a$)

$$\dfrac{\partial}{\partial x_i}\left(D_{ij}\dfrac{\partial c}{\partial x_j}\right) - \dfrac{\partial}{\partial x_i}(v_i c) = \dfrac{\partial c}{\partial t}$$ (4)

Or expanding to 2-D case, then,

$$\underbrace{D_x \dfrac{\partial^2 c}{\partial x^2} + D_y \dfrac{\partial^2 c}{\partial y^2}}_{\text{Diffusive/dispersive flux}} \underbrace{- v_x \dfrac{\partial c}{\partial x} - v_y \dfrac{\partial c}{\partial y}}_{\text{Advection flux}} = \dfrac{\partial c}{\partial t}$$

ENVIRONMENTAL FLOW & TRANSPORT EQUATIONS

MOMENTUM!

$$\frac{\partial u_i}{\partial t} + u_j \frac{\partial u_i}{\partial x_j} = \nu \frac{\partial^2 u_i}{\partial x_k^2} - \frac{1}{\rho}\frac{\partial P}{\partial x_i} + \frac{gT}{T_0} - \frac{\partial \tau_{ij}}{\partial x_j}$$

(TIME)   (SPACE)

MOMENTUM   VISCOUS   BUOYANCY   REYNOLDS
                DISSIPATION   STRESS TENSOR
                                                 for TURBULENCE

CONTINUITY:

$$\frac{\partial u_i}{\partial x_i} = 0$$

MASS IN ≡ MASS OUT

(INCOMPRESSIBLE)

ENERGY!

THERMAL DIFFUSIVITY (L^2/T)

$$\frac{\partial T}{\partial t} + u_j \frac{\partial T}{\partial x_j} = D_H \frac{\partial^2 T}{\partial x_k^2} - \frac{\partial H_j}{\partial x_j}$$

ADVECTION   DIFFUSION   TURBULENT   Turbulence models
                                  HEAT FLUX

MASS:

BINARY DIFFUSIVITY (L^2/T)

$$\frac{\partial C_\alpha}{\partial t} + u_j \frac{\partial C_\alpha}{\partial x_j} = D \frac{\partial^2 C_\alpha}{\partial x_k^2} - \frac{\partial H_j}{\partial x_j} + \sum_\beta K_{\alpha\beta} R_\beta$$

ADVECTION   MASS DIFFUSION   Stoichiometric coeff
                                       of αth species involved
                 TURBULENT   in reaction R_β
                 MASS FLUX

Solve simultaneously for unknowns

$\left.\begin{array}{c} U_1, U_2, U_3 \\ P \end{array}\right\}$ Navier-Stokes and
Continuity = 4 eqn

T   Energy   1 eqn

$(5+n)$ eqns for $(5+n)$ unknowns.

$C_1, C_2 .. C_\alpha .. C_n$ Mass n eqn

5.6 ANALYTICAL SOLUTIONS.

Why? — Determine off-site migration
       — Approximate geometries

What parameters are important?

1. Diffusion } hydrodynamic dispersion
2. Mechanical dispersion $D_L = \alpha_L v^2 + D^*$
3. Groundwater velocity field, v^a

Solutions:

Fetter section 2.8 pp 56-64.

Analytical Solutions

1. Simplify geometry 1-D etc
2. Simplify heterogeneity (assume an equivalent magnitude of dispersion).
3. Simple solutions (but accurate).

Numerical Solutions

1. Enable complex 'real' geometries
2. Complex heterogeneity incorporated
3. Computer solutions — may include "numerical" dispersion.

Philosophical Trade:

• Data accuracy / reliability
• Sensitivity studies.

LIMITS OF APPLICABILITY OF APPROXIMATIONS
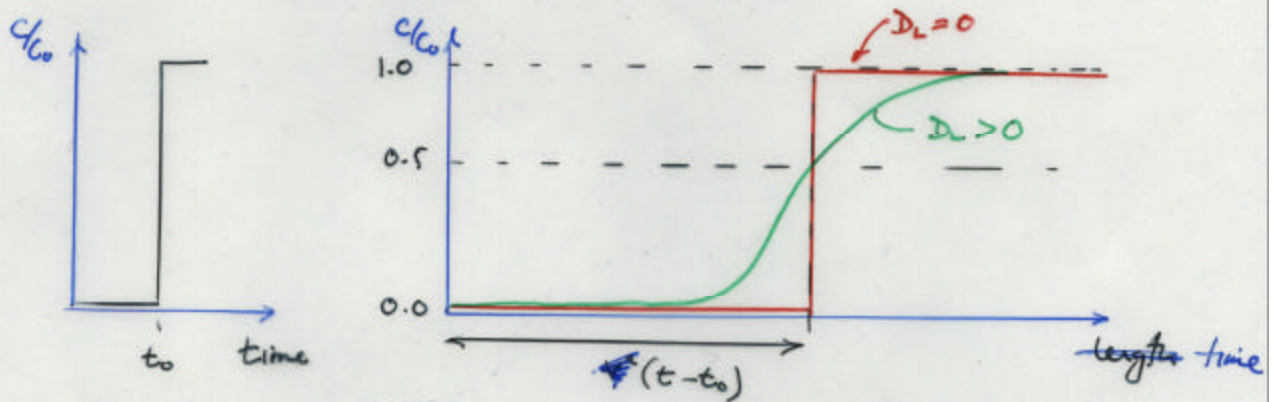
This view of the RTD curve is true only for large Peclet No.s (Pe)

$$Pe \geqslant 10$$

$$Pe = \frac{V^a L}{D_L} \longleftarrow D_L = D^* {}^{\nearrow 0} + \alpha_L V^a$$

$$\alpha_L \simeq \frac{1}{10} L$$

$$\therefore D_L \cong \frac{L V^a}{10}$$

Resubstituting then

$$Pe = \frac{V^a L}{L V^a} \cdot 10 \qquad = 10$$

$$\therefore \text{ ok to use approximations.}$$

ANALYTICAL SOLUTIONS (1-D)

Equation:

$$D \frac{\partial^2 c}{\partial x^2} - V_x \frac{\partial c}{\partial x} = \frac{\partial c}{\partial t}$$

or Temperature, T.

Inlet boundary condition

$x=0$

V_x

L

Outlet boundary condition
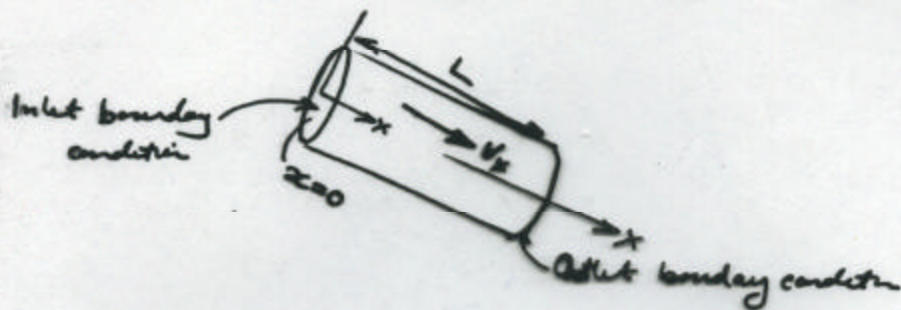
Boundary Condition Types:

First type: Fixed concentration: $C = C_0$

Second type: Fixed gradient $\left. \frac{\partial c}{\partial x} \right|_{x=?} = $ constant

includes zero flux $\partial c / \partial x = 0$
(accumulating mass).

Third type: Variable flux $-D \frac{\partial c}{\partial x} + V_x c = V_x c(t)$

i.e. input flux of constant
concentration as $V C_0$ = prescribed ma

ONE-DIMENSIONAL STEP CHANGE IN CONCENTRATION (Ogata & Banks, 1961)

Step input (Heaviside function)
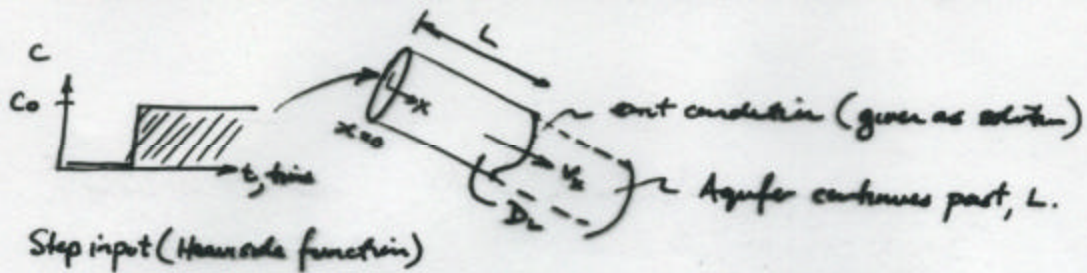
Initial conditions: $\quad\quad c(x,0) = 0 \quad\quad x \geq 0$

Boundary conditions: $\quad\quad c(0,t) = C_o \quad\quad t \geq 0^+$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad c(\infty,t) = 0 \quad\quad t \geq 0^+$

$$c = \frac{1}{2} C_o \left[erfc\left(\frac{L - V_x t}{2\sqrt{D_L t}}\right) + exp\left(\frac{V_x L}{D_L}\right) erfc\left(\frac{L + V_x t}{2\sqrt{D_L t}}\right) \right]$$

Non-dimensionalize: $\quad\quad Pe = \dfrac{V_x L}{D_L} \quad ; \quad t_R = \dfrac{V_x t}{L} \equiv$ 'pore' volumes. as $V_x =$!

$$\frac{c}{C_o} = \frac{1}{2}\left[erfc\left[\left(\frac{Pe}{4 t_R}\right)^{1/2}(1 - t_R)\right] + exp(Pe)\, erfc\left[\left(\frac{Pe}{4 t_R}\right)^{1/2}(1 + t_R)\right]\right]$$

Observe change in c/C_o at location, L, downstream (with time).

$erfc(0) = 1$

$erfc(\infty) = 0$
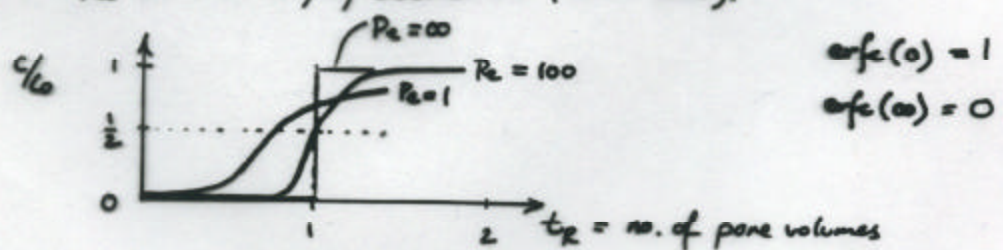
ONE – DIMENSIONAL CONTINUOUS INJECTION AT CONSTANT CONCENTRATION, C_0.

(Santy, 1980)

Mass flux in
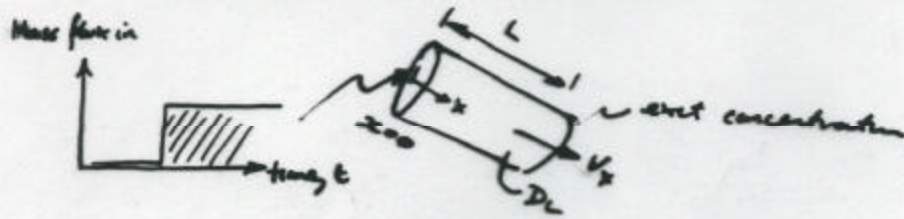
Initial conditions: $\qquad C(x,0) = 0 \qquad -\infty < x < +\infty$

Boundary conditions: $\qquad \int_{-\infty}^{+\infty} n_e\, C(x,t)\, dx = C_0\, n_e\, V_x\, t \qquad t > 0$

Dispersion occurs both downstream and upstream

$C(\infty, t) = 0 \qquad t \geq 0$

$$C = \frac{1}{2} C_0 \left[\operatorname{erfc}\left(\frac{L - V_x t}{2\sqrt{D_L t}} \right) - \exp\left(\frac{V_n L}{D_L} \right) \operatorname{erfc}\left(\frac{L + V_x t}{2\sqrt{D_L t}} \right) \right]$$

Non-dimensional:

Same as step injection but –ve.

$$\frac{C}{C_0} = \frac{1}{2} \left[\operatorname{erfc}\left\{ \left(\frac{P_e}{4 t_R} \right)^{1/2} (1 - t_R) \right\} - \exp(P_e)\, \operatorname{erfc}\left\{ \left(\frac{P_e}{4 t_R} \right)^{1/2} (1 + t_R) \right\} \right]$$

For $P_e \to \infty$
$$\frac{C}{C_0} \simeq \frac{1}{2} \operatorname{erfc}\left\{ \left(\frac{P_e}{4 t_R} \right)^{1/2} (1 - t_R) \right\}$$

Solution identical for both $\begin{cases} C_0 = \text{constant} \\ V C_0 = \text{constant} \end{cases}$

i.e. @ $P_e \to \infty$ Dispersive effects $\to 0$.

ONE – DIMENSIONAL – SLUG INJECTION   (Sauty, 1980)
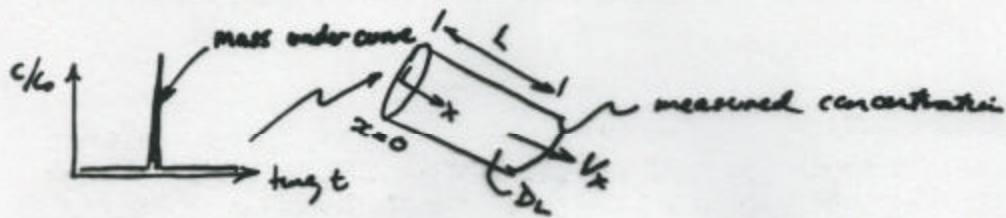
Mass slug injected: At some later time, a maximum concentration, C_{max}, results at time, t_{max}.

$$C_R = \frac{E}{(t_R)^{1/2}} \exp\left\{-\frac{P_e}{4t_R}(1-t_R)^2\right\}$$

$$E = (t_{R_{max}})^{1/2} \cdot \exp\left\{\frac{P_e}{4t_{R_{max}}}(1-t_{R_{max}})^2\right\}$$

$t_{R_{max}}$ = time of peak concentration
$\phantom{t_{R_{max}}}$ = $(1 + P_e^{-2})^{1/2} - P_e^{-1}$

$C_R = C/C_{max}$

5.6.6 3-D Flow field — Slug Injection

$(c_0 \times \text{volume})$

$$C(x, y, z, t) = \frac{M}{8(\pi t)^{3/2}\sqrt{D_x D_y D_z}} \exp\left\{ - \frac{(x - (x_0 + Vt))^2}{4D_x t} - \frac{(y - y_0)^2}{4D_y t} - \frac{(z - z_0)^2}{4D_z t} \right.$$
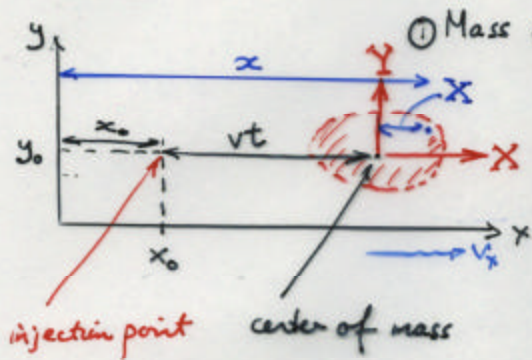
① Mass of injection at location x_0, y_0, z_0

② Moves downstream @ velocity V

③ At time, t, center of mass at $x = x_0$

Note coordinates: $x_0 + vt + X = x$

~ $\qquad X = x - (x_0 +$

∴ resubstitute into (1)

$$c = \frac{M}{8(\pi t)^{3/2}\sqrt{D_x D_y D_z}} \exp\left\{ - \frac{X^2}{4D_x t} - \frac{Y^2}{4D_y t} - \frac{z^2}{4D_z t} \right\}$$

Max concentration; set $X = Y = z = 0$

$$C_{max} = \frac{M}{8(\pi t)^{3/2}\sqrt{D_x D_y D_z}}$$

injection point   center of mass

Note downgradient form:
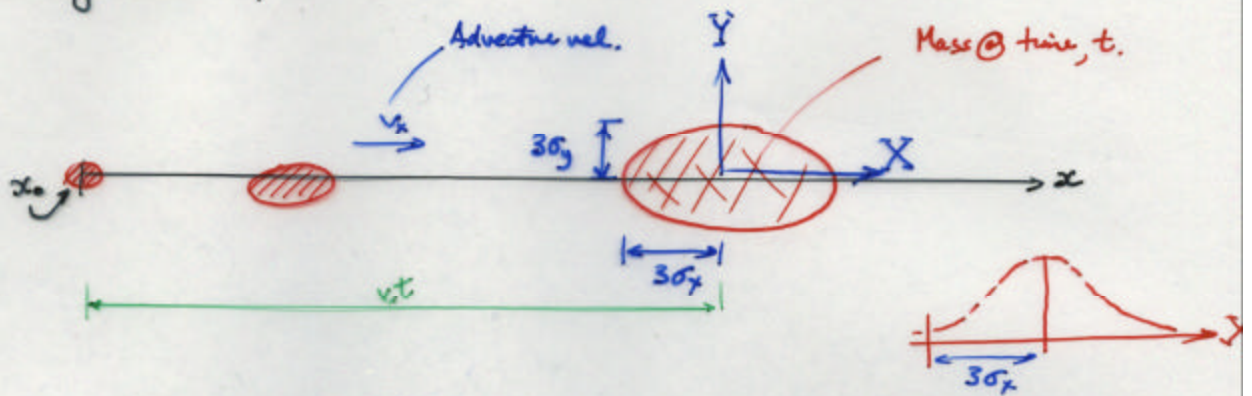
Zone consisting of 99.7% of Mass
contained in the 3-D ellipsoid of
dimensions:

$$3\sigma_x = 3\sqrt{2D_x t} \quad = 3(2D_x t)^{1/2} \text{ etc.}$$
$$3\sigma_y = 3\sqrt{2D_y t}$$
$$3\sigma_z = 3\sqrt{2D_z t}$$

∴ ① Measure ellipsoid in field
   and ② evaluate D_x etc.

Preferable method since includes large scale heterogeneity

5.7 EVALUATING DISPERSIVITY

Note: transverse dispersion will affect the
resulting form of the plume due to lateral attenuation
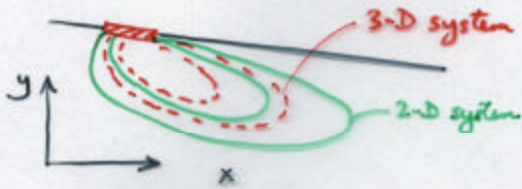
— No lateral dispersion (2-D)

--- Lateral dispersion (3-D)

This is important if:

   3-D systems are represented as 2-D

   2-D systems are represented as 1-D

Have to incorporate these effects
when they are important.
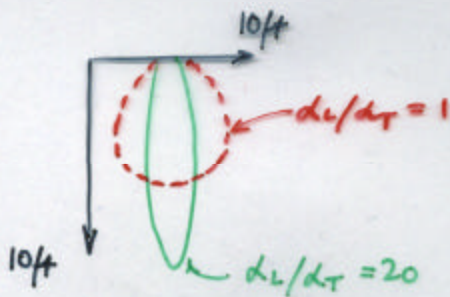
- Large ratio gives greater linear
       propagation length
- Small ratio gives lateral attenuation

Methods:

    - Laboratory
    - Field — Induced gradient
                — Natural gradient — $\begin{cases} \text{Contaminated sites.} \\ \text{Tests will remobilize} \\ \text{contaminants.} \end{cases}$

GEOMETRY
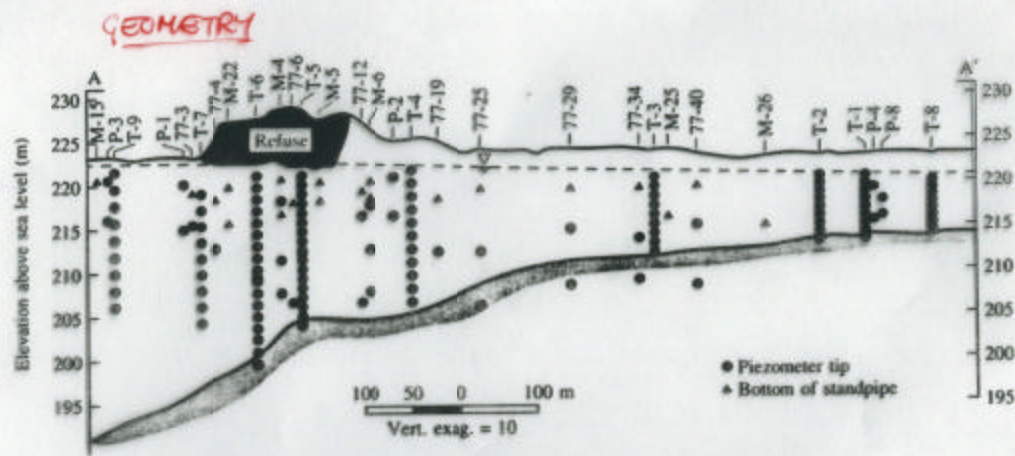
FIGURE 2.33   Cross section of aquifer at the Borden landfill showing the location of multilevel monitoring devices. *Source:* E. O. Frind and G. E. Hokkanen, *Water Resources Research* 23, no. 5 (1987):918–30. Copyright by the American Geophysical Union.
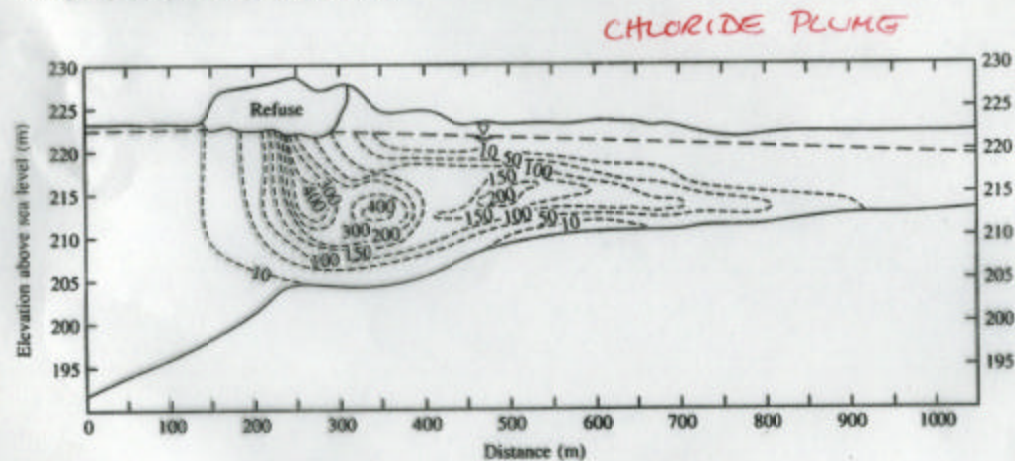
CHLORIDE PLUME

FIGURE 2.34   Chloride plume along the Borden landfill cross section in 1979. Values are in milligrams per liter. *Source:* E. O. Frind and G. E. Hokkanen, *Water Resources Research* 23, no. 5 (1987):918–30. Copyright by the American Geophysical Union.

CONSTANT α_L; VARIABLE α_T

$\alpha_L = 10$ m $\alpha_T = 1.0$ m

$\alpha_L = 10$ m $\alpha_T = 0.10$ m

$\alpha_L = 10$ m $\alpha_T = 0.01$ m

$\alpha_L = 10$ m $\alpha_T = 0.005$ m
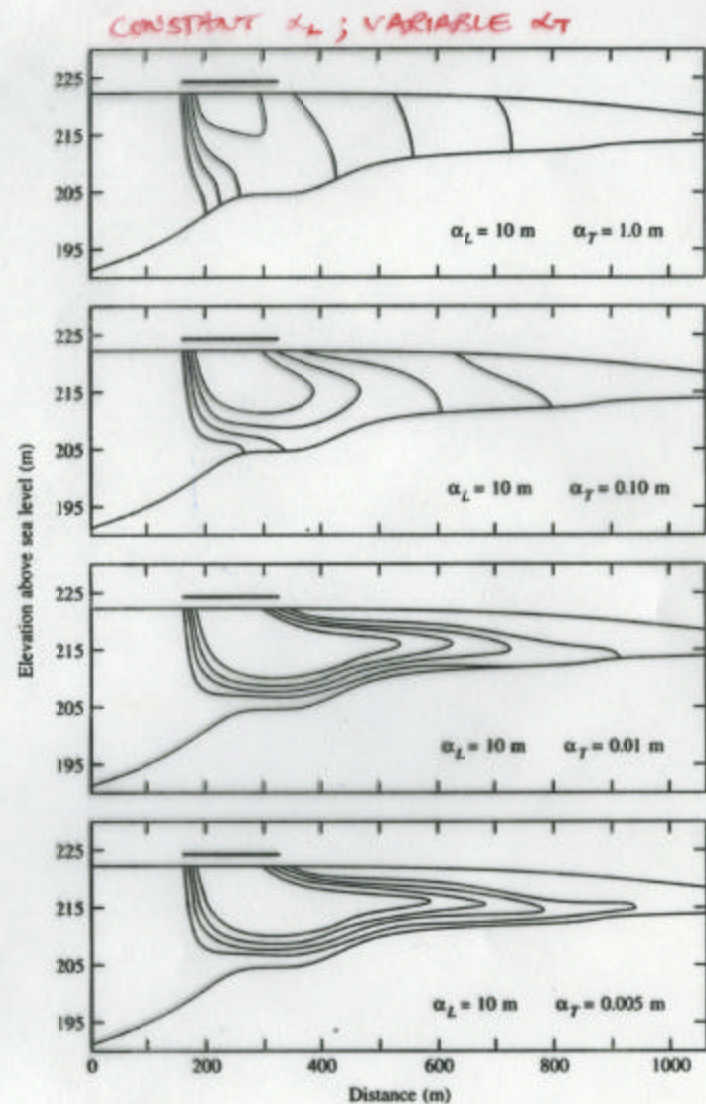
Reducing α_T enables longer propagation since less lateral loss $\perp$ to profile

5.7.1 Laboratory Tests:

- Not very useful since scale dependent!
- General method
  - Inject solute of known concentration and measure outlet concentration w/ time.
  - Fit to curve.

Q_{in}
@
Concentration C_0.
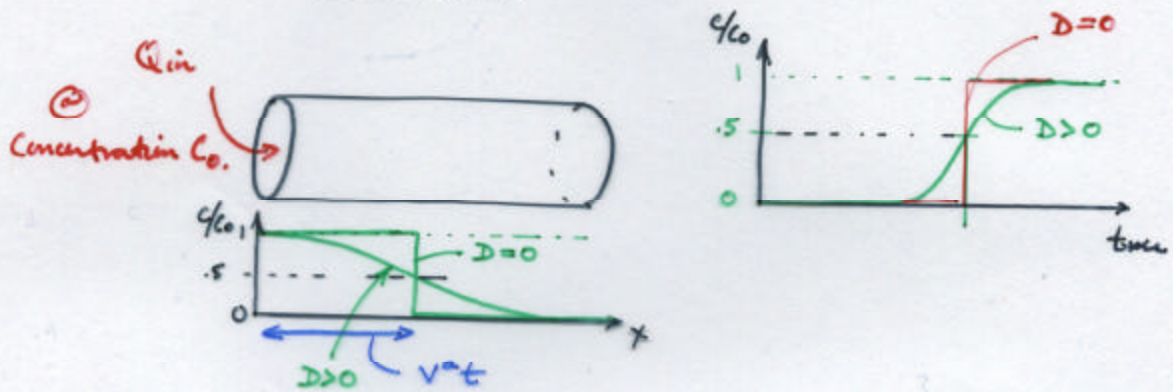
Define flow rate relative to number of pore volumes —
  - When x1 pore volume flushed through, the flow of the contaminant should also break through at
  $$c = \tfrac{1}{2} C_0$$

Define No. of pore volumes of sample, as U

$$U = \frac{\text{total discharge}}{\text{pore volume}} = \frac{\overset{a}{v_x} A \, n \, t}{A L n} = \frac{\overset{a}{v_x} t}{L} = t_R$$

advective vel
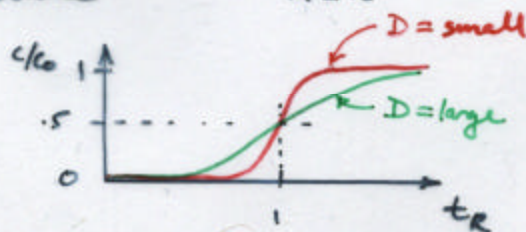
$$\frac{C}{C_0} \approx \tfrac{1}{2} \, \text{erfc} \left[\frac{1-U}{2(U D_L / v_x L)^{1/2}} \right]$$

$$\text{erfc}(0) = 1$$

5.7.2 Single Well Tracer Test

- Higher than natural gradient
- Incorporates scale effects
- Needs only single wellbore — Injection then recovery of fluid
- Neglects diffusion — incorporates dispersion
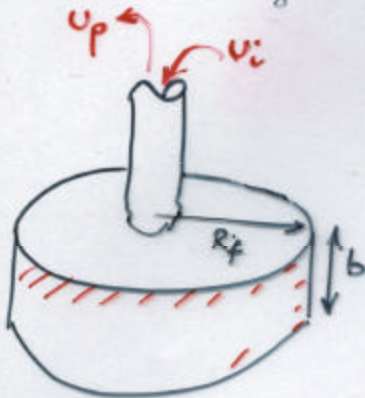
U_p = cumulative volume recovered at initial concentration, C_0.

U_i = total volume injected

R_f = average frontal position of injected water at end of injection

n = porosity
b = aquifer thickness or wellbore zone.

Volume in $= Qt$

Volume occupied $= \pi R_f^2 b n$

$$Qt = \pi R_f^2 b n$$

$$R_f^2 = \frac{Qt}{\pi b n}$$

$$\frac{c}{c_0} = \frac{1}{2} \, erfc\left\{ \frac{(U_p - U_i) - 1}{\left\{ \frac{16}{3}(d_L/R_f)\left[2 - (1 - U_p/U_i) \right]^{1/2} \left[1 - (U_p/U_i) \right] \right\}^{1/2}} \right\}$$

5.7.3 Twin Well Tracer Test
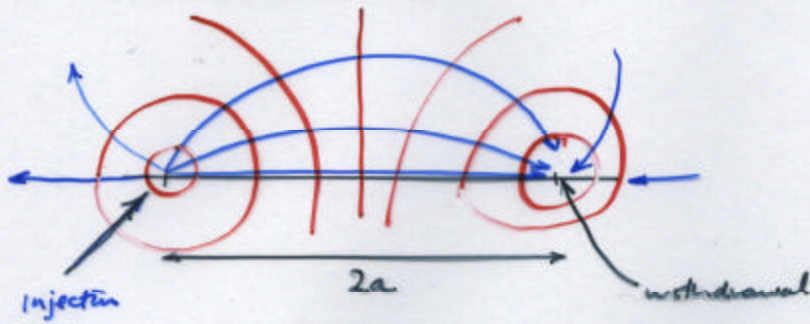
1. Inject tracer
2. Record outlet at withdrawal well.

Transit time for plug flow: along a given streamline
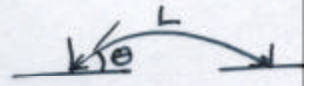
$$t_\theta = \frac{4\pi a^2 b}{q \sin^2 \theta}\left(1 - \frac{\theta}{\tan\theta}\right)$$

q = injection rate
θ = streamtube "angle"
b = aquifer thickness
a = half separation of wells

$$L = \frac{2a\theta}{\sin\theta}$$

Fit measured curve to theoretical curve

First breakthrough
continuous source
spike source
Long tail
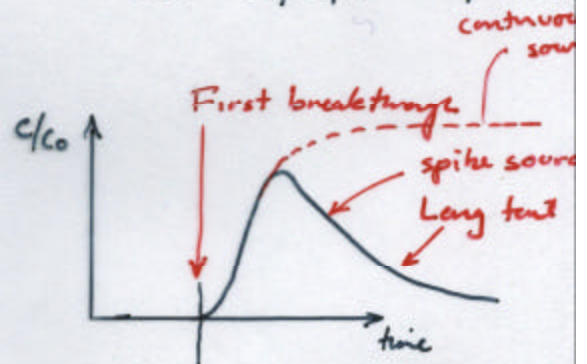
$$t_\theta = \frac{4\pi a^2 b}{q \sin^2\theta}\left(1 - \frac{\theta}{\tan\theta}\right)\bigg|_{\theta = 0}$$

Problems:

- Test induces dispersion due to nature of test, alone.
  ∴ obscures actual dispersion due to the porous medium.

plug flow
due to dispersion

- Natural gradient tests preferred
- Avoids this "geometric" dispersion due to severe flow-field
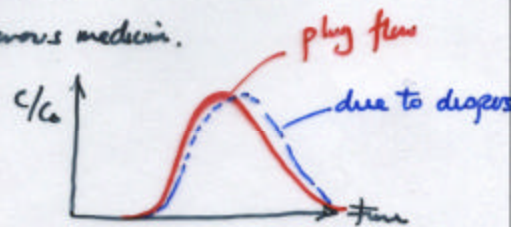
NATURAL GRADIENT

Evaluation of advective vel, $V_x = \ell/t$

$t(d)$	$\ell(m)$	$V(m/d)$
85	9.5	0.11
462	38	0.08
647	61	0.09

$$\bar{V} \cong 0.09 \, m/d$$

Evaluation of Dispersivity, D_x

$$3\sigma_x = 3\sqrt{2 D_x t} \qquad D_x = (3\sigma_x)^2/18t$$

Half length $(3\sigma_x)$	Time (t)	Dispersivity D_x
5m	85	$.016 \, m^2/d$
14m	462	$.023$
15m	647	$.019$

$$\bar{D}_x = .019$$

FIGURE 2.13 Vertically averaged chloride concentration at 1 day, 85 days, 462 days, and 647 days after the injection of a slug into a shallow aquifer. Source: D. M. Mackay et al. Water Resources Research 22, no. 13 (1986):2017–29. Copyright by the American Geophysical Union.

Transverse Dispersivity, D_y

Half length $(3\sigma_y)$	Time (t)	Dispersivity D_y
4.5m	85	$.013 \, m^2/d$
6.0	462	$.004$
6.5	647	$.004$

$$\bar{D}_y \simeq .007 \, m^2/d$$

Compare with estimate: $\alpha_L = \frac{1}{10} x$

$x =$ scale of measurement $\cong 61m$

$$D_L = \cancel{D_x^0} + \alpha_L V_x = (6.1m)(0.09 \, m/d)$$

$$D_L = 0.55 \, m^2/d$$

not very close to $0.019 \, m^2/d$.

5.7.4 SCALE EFFECTS OF DISPERSION

Flow →

— high K lenses
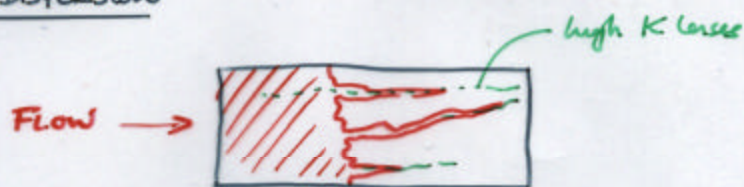
Macrodispersion — variability in conductivity field → variability in velocity field.
      — Gives enhanced dispersion — at all scales.

Hence scale effect:
    Larger scale → larger variation in conductivity distribution
            → increasing dispersivity

Some controversy over upper limit (of scale)
        scale of 10,000 m ?
        new sources of heterogeneity — regional geology.

Stochastic methods may be applied
      — Treat heterogeneity as the defining parameter
      — define heterogeneity → define dispersion characteristics

Approx magnitudes:
$$\alpha_L = \tfrac{1}{10} x$$
$$\alpha_T = \tfrac{1}{10}\alpha_L \quad \text{to} \quad \tfrac{1}{3}\alpha_L$$
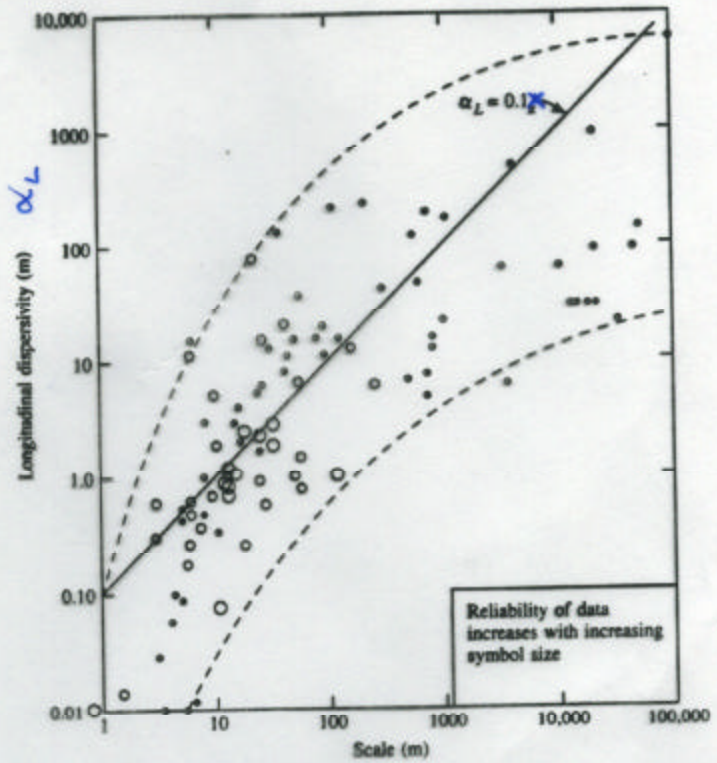
FIGURE 2.18 Field-measured values of longitudinal dispersivity as a function of the scale of measurement. The largest circles represent the most reliable data. Source: L. W. Gelhar, *Water Resources Research* 22, no. 9 (1986): 135S–145S. Copyright by the American Geophysical Union.
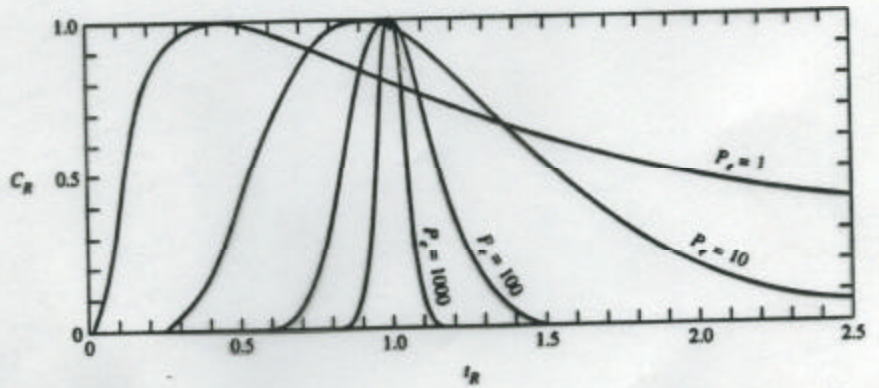
FIGURE 2.10 Dimensionless-type curve for the injection of a slug of a tracer into a one-dimensional flow field. Source: J. P. Sauty, *Water Resources Research* 16, no. 1 (1980): 145–58. Copyright by the American Geophysical Union.

6. RETARDATION & ATTENUATION

Reversible

Non-reversible

Advection ⎫ mechanisms of propogation of
Dispersion ⎭ a "conservative" solute.

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x}$$

Consequences:
1. Center of mass moves at velocity, V^a.
2. $c/c_o = \frac{1}{2}$ moves @ V^a.

Potential for retardation:

Changes in concentration due to "reactions": — Within aqueous phase
— With solid grains
— With gas in unsaturated zone.

Reactions group as:

Sorption (Removal).
1. Adsorption - desorption
   eg. Organic solvents sorbing onto organic matter

Reactions (transformation)
2. Acid - base reactions. eg. AMD on limestone/carbonate
3. Solution - precipitation reactions. eg. Silica dissolution/feldspar in HDS
4. Oxidation - reduction reactions. eg. Oxidation of Fe in AMD
5. Ion-pairing and complexation reactions
6. Microbial cell synthesis reactions: eg. Biodegradation of gasoline und solvents. → methane

+ Radioactive decay

CLASSIFICATION OF CHEMICAL REACTIONS

c^* — Non-equilibrium (long time to equilibrate).
— Equilibrium
→ time

i.e. Equilibrium

Non-equilibrium

Reversible:
eg. Re-dissolution of precipitates

	Chemical reactions	
Level A	"Sufficiently fast" and reversible	"Insufficiently fast" and/or irreversible
Level B	Homogeneous / Heterogeneous	Homogeneous / Heterogeneous
Level C	Surface / Classical	Surface / Classical
Class	I, II, III	IV, V, VI

Level A
Level B
Single phase   Solid & Aqueous Phase
Level C
Class
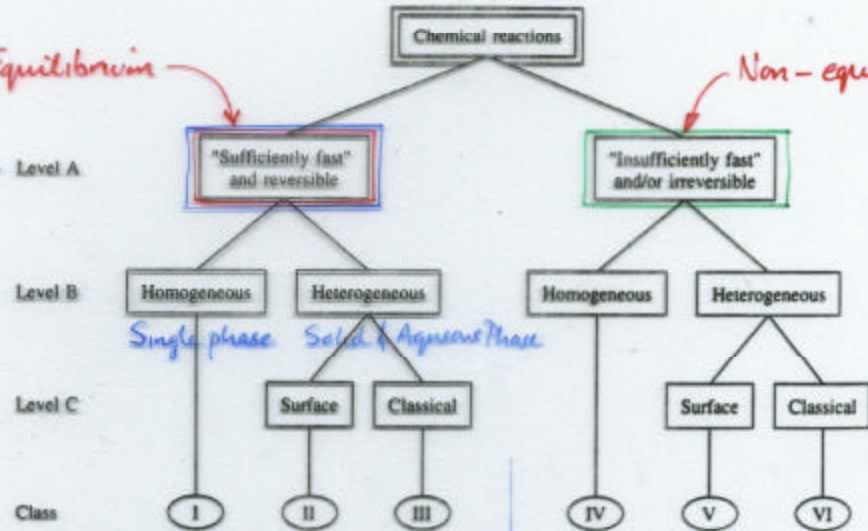
FIGURE 3.1 Classification of chemical reactions useful in solute transport analyses. Source: J. Rubin, *Water Resources Research* 19, no. 5 (1983): 1231–52. Published by the American Geophysical Union.

←————— SORPTION PROCESSES —————→   ←———— NON-EQUILIBRIUM REACTIONS ————→

All these reactions accommodated by simple retardation type models.

Use

$$\frac{\partial c}{\partial t} = \frac{D_L}{R}\frac{\partial^2 c}{\partial x^2} - \frac{V}{R}\frac{\partial c}{\partial x}$$

6.1 SORPTION PROCESSES

Adsorption: Solute clings to surface — chemical capture on clay particles

Absorption: Solute diffuses into interior of a particle.

→ Both result in "partitioning" of solute to solid phase i.e. removed.

Test: Mix solid with solute at known concentration

— measure amount removed per unit volume of solid

→ Equilibrium sorption isotherm.

also: Kinetic sorption isotherm (reaction slow but not reaching equilibrium).

Isotherms provide a convenient way of accommodating sorption in the "advection – dispersion" equation representing retardation effects.

Rewrite "advection – dispersion" equation for reactive (non conservative) system to accommodate retardation.

(solute is removed)

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v_x^a \frac{\partial c}{\partial x} - \frac{\rho_d}{\theta} \frac{\partial c^*}{\partial t} + \left(\frac{\partial c}{\partial t}\right)_r \qquad (1)$$

(Dispersion)　　(Advection)　　(Sorption)　　　(Reaction)

"equilibrium"

ρ_d = bulk density of aquifer

θ = volumetric moisture content (n if saturated)

c^* = amount of solute sorbed per unit weight of solid (aquifer

r = subscript for biological or chemical reaction

Assume that reactions in groundwater are fast compared to flow rates. Then amount of solid sorbed is related to solute concentration, directly.

small in comparison to travel time.
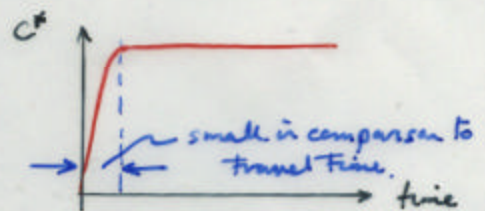
the　　$c^* = f(c)$

Therefore　　$\frac{\partial c^*}{\partial t} = \left(\frac{\partial c^*}{\partial c}\right) \frac{\partial c}{\partial t}$

Resubstitute into (1) and defines c (concentration in solute) as only variable

Linear

Freundlich

∴ Determine　$\frac{\partial c^*}{\partial c}$　⟹
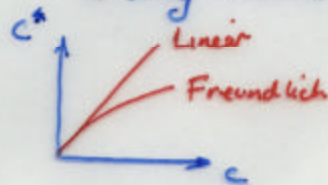
Defined as distribution coefficient, $k_d = \frac{\partial c^*}{\partial c}$

6.2 EQUILIBRIUM SURFACE REACTIONS

Linear Isotherm

$$c^* = k_d C$$
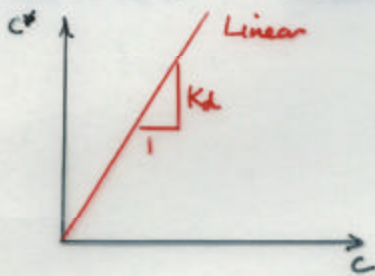
c^* (mg/kg) solute sorbed onto surface

c (mg/L) concentration of solute in equilibrium with solid

K_d (L/kg) distribution coefficient.

Freundlich Isotherm

$$c^* = k_d c^N$$

$$\log c^* = \log k_d + N \log c$$
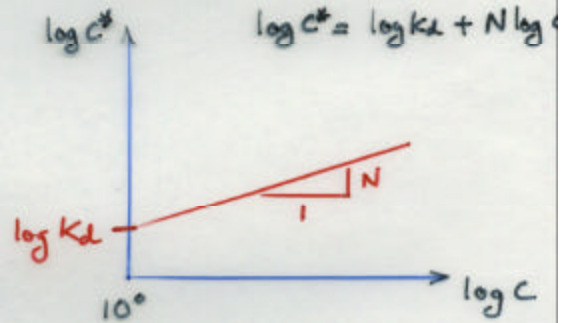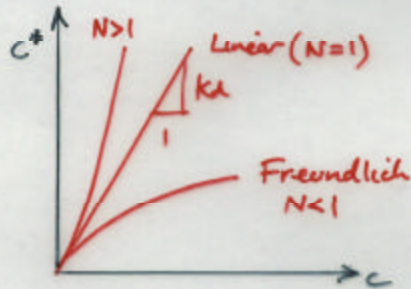
Langmuir Isotherm
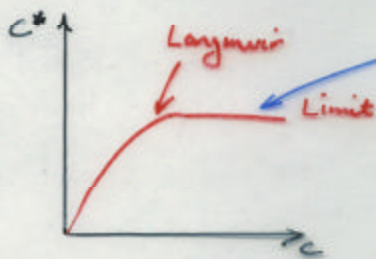
Represents a finite no. of sorption sites

$$\frac{c}{c^*} = \frac{1}{\alpha\beta} + \frac{c}{\beta} = \frac{\alpha\beta c}{1+\alpha c}$$

α = absorption coefficient related to binding energy

β = max amount of solute that may be absorbed to solid (mg/kg)

Why interested in Isotherms

Recall:

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v_x^a \frac{\partial c}{\partial x} - \frac{\rho_d}{\theta} \frac{\partial c^*}{\partial t} + \left(\frac{\partial c}{\partial t}\right)_r^{\nearrow 0}$$

$$\frac{\partial c^*}{\partial t} = \frac{\partial c^*}{\partial c}\left(\frac{\partial c}{\partial t}\right) = K_d \frac{\partial c}{\partial t}$$

Move retardation term to L.H.S.

$$\frac{\partial c}{\partial t} + \frac{\rho_d}{\theta}\underbrace{\left(\frac{\partial c^*}{\partial c}\right)}_{K_d} \frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v_x^a \frac{\partial c}{\partial x}$$

$$\underbrace{\left[1 + \frac{\rho_d}{\theta} K_d\right]}_{\text{Retardation coefficient, } R} \frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v_x^a \frac{\partial c}{\partial x}$$

$$\frac{\partial c}{\partial t} = \frac{D_L}{R} \frac{\partial^2 c}{\partial x^2} - \frac{v_x^a}{R} \frac{\partial c}{\partial x}$$

Effective (retarded) parameters.

Effect:

1. Retards velocity as $V_{effective} = v_x^a/R$ ⎫ Apply these to all
2. Reduces effective dispersion as D_L/R ⎭ previous expressions.
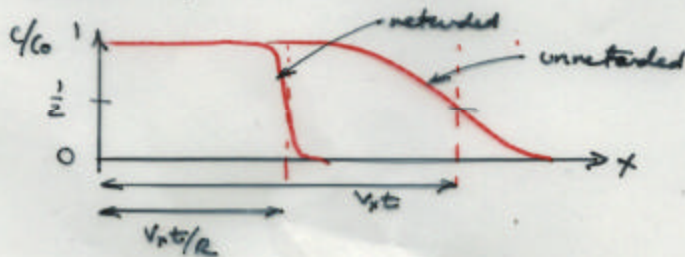
DISTRIBUTION COEFFICIENTS

Form	Relation	$K_d = \partial c^* / \partial c$	
Linear	$c^* = K_d c$	$\dfrac{\partial c^*}{\partial c} = K_d$	$R = \left[1 + \dfrac{\rho_d}{\theta} K_d\right]$
Freundlich	$c^* = K_d c^N$	$\dfrac{\partial c^*}{\partial c} = N K_d c^{N-1}$	$R = \left[1 + \dfrac{\rho_d}{\theta} N K_d c^{N-1}\right]$
Langmuir	$c^* = \dfrac{\alpha \beta c}{1 + \alpha c}$	$\dfrac{\partial c^*}{\partial c} = \dfrac{\alpha \beta}{(1 + \alpha c)^2}$	$R = 1 + \dfrac{\rho_d}{\theta} \dfrac{\alpha \beta}{(1 + \alpha c)^2}$

Typical magnitudes of R

K_d in the range 0 to 10^3 ml/g

$$\rho_d = 2500 \ kg/m^3 \longrightarrow 2.5 \ g/ml$$
$$\theta = 0.2 \ to \ 0.4$$

$$R \doteq \left(1 + \frac{2.5}{.25} K_d\right)$$

$$R \doteq (1 + 10 K_d) \implies 1 \ to \ 10^4$$

Range.

Conservative — Chloride

Cl
647 days

57m

13m   23.5m

CTET
633 days

Non-conservative or reactive

PCE
633 days

Source location
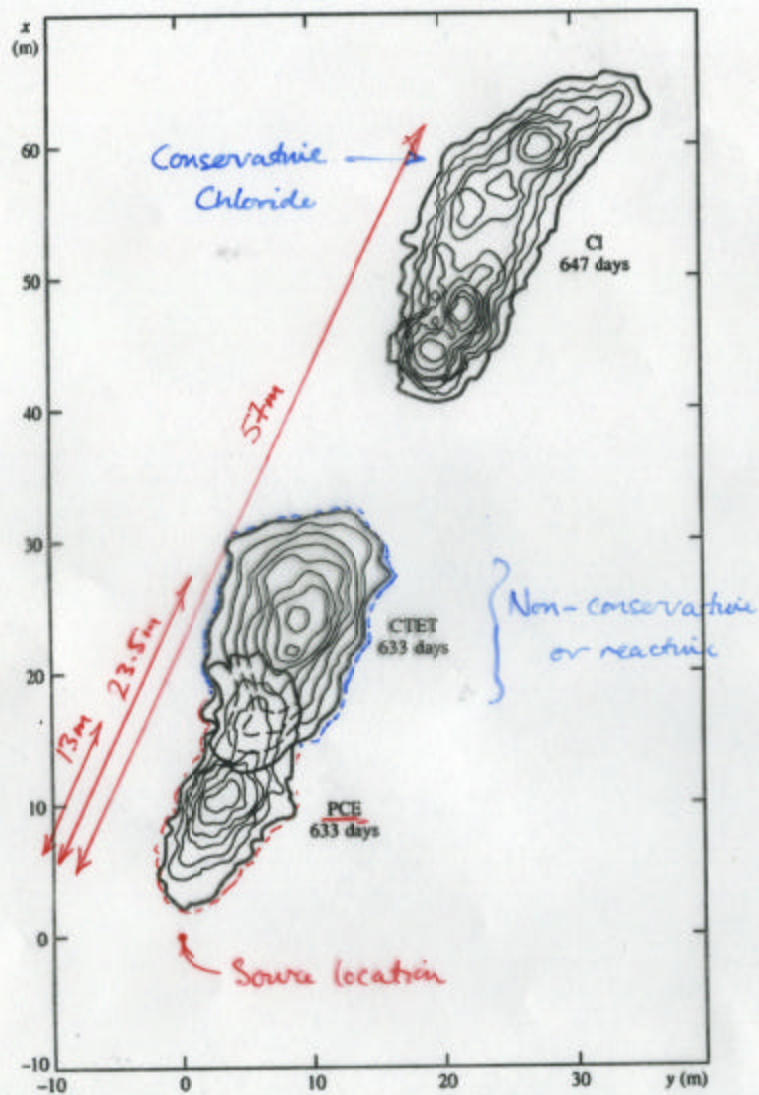
FIGURE 3.16 Plumes of chloride, carbon tetrachloride, and tetrachloroethylene at the end of the experimental period. The plumes are based on depth-averaged values. Source: P. V. Roberts, M. N. Goltz, and D. M. Mackay, Water Resources Research 22, no. 13 (1986): 2047–59. Copyright by the American Geophysical Union.

CTET Plume Movement.

TETRACHLOROETHYLENE (PCE) Movement (Dissolved plume)

633 days
380 days
16 days

633 days
380 days
16 days

(a)   (b)
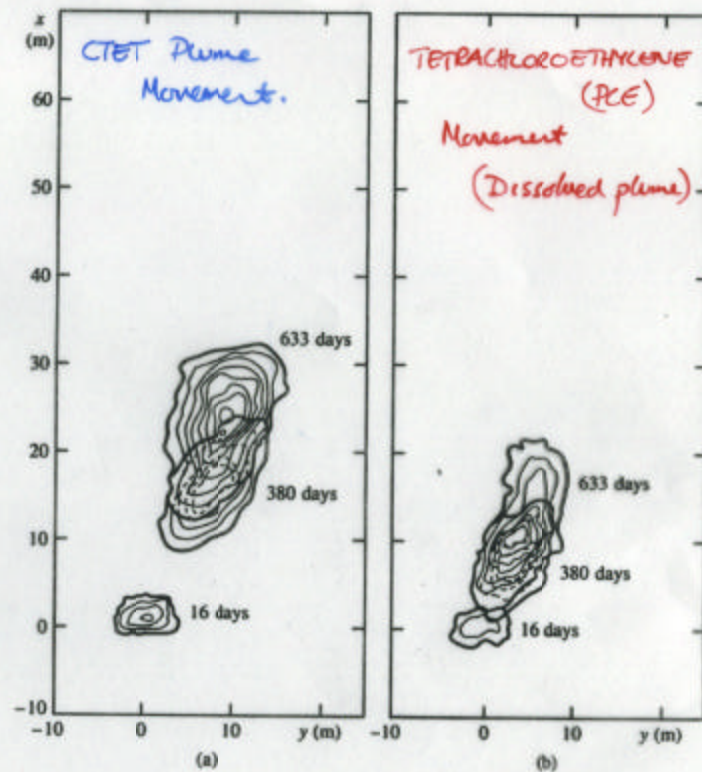
FIGURE 3.17 (a) Growth of carbon tetrachloride plume with time; (b) growth of tetrachloroethylene plume with time. Source: P. V. Roberts, M. N. Goltz, and D. M. Mackay, Water Resources Research 22, no. 13 (1986): 2047–59. Copyright by the American Geophysical Union.

Why are different compounds differentially mobile ??

Assuming Cl is unretarded: $R = \dfrac{V^a_{cl}}{V^a} = \dfrac{l_{cl}}{t} \dfrac{t}{l}$

CTET ⟹ R = 2.42

PCE ⟹ R = 4.38

$$2000 \text{ Kg}/m^3 = 2000 \frac{\text{Kg}}{m^3} \cdot \frac{1m^3}{1000 L} = \frac{2 \text{ Kg}}{L} = 2 \frac{g}{mL}$$

$1 m^3 = 1000 L$

$$\frac{\theta}{\rho_d} = \frac{.3}{2} \frac{L}{Kg} = .15$$

Rearranging $\quad R = \left[1 + \frac{\rho_d}{\theta} K_d \right]$

$$(R-1) \frac{\theta}{\rho_d} = K_d$$

Solute	$(R-1)$	$(R-1)\frac{\theta}{\rho_d} = K_d$ (L/kg or mL/g)
CTET	1.42	.213
PCE	3.38	.507 (tetrachloroethylene)
		K_d

(Note can also check dispersion)

Note: organic content very low ~ 0.02%

∴ absorption limited

Estimates

octanol-water partition

Solute	Solubility	log K_{ow}
CTET	805 mg/L @ 30°C	2.7
(Tetrachloroethylene) PCE	1503 mg/L @ 25°C	2.6

6.3 FRACTURED ROCK

- Retardation in fractured rock may be considered as a non-equilibrium rea[c]
- Conditioned by fracture surface area.
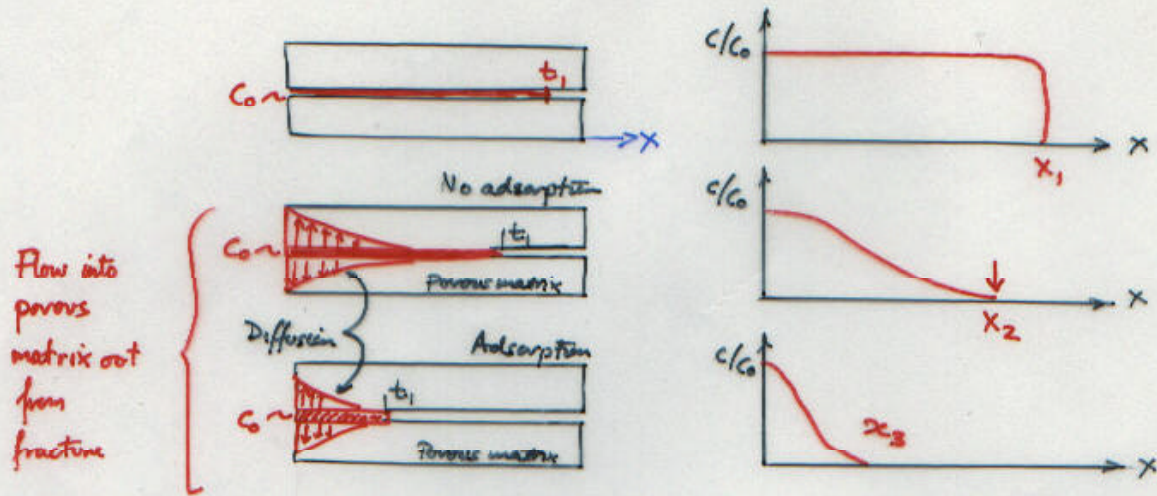
Diffusive process — is reversible
         — is not in equilibrium with the groundwater flow

Approximate representation as a linear isotherm

$$K_d = \frac{\text{mass of solute on solid phase per unit "area" of solid phase}}{\text{concentration of solute in solution}}$$

i.e. K_d per unit surface area, not volume $\dfrac{\bar{V}}{V_c} = 1 + A K_d = R$

A = surface area/void volume of fracture $= \dfrac{2A}{A b} = \dfrac{2}{b}$

Planar fracture $\dfrac{\bar{V}}{V_c} = \underbrace{1 + \dfrac{2}{b} K_d}_{R}$ Small fractures have greater retardation capacity.

6.4 SORPTION OF HYDROPHOBIC (ORGANIC) COMPOUNDS

1. Low solubility in water   eg. CTET   Solubility $805 \, mg/L \rightarrow 805 \, ppm$

   Drinking H_2O limit $5 \, ppb$.

2. Adsorbed onto • solid surfaces (since hydrophobic)

   • organic matter (important sink)

   exclusively sorbed onto organic if $f_{oc} \geqslant 0.1\%$

   $f_{oc} = \dfrac{organic \; carbon \; wt}{bulk \; wt.}$

Two limits for behaviour:

If $f_{oc} \geqslant 0.1\%$ then $K_{oc} = \dfrac{K_d}{f_{oc}}$

K_{oc} = organic carbon partition coefficient.

If only know wt of organic matter, $K_{oc} = 1.724 \, K_{om}$
since organic carbon less wt than organic matter

If $f_{oc} \leqslant 0.1\%$ then   mineral surfaces are an important
(relatively) sink for the hydrophobic
compounds.

$\therefore$ $K_d = K_{oc} f_{oc}$ does not apply.

This table sheds some insight into the f_{oc} contents of typical sands and gravels

TABLE 4.1 Field Studies that Have Yielded Reliable Estimates Of Organic Contaminant Retardation in Sand/Gravel Aquifers

Site Location and Test Type (reference)[a]	Retardation Factors Determined For Listed Contaminants		Organic Carbon Content Of Solids (reference)
	Contaminant	Factor	
Palo Alto, California Forced gradient (1)	Chloroform	2.5-3.5	nr[c]
	Bromoform	6.0	
	1,1,1-Trichloroethane	12.0	
	Chlorobenzene	33.0	
R. Aare, Switzerland River infiltration (2)	Tetrachloroethene	5.0	nr
Gloucester, Ontario Forced gradient (3, 4)	1,4-Dioxane	1.4	0.1-0.25% (4, 5)
	Tetrahydrofuran	2.2	
	Diethyl ether	3.0	
Plume interpretation (4, 5)	1,4-Dioxane	1.6	
	Tetrahydrofuran	2.2	
	Diethyl ether	3.3	
	1,2 Dichlorobenzene	7.6	
	Benzene	8.8	
	Carbon tetrachloride	23.0	
Borden, Ontario Natural gradient (6, 7)	Bromoform	1.9-2.7	0.02% (6, 11)
	Carbon tetrachloride	1.8-2.5	
	Tetrachloroethene	2.7-5.9	
	1,2-Dichlorobenzene	3.9-9.0	
	Hexachloroethane	5.0-7.0	
Moffett Naval Air Station, California Forced gradient (8)	Trichloroethene	5-9	0.11% (8)
	1,1,1-Trichloroethane	1.4-3.0	
Otis Air Force Base, Massachusetts Plume interpretation (9)	Trichloroethene	1.0	0.01-0.75% (9)
	Tetrachloroethene	1.0	
	Dichlorobenzene	1.0-1.1	
	DTBB[b]	2.4-2.6	
	P-Nonylphenol	1.1-3.3	
Rocky Mountain Arsenal, Colorado Forced gradient (10)	Trichloroethene	1-2	0.005% (12)
	1,1,1-Trichloroethane	1-2	

a References: (1) Roberts et al., 1985; (2) Schwarzenbach et al., 1983; (3) Whiffin and Bahr, 1985; (4) Patterson et al., 1985; (5) Jackson et al., 1985; (6) Mackay et al., 1986; (7) Roberts et al., 1986; (8) Semprini et al., 1987; (9) Barber et al., 1988; (10) Mackay et al., 1986; (11) Ball et al., 1989; (12) Mackay et al., unpublished results.

b DTBB is 2,6-di-tert-butyl-p-benzoquinone.

c nr: not reported.

1986 b

1986 a

Source: Mackay, D. Characterization of the Distribution and Behavior of Organic Contaminants in the Subsurface. In Proceedings of a National Research Council Symposium. National Academy Press (in press 1990)

4-18

Rocky mtn Arsenal $\Rightarrow f_{oc} = 0.005\%$
TCE @ 5 mg/l
$K_dTCE = 0.2 cm^3/g$

$\Rightarrow S = k_dC = 10^{-8} \frac{gms TCE}{gm solid}$ i.e. f_{oc} from TCE $\approx 10^{-8}$ i.e. no appreciable contribution of TCE to the organic carbon content.

TAKE CARE IN APPLYING $f_{oc} \geq .1\%$ where $\underline{f_{oc} < 0.1\%}$.

eg. Border results: $\qquad f_{oc} = 0.02\%$

$$K_d = K_{oc} \, f_{oc}$$

For Carbon Tetra Chloride (CTET) $\qquad$ Solubility, $S = 805 \, mg/L$

Using (T14) $\qquad \log K_{oc} = 3.64 - 0.55 \log S$
$$= 3.64 - 0.55(2.9) = 2.04$$

$$K_{oc} = 110 \, \frac{mg/L}{} \, mL/g$$

From calculation $f_{oc} > 0.1\%$ $\boxed{K_d = 110 \, (0.0002) = 0.02 \, \frac{mg/L}{} \, mL/g}$

From plume $\boxed{R = 2.42 \, ; \quad K_d = 0.213 \, \frac{mg/L}{} \, mL/g}$

1. Estimated value is too low — neglects the significant of the mineral surfaces.

2. Reasonable correspondence.

Handwritten notes (left side):

$\log K_{oc} = 3.64 - 0.55 \log S$

$S_{ETHYL\ BENZENE} = 140\ mg/L$

$\log S = 2.15$

$\log K_{oc} = 3.64 - 0.55(2.15) = 2.46$

$\therefore K_{oc} = 288\ L/kg \sim (mL/g)$

TABLE 3.5 Empirical equations by which K_{oc} can be estimated from S.

Equation Number	Equation	Reference
(T13)	$\log K_{oc} = 0.44 - 0.54 \log S$ S in mole fraction, $r^2 = 0.94$	Karickhoff, Brown, and Scott 1979
(T14)	$\log K_{oc} = 3.64 - 0.55 \log S$ S in mg/L	Kenaga 1980
(T15)	$\log K_{oc} = 4.273 - 0.686 \log S$ S in mg/L	Means et al. 1980
(T16)	$\log K_{oc} = 3.95 - 0.62 \log S$ S in mg/L	Hassett et al. 1983
(T17)	$\log K_{on} = 0.001 - 0.729 \log S$ S in moles/L, $r^2 = 0.996$	Chiou, Porter, and Schmedding 1983

TABLE 3.6 K_{oc} values estimated from the aqueous solubility.

Compound:	Dichloroethane	Benzene	Trichloroethene	Ethyl Benzene	Tetrachloroethene	Napthalene	2,2'-Dichlorobiphenyl	Pyrene
Molecular weight:	98.96	78.12	131.38	165.82	106.18	128.18	223.10	202.26
Solubility (mg/L)								
	5500	1780	1100	140	150	31	1.86	0.032
Log S:	3.74	3.25	3.04	2.15	2.18	1.49	0.269	−1.50
Solubility (moles/L)								
	5.56×10^{-2}	2.28×10^{-2}	8.37×10^{-3}	8.44×10^{-4}	1.41×10^{-3}	2.42×10^{-4}	8.32×10^{-6}	1.58×10^{-7}
Log S:	−1.25	−1.64	−2.08	−3.07	−2.85	−3.62	−5.08	−6.80
Solubility (Mole Fractions)								
	1.00×10^{-3}	4.10×10^{-4}	1.51×10^{-4}	1.52×10^{-5}	2.54×10^{-5}	4.35×10^{-6}	1.49×10^{-7}	2.84×10^{-9}
Log S:	−3.00	−3.39	−3.82	−4.82	−4.60	−5.36	−6.83	−8.55
Equation Number[a]				**Estimated log K_{oc}**				
(T13)	2.06	2.27	2.50	3.04	2.87	3.33	4.13	5.06
(T14)	1.58	1.85	1.97	2.46	2.44	2.82	3.79	4.47
(T15)	1.67	2.01	2.15	2.76	2.74	3.21	4.46	5.27
(T16)	1.63	1.94	2.07	2.62	2.60	3.03	4.12	4.88
(T17)	1.15	1.43	1.75	2.47	2.31	2.88	3.93	5.19
Range	1.15–2.06	1.43–2.27	1.75–2.50	1.80–3.04	2.31–2.87	2.82–3.33	3.79–4.46	4.47–5.27
Mean	1.62	1.90	2.09	2.67	2.59	3.05	4.09	4.97
St. dev.	0.32	0.31	0.27	0.24	0.22	0.22	0.25	0.32
Coef. var	0.08	0.07	0.06	0.05	0.04	0.04	0.05	0.08

[a] The equation numbers in his table refer to Table 3.5.

Equation Number	Equation	Chemicals Used	Reference
(T1)	$\log K_{oc} = 0.52 \log K_{ow} + 0.62$	72 substituted benzene pesticides	Briggs, 1981
(T2)	$\log K_{oc} = 1.00 \log K_{ow} - 0.21$	10 polyaromatic hydrocarbons	Karickhoff, Brown, and Scott 1979
(T3)	$K_{oc} = 0.63 K_{ow}$	Miscellaneous organics	Karickhoff, Brown, and Scott 1979
(T4)	$\log K_{oc} = 0.544 \log K_{ow} + 1.377$	45 organics, mostly pesticides	Kenaga and Goring 1980
(T5)	$\log K_{oc} = 1.029 \log K_{ow} - 0.18$ $r^2 = 0.91; n = 13$	13 pesticides	Rao and Davidson 1980
(T6)	$\log K_{oc} = 0.94 \log K_{ow} + 0.22$	s-triazines and dinitroanalines	Rao and Davidson 1980
(T7)	$\log K_{oc} = 0.989 \log K_{ow} - 0.346$ $r^2 = 0.991; n = 5$	5 polyaromatic hydrocarbons	Karickhoff 1981
(T8)	$\log K_{oc} = 0.937 \log K_{ow} - 0.006$	Aromatics, polyaromatics, triazines	Lyman 1982
(T9)	$\ln K_{oc} = \ln K_{ow} - 0.7301$	DDT, tetrachlorobiphenyl, lindane, 2,4-D, and dichloropropane	McCall, Swann, and Laskowski 1983
(T10)	$\log K_{oc} = 0.904 \log K_{ow} - 0.779$ $r^2 = 0.989; n = 12$	Benzene, chlorinated benzenes, PCBs	Chiou, Porter, and Schmedding 1983
(T11)	$\log K_{oc} = 0.72 \log K_{ow} + 0.49$ $r^2 = 0.95; n = 13$	Methylated and chlorinated benzenes	Schwarzenbach and Westall 1981
(T12)	$\log K_{oc} = 1.00 \log K_{ow} - 0.317$ $r^2 = 0.98; n = 22$	22 polynuclear aromatics	Hassett et al. 1980

TABLE 3.4 Experimentally derived (K) values.

log(K_{oc})

Compound	log(K_{oc})	Reference
Benzene	1.50	Chiou, Porter, and Schmedding 1983
	1.92	Karickhoff, Brown, and Scott 1979
	1.98	Rogers, McFarlane, and Cross 1980
Ethylbenzene	2.22	Chiou, Porter, and Schmedding 1983
2,2'-Dichlorobphenyl	3.92	Chiou, Porter, and Schmedding 1983
Tetrachloroethene	2.32	Chiou, Peters, and Freed 1979
Napthalene	3.11	Karickhoff, Brown, and Scott 1979
Pyrene	4.92	Karickhoff, Brown, and Scott 1979
	4.80	Means et al. 1980

EXPERIMENTAL VALUES

COMPARE?

TABLE 3.3 Estimated values of K_{oc} based on published K_{ow} values.

	Dichloroethane	Benzene	Trichloroethene	Ethyl Benzene	Tetrachloroethene	Napthalene	2,2'-Dichlorobiphenyl	Pyrene
Log K_{ow}	1.79	2.13	2.29	3.14	3.40	3.37	4.80	5.32
Equation Number[a]				Estimated log K_{oc}				
(T1)	1.79	1.96	2.05	2.49	2.62	2.61	3.35	3.62
(T2)	1.58	1.92	2.10	2.93	3.19	3.16	4.59	5.11
(T3)	1.13	1.34	1.44	1.98	2.14	2.16	3.07	3.35
(T4)	2.35	2.54	2.62	3.09	3.23	3.21	3.99	4.27
(T5)	1.66	2.01	2.18	3.05	3.32	3.29	4.76	5.29
(T6)	1.90	2.22	2.37	3.17	3.42	3.39	4.73	5.22
(T7)	1.42	1.76	1.92	2.76	3.02	2.99	4.40	4.92
(T8)	1.67	1.99	2.14	2.94	3.18	3.15	4.49	4.98
(T9)	1.06	1.40	1.56	2.41	2.67	2.64	4.07	4.59
(T10)	1.08	1.39	1.53	2.06	2.30	2.51	3.80	4.27
(T11)	1.78	2.02	2.14	2.75	2.94	2.92	3.95	4.32
(T12)	1.47	1.81	1.97	2.82	3.08	3.05	4.48	5.00
Range	1.06–2.35	1.34–2.54	1.44–2.62	1.98–3.17	2.14–3.42	2.16–3.39	3.07–4.76	3.35–5.29
Mean	1.57	1.86	2.00	2.70	2.93	2.92	4.14	4.58
St. dev.	0.38	0.35	0.33	0.39	0.41	0.37	0.54	0.63
Coef. var.	0.24	0.19	0.17	0.14	0.15	0.13	0.13	0.14

[a] The equation numbers in this table refer to Table 3.2

log

Handwritten notes:

log K_{ow} = 2.13

10^x it !!

K_{ow} = 135

K_{oc} = 0.63 K_{ow}

= 84.98

log K_{oc} = 1.92

If $f_{oc} \geq 0.1\%$ then

Koc may be estimated from two methods:

    1. Kow — octanol-water partition coefficient defines solubility of octanol in water

    2. Solubility data specific to the solvent compound.

For example: ($f_{oc} > 0.1\%$)

$$Kd = Koc \, f_{oc}$$

eg. $Koc = 0.63 \, Kow$ Tables $\begin{cases} 3.2 \\ 3.3 \\ 3.4 \end{cases}$

eg. $\log Koc = 3.64 - 0.55 \log S$

Solubility in mg/L

see Table $\begin{matrix} 3.5 \\ 3.6 \end{matrix}$

6.4.1 Multiple Solutes

- Solubility is reduced where multiple hydrophobic components are encountered.
- Concentration is lower than if solute is alone.

$$S_i^e = X_i \, S_i$$

S_i = pure phase solubility, (mg/L) for compound i

X_i = mole fraction of component i in DNAPL

ie Lab analysis of course

Mole fraction = $\dfrac{\text{Moles of compound } i}{\text{Total moles of soln.}}$

* Mole fraction since solubility controlled by available molecules

S_i^e = effective solubility of i

□ Effective solubility is an <u>upper</u> theoretical bound.

□ Does not account for co-solvency and other non-ideal behaviors

Smithville Compound	"Free phase" %by wt	Formula Wt (g)	Moles per 100g of cocktail	Mole fraction X_i	Pure phase Solubility (mg/L)	S_i^e
TCE	2%	131.4	$\frac{2}{131}$ = 0.0152	$\frac{.0152}{.677}$ = 2.2%	1060	23
TCB	10	181.45	.055	8.12%	19	1.5
PCB	50	220 (average)	.227	33.5%	.2	.0
Mineral oils	38	100 (guess)	.38	56.1%		
			$\overline{.677}$			

moles per 100g

i.e. $.677 \times 10^{23}$ molecules

$1 \, mg/L = 1 \, ppm$.

Mole of substance = formula wt in g.

Moles of solute per liter of solution = MOLARITY = $\dfrac{\text{Density}}{\text{Formula wt}}$

Water = $\dfrac{1000 g/L}{(16+2)}$ = 55.

Worksheet 7-1: Calculation of Effective Solubility (from Newell and Ross, 1992; after Shiu et al., 1988; and Feenstra et al., 1991)

For a single-component DNAPL, the pure-phase solubility of the organic constituent can be used to estimate the theoretical upper-level concentration of organics in aquifers or for performing dissolution calculations. For DNAPLs comprised of a mixture of chemicals, however, the effective solubility concept should be employed:

$$S_i^* = X_i S_i$$

where

S_i^* = the effective solubility (the theoretical upper-level dissolved-phase concentration of a constituent in groundwater in equilibrium with a mixed DNAPL; in mg/l)

X_i = the mole fraction of component i in the DNAPL mixture (obtained from a lab analysis of a DNAPL sample or estimated from waste characterization data)

S_i = the pure-phase solubility of compound i in mg/l (usually obtained from literature sources)

For example, if a laboratory analysis indicates that the mole fraction of trichloroethylene (TCE) in DNAPL is 0.10, then the effective solubility would be 110 mg/l. This is derived by multiplying the pure phase solubility of TCE by the TCE mole fraction:

$$1100 \text{ mg/l} * 0.10 = 110 \text{ mg/l}$$

Effective solubilities can be calculated for all components in a DNAPL mixture. Nearly insoluble organics in the mixture (such as long-chained alkanes) will reduce the mole fraction and effective solubility of more soluble organics, but will contribute little dissolved-phase organics to groundwater.

Please note that this relationship is approximate and does not account for non-ideal behavior of mixtures, such as co-solvency. etc.

Worksheet 7-2: Method for Assessing Residual NAPL Based on Organic Chemical Concentrations in Soil Samples (from Newell and Ross, 1992; after Feenstra et al, 1991)

To estimate if NAPLs are present, a partitioning calculation based on chemical and physical analyses of soil samples from the saturated zone (from cores, excavation, etc.) can be applied. This method tests the assumption that all the organics in the subsurface are either dissolved in groundwater or adsorbed to soil (assuming dissolved-phase sorption, not the presence of NAPL). By using the concentration of organics on the soil and the partitioning calculation, a theoretical pore-water concentration of organics in groundwater is determined. If the theoretical pore-water concentration is greater than the estimated solubility of the organic constituent of interest, then NAPL may be present at the site. A worksheet for performing this calculation is presented below; see Feenstra et al. (1991) for the complete methodology.

Step 1: Calculate S^e_t, the effective solubility of organic constituent of interest. See Worksheet 7-1.   [S_e]

Step 2: Determine K_{oc}, the organic carbon-water partition coefficient from one of the following: [K_{oc}]

- Appendix A and associated references or

- Empirical relationships based on K_{ow}, the octanol-water partition coefficient, which also is found in Appendix A. For example, K_{oc} can be estimated from K_{ow} using the following expression developed for polyaromatic hydrocarbons:

$$\text{Log } K_{oc} = 1.0 * \text{Log } K_{ow} - 0.21$$
[K_{oc}]   [K_{ow}]

Step 3: Determine f_{oc}, the fraction of organic carbon on the soil, from a laboratory analysis of clean soils from the site. Values for f_{oc} typically range from 0.03 to 0.00017 mg/mg. Convert values reported in percent to mg/mg.

Step 4: Determine or estimate ρb, the dry bulk density of the soil, from a soils analysis. Typical values range from 1.8 to 2.1 g/ml(kg/l). Determine or estimate θw, the water-filled porosity.

Step 5: Determine Kd, the partition (or distribution) coefficient between the pore water (ground water) and the soil solids:

$$Kd = K_{oc} * f_{oc}$$
[$K_{oc}\, f_{oc}$]

Step 6: Using Ct, the measured concentration of the organic compound in saturated soil in mg/kg, calculate the theoretical pore water concentration assuming no DNAPL (i.e., Cw in mg/l):

$$Cw = \frac{(Ct * \rho b)}{(Kd * \rho b + \theta w)}$$

C_t = total concentration in saturated soil

Cw = concentration in water only. ——— Equilibrium concentration

Step 7: Compare Cw and S^e_t (from Step 1):

Cw > S^e_t suggests possible presence of DNAPL ← Remaining source of DNAPL. (in the sample)
Cw < S^e_t suggests possible absence of DNAPL

* May measure Cw directly by pore-water extraction

6.4.3 TIME REQUIRED FOR DISSOLUTION — two forms { Distributed, Pool }

a) Distributed throughout volume

- Slow dissolution rates
- Decreases with time due to reduction in contact area.

$$t = \frac{\text{Mass of NAPL}}{\text{Mass rate of removal}} = \frac{m}{V^a \, n_e \, C_w \, A}$$
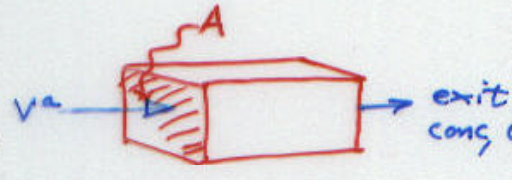
V^a = advective velocity

n_e = effective porosity

A = c/s area of flow

m = NAPL mass

C_w = dissolved exit concentration

g.

1 m³ sandy soil

$$\left. \begin{array}{l} K = 10^{-3} \text{ cm/s} \\ i = 0.01 \\ n_e = 0.3 \end{array} \right\}$$
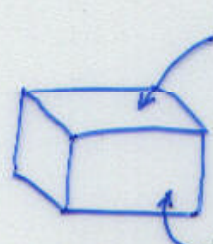
$$V^a = \frac{Ki}{n} = \frac{10^{-3} \, 10^{-2}}{.3}$$

Residual @ 30 L/m³

of PCE $\rho = 1.63 \, g/cm^3$

Solubility = 200 mg/L

Assume solubility @ 10% → 20 mg/L

$$= 3 \times 10^{-5} \text{ cm/s}$$

$$= 3 \text{ cm/d} = .03$$

$$t = \underline{744 \text{ years}}$$

Magnitudes consistent with persistent DNAPL contamination problem in 40s, 50s, 60s.

b) **Residual Pool Sources**

Diffusion/Dispersion
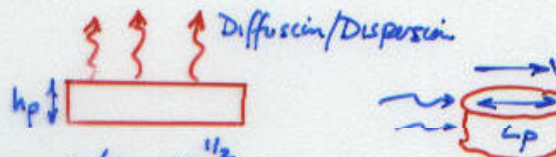
M_a = Surface area averaged mass transfer rate $(M/L^2/T)$

$$M_c = \left[(4 D_v V^a) / (\pi L_p) \right]^{1/2} C_{sat} \, n_e$$

D_v = coef of vertical dispersion
$$= D^* + V^a \alpha_T \qquad (L^2/T)$$

V^a = average advection g/w velocity

L_p = pool length

n_e = effective porosity

C_{sat} = saturation concentration (solubility)
(may be 10% of this due to mass transfer rate effects)

Assuming pool area remains constant:

$$t_d = \underbrace{P_h \; n \; \rho_{nw} \; S_n}_{\substack{\text{Mass of NAPL present} \\ \text{area}}} / \underbrace{M_a}_{\substack{\text{Mass rate of} \\ \text{removal}}}$$

t_d = dissolution time

P_h = pool height

S_n = NAPL saturation

ρ_{nw} = Density of NAPL

eg TCE in sand

Schwille experiment.

SCHWILLE POOL DISSOLUTION EXPERIMENT

From Schwille (1988)

TCE Solubility, S ≃ 1100 mg/ℓ
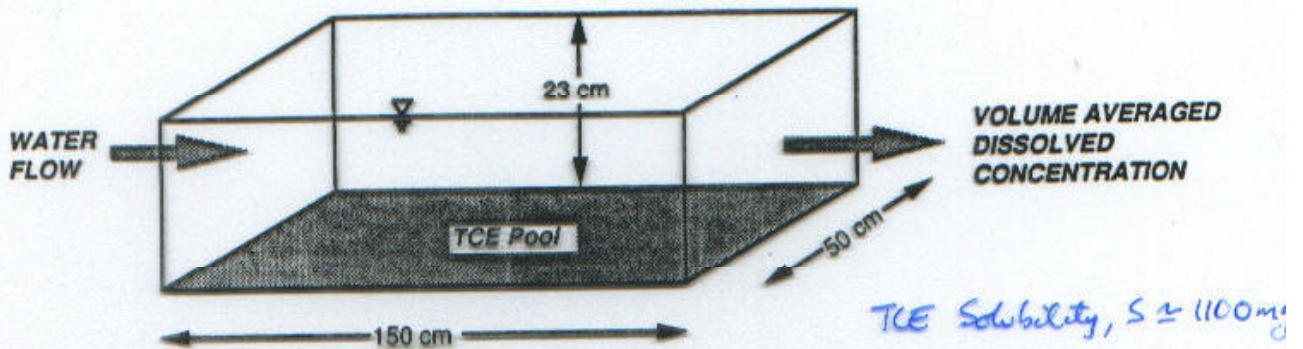
RESULTS OF POOL DISSOLUTION EXPERIMENT:

Linear Velocity (m/day)	Concentration (mg/L)	Relative Concentration
1.1	90	8.2 %
2.3	67	6.1 %
2.3	87	7.9 %
4.5	73	6.6 %
6.8	77	7.0 %

Much lower than absolute solubility

CONCLUSION FROM POOL DISSOLUTION EXPERIMENT:

* Dissolved concentrations can be considerably less than saturation concentrations

→ Contact time of groundwater with solvent

→ Area of contact (Related to pool size).

Table 5.3. Equivalent DNAPL mass associated with some relatively well-documented organic contaminant plumes in sand-gravel aquifers (modified from Mackay and Cherry, 1989).

SITE LOCATION AND PLUME MAP	PRESUMED SOURCES	PREDOMINANT DNAPL CONTAMINANTS	PLUME VOLUME (LITERS)	ESTIMATED CHEMICAL MASS DISSOLVED IN PLUME (AS EQUIVALENT DNAPL VOLUME IN LITERS OR 55-GAL DRUMS)
Ocean City, NJ	chemical plant	Trichloroethene 1,1,1-Trichloroethane Tetrachloroethene	5,700,000,000	15,000 (72 drums)
Mountain View, California	electronics plant	Trichloroethene 1,1,1-Trichloroethane	6,000,000,000	9800 (47 drums)
Cape Cod, Ma.	sewage infiltration beds	Trichloroethene Tetrachloroethene	40,000,000,000	1500 (7 drums)
Gloucester, Ont.	special waste landfill	1,4-Dioxane Freon 113	102,000,000	190 (0.9 drum)
San Jose, Cal.	electronics plant	1,1,1-Trichloroethane Freon 113 1,1-Dichloroethene	5,000,000,000	130 (0.6 drum)
Denver, Colorado	trainyard, airport	1,1,1-Trichloroethane Trichloroethene Dibromochloropropane	4,500,000,000	80 (0.4 drum)

0 ———— 5 km

Flow ⟶

Evaluate total NAPL (dissolved) in plume ⟶ Evaluate source NAPL (volume).

Plume = Dissolved mass + Sorbed mass

$$M_T = C \, n \, V_T + C^* \rho_b V_T$$

$$C^* = K_d C \left(\frac{n}{n}\right)$$

$$\boxed{M_T = C n V_T R} \longleftarrow R = \left[1 + \frac{\rho_b}{n} K_d\right]$$

6.5 RADIOACTIVE DECAY

Recall:

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v^a \frac{\partial c}{\partial x} - \frac{\rho_d}{\theta} \frac{\partial c^*}{\partial t} + \left(\frac{\partial c}{\partial t}\right)_{rxn}$$

Retardation   Reaction

◻ Radioactive chain decay

◻ Abiotic hydrolysis (natural degradation of hydrocarbons

$$\left(\frac{\partial c}{\partial t}\right)_{decay} = \frac{-\ln(2)}{\lambda} c$$

λ = half life (in same units as time)

The previous figure introduced the concept of half-life to define the abiotic rxn rate. You will recall that this derives from the first-order rate laws, which is often assumed to apply to abiotic rxns:

$$- \frac{d(RX)}{dt} = k_T [RX]$$

where half life, $t_{1/2} = 0.693/k_T$

Vogel et al (1987) give the following table of half-lives:

TABLE 3
Environmental half-lives and products from abiotic hydrolysis or dehydrohalogenation of halogenated aliphatic compounds at 20 °C

Compound	Half-life years (reference)	Product(s) (reference)
Methanes		
Dichloromethane	1.5 (10), 704 (8)	
Trichloromethane	1.3 (10), 3500 (8)	
Tetrachloromethane	7000 (8)	
Bromomethane	0.10 (8)	
Dibromomethane	183 (8)	
Tribromomethane	686 (8)	
Bromochloromethane	44 (8)	
Bromodichloromethane	137 (8)	
Dibromochloromethane	274 (8)	
Ethanes		
Chloroethane	0.12 (11)[a]	Ethanol (11)[a]
1,2-Dichloroethane	50 (12)	
1,1,1-Trichloroethane	0.5 (10), 1.7 (12)	Acetic acid (12–14)
	0.8 (15)[a], 2.5 (16)[a]	1,1-Dichloroethylene (14–16)
1,1,2-Trichloroethane	170 (12)	1,1-Dichloroethene (17)
1,1,1,2-Tetrachloroethane	384 (12)	Trichloroethene (12)
1,1,2,2-Tetrachloroethane	0.8 (12)	Trichloroethene (12)
1,1,2,2,2-Pentachloroethane	0.01 (12)	Tetrachloroethene (12)
Bromoethane	0.08 (8)	
1,2-Dibromoethane	2.5 (9)	Bromoethene (9)
	2.5 (18)	Ethylene glycol (18)
Ethenes		
Trichloroethene	0.9 (10), 2.5 (15)[b]	
Tetrachloroethene	0.7 (10), 6 (15)[b]	
Propanes		
1-Bromopropane	0.07 (8)	
1,2-Dibromopropane	0.88 (9)	Bromopropene (9)
1,3-Dibromopropane	0.13 (9)	Bromopropanol (9)
1,2-Dibromo-3-chloropropane	35 (19)	Bromochloropropene (19)

[a]Extrapolated by 2 from Reference 11.   [b]At 10 °C in sea water.   [c]At 20 °C.

6.6 BIODEGRADATION

In addition to <u>abiotic</u> processes → Biodegradation of hydrocarbons

Biofilm + Oxygen → Aerobic biodegradation

→ Growth of microbial population

AEROBIC

Need oxygen sources – dissolved in water

– pumped in for remediation

<u>Monod</u> – function governs rates!

3 rate laws (coupled) (H) Hydrocarbon concentration

(O) Oxygen availability in fluid

(M) Biofilm mass

→ 3 conservation equations and 3 unknowns

Solve for (H).

ANAEROBIC

Microbes use other metabolic source e.g. nitrate available from

fertilizer

1 rate law required only

1 conservation equation } solve for hydrocarbon concentration.

BIODEGRADATION — More complex than simple reaction — Since requires

AEROBIC

3 Growth/Decay laws — Inter-relate

$$\frac{dH}{dt} = -M_t k_h \left(\frac{H}{K_s + H}\right)\left(\frac{O}{K_c + O}\right) \qquad (3.59) \quad \text{Hydrocarbon}$$

$$\frac{dO}{dt} = -M_t k_h G \left(\frac{H}{K_s + O}\right)\left(\frac{O}{K_c + O}\right) \qquad (3.60) \quad \text{Oxygen}$$

$$\frac{dM_t}{dt} = M_t k_h Y \left(\frac{H}{K_s + H}\right)\left(\frac{O}{K_c + O}\right) + k_s Y C_{oc} - b M_t \qquad (3.61) \quad \text{Microbial population}$$

where

H = hydrocarbon concentration in pore fluid (ML^{-3})

O = oxygen concentration in pore fluid (ML^{-3})

M_t = total aerobic microbial concentration (ML^{-3})

k_h = maximum hydrocarbon utilization rate per unit mass of aerobic microorganisms (T^{-1})

Y = microbial yield coefficient (g cells/g hydrocarbon)

K_s = hydrocarbon half-saturation constant (ML^{-3})

K_c = oxygen half-saturation constant (ML^{-3})

k_s = first-order decay rate of natural organic carbon (T^{-1})

C_{oc} = natural organic carbon concentration (ML^{-3})

b = microbial decay rate (T^{-1})

G = ratio of oxygen to hydrocarbon consumed

The microorganisms will grow on both naturally occurring organic carbon as well as hydrocarbon contaminants. The microorganisms tend not to move in the aquifer because they generally adhere to aquifer materials (Harvey, Smith, and George 1984). Even if the microbes are free to move, the natural tendency of the aquifer matrix will be to filter them out. There will be some tendency for microbes to transfer from the solid surface to solution. As a first approximation this can be considered to be a linear function of the total mass of microorganisms.

We can combine Equations 3.59, 3.60, and 3.61 individually with Equation 3.1 to obtain solute transport equations for hydrocarbon, oxygen and microorganisms. The hydrocarbon is assumed to sorb onto the solid surfaces following a linear sorption

3 Conservation equations — inter-related

isotherm. The resulting equations are (Borden and Bedient 1986)

$$\frac{\partial H}{\partial t} = \frac{1}{r_h}\left(D_h \frac{\partial^2 H}{\partial x^2} - v_x \frac{\partial H}{\partial x}\right) - \frac{h_h M_t}{r_h}\left(\frac{H}{K_s + H}\right)\left(\frac{O}{K_c + O}\right) \qquad (3.62)$$

$$\frac{\partial O}{\partial t} = D_o \frac{\partial^2 O}{\partial x^2} - v_x \frac{\partial O}{\partial x} - k_h M_t F \left(\frac{H}{K_s + H}\right)\left(\frac{O}{K_c + O}\right) \qquad (3.63)$$

$$\frac{\partial M_t}{\partial t} = \frac{1}{r_m}\left(D_t \frac{\partial^2 M_t}{\partial x^2} - v_x \frac{\partial M_t}{\partial x}\right) + h_h M_t Y \left(\frac{H}{K_s + H}\right)\left(\frac{O}{K_c + O}\right) + \frac{k_s Y C_{oc}}{r_m} - b M_t \qquad (3.64)$$

where

M_t = concentration of aerobic microbes in solution

r_h = retardation factor for hydrocarbon

r_m = microbial retardation factor

v_x = average linear ground-water velocity

ANAEROBIC

Some microorganisms can degrade hydrocarbons in the absence of oxygen. These microbes use another electron acceptor, such as nitrate (Major, Mayfield, and Barker 1988). Anaerobic decomposition of hydrocarbons can be described by another variation of the Monod function, which describes two-step catalytic chemical reactions (Bouwer and McCarty 1984). This function is

1 Rate law

$$\frac{dH}{dt} = -h_a M\left(\frac{H}{K_s + H}\right) \qquad (3.65)$$

where

M_t = total mass of anaerobic microbes

h_{va} = maximum hydrocarbon utilization rate per unit mass of anaerobic microbes

K_s = half-maximum rate concentration of the hydrocarbon for anaerobic decay

The solute transport and decay equation for anaerobic biodegradation in the aqueous phase is

Conservation eqn.

$$\frac{\partial H}{\partial t} = \frac{1}{r_h}\left(D_h \frac{\partial^2 H}{\partial x^2} - v_x \frac{\partial H}{\partial x}\right) - \frac{h_a M}{r_h}\left(\frac{H}{K_s + H}\right) \qquad (3.66)$$

If the concentration of the hydrocarbon, H, is much less than K_s, the half-maximum rate concentration, then Equation 3.65 can be simplified to a linear form by neglecting H in the denominator (Bouwer and McCarty 1984). This results in a first-order decay term.

Under these conditions the solute-transport equation with anaerobic biodegradation becomes

$$\frac{dH}{dt} = -\left(\frac{h_a M}{K_s}\right) H \qquad (3.67)$$

$$\frac{\partial H}{\partial t} = \frac{1}{r_h}\left(D_h \frac{\partial^2 H}{\partial x^2} - v_x \frac{\partial H}{\partial x}\right) - \left(\frac{h_a M}{r_h K_s}\right) H \qquad (3.68)$$

Reaction term to equation.

LINEARIZED ANAEROBIC

Hydrocarbon conc $\ll K_a$ then rearrange as

$$\frac{dH}{dt} = -h_{va} M_a \left(\frac{H}{K_a + H}\right) \Rightarrow -h_{va} M_a \frac{H}{K_a}$$

6.7 COLLOID TRANSPORT

- □ Particles with diameters < 1 μm — Organic macromolecules
  - Metal complexes
  - Radioactive complexes (eg Plutonium)
- □ Colloids may sorb other solutes and mobilize
- □ Solutes with high retardation may sorb onto colloids and
  be mobile with very low retardation

  eg Plutonium — low R for colloids
  high R for soil

Main issues

1. Retardation/attenuation mechanisms do not operate
   a) No sorption and reduced concentration
   b) No slowing down due to v/R

2. Presence in monitoring wells may be due to
   accidental introduction of colloids — from equipment
   — precipitation of iron when O_2 added.

3. Some evidence to suggest some attenuation mechanisms
   a) Multiphase interfaces trap due to surface tension
      air/water   water/solvent etc.
   b) Non-neutral charges → electrical attraction & capture
      especially clays
   c) Mechanical straining in fine grained media.

4. Lack of attenuation make colloids attractive as Tracers (conservative)
   and unretarded.

HEAT FLOW — RETARDATION ANALOG

cold fluid, Q

COLD WARM HOT

porosity, n

$\left.\begin{array}{c}\rho_f, c_f \\ \rho_s, c_s\end{array}\right\}$ $\rho_a c_a = n\rho_f c_f + (1-n)\rho_s c_s$

Hydrodynamic front. Front of injected water

Thermal front. Cold to left, warm to right

$(cooled) - V_{th}$
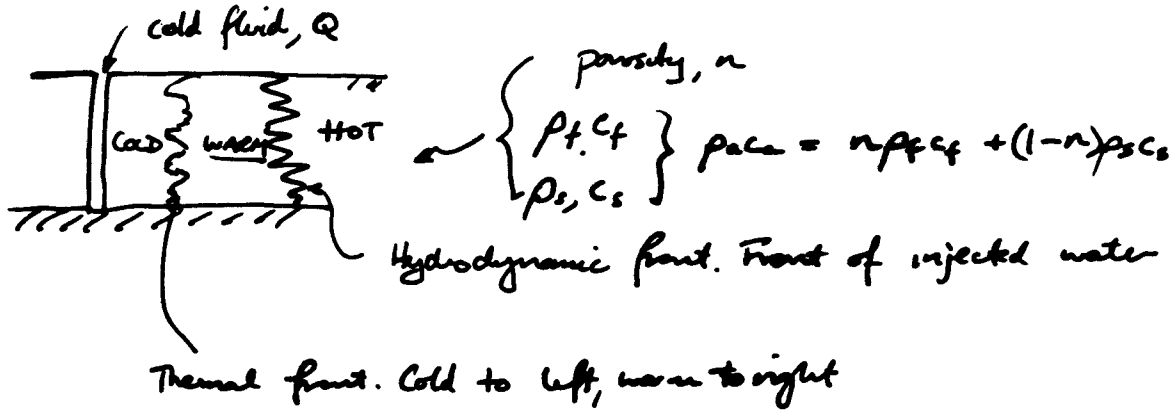
Relate volume of heated aquifer to volume injected and occupied by injected water; V_{hyd}.

Energy balance:

$$\rho_f c_f \, Q \, \Delta T = V_{th} \, \underbrace{\rho_a c_a}_{\text{heat capacity of aquifer}} \, \Delta T$$

$$Q = n \, V_{hyd}$$

$$\rho_f c_f \, n \, V_{hyd} \, \cancel{\Delta T} = V_{th} \left[n\rho_f c_f + (1-n)\rho_s c_s \right] \cancel{\Delta T}$$

$$\frac{V_{th}}{V_{hyd}} = \frac{n\rho_f c_f}{n\rho_f c_f + (1-n)\rho_s c_s} = \left[1 + \frac{(1-n)}{n} \underbrace{\frac{\rho_s c_s}{\rho_f c_f}}_{\sim \frac{1}{2}} \right]^{-1}$$

	V_{hyd}/V_{th}
$n = 10\%$	5.5
20%	3.0
30%	2.2

$\llcorner$ Analogous to retardation, R.

Reactive transport analog: $R_{mass} = \dfrac{V_{hyd}}{V_{tracer}}$; $R_{thermal} = \dfrac{V_{hyd}}{V_{thermal}}$

RETARDATION ANALOG FOR PDE

For a porous bed where $T_{solid} = T_{fluid}$ at all times — equilibrium

$$D^* \frac{\partial^2 T}{\partial x^2} - \rho_f c_f q_D \frac{\partial T}{\partial x} = [\rho_f c_f n + (1-n)\rho_s c_s] \frac{\partial T}{\partial t}$$

Darcy flux $q_D = -\frac{k}{\mu}\frac{\partial p}{\partial x}$

Aggregate thermal conductivity, $D^* = n D_f + (1-n) D_s$

Divide through both sides by $n\rho_f c_f$

$$\frac{D^*}{n\rho_f c_f}\frac{\partial^2 T}{\partial x^2} - \frac{\rho_f c_f q_D}{n\rho_f c_f}\frac{\partial T}{\partial x} = \underbrace{\frac{[\rho_f c_f n + (1-n)\rho_f c_s]}{n\rho_f c_f}}\frac{dT}{dt}$$

Thermal retardation, R_{th}.

Rearrange as:

$$\left(\frac{1}{R_{th}}\frac{D^*}{n\rho_f c_f}\right)\frac{\partial^2 T}{\partial x^2} - \left(\frac{1}{R_{th}}\frac{q_D}{n}\right)\frac{\partial T}{\partial x} = \frac{\partial T}{\partial t}$$

advection flux.

- Solve as Advection - dispersion equation
- Thermal front lags hydraulic front by factor, R_{th}.
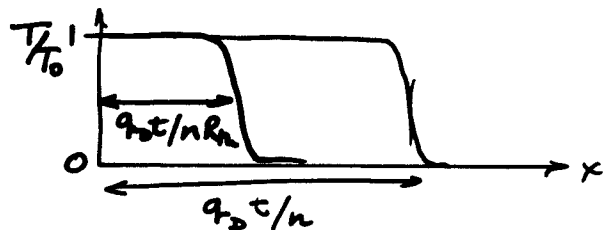
RESIDENCE TIME DISTRIBUTION (RTD) CURVES & ANALYSIS

USE: ① TO deconvolve tracer data (at output) to determine system parameters.

② Useful **only** if: Capture the full flow.

i.e. a producing well or output of reactor.

Other options are to fit model data to observed concentration profile.
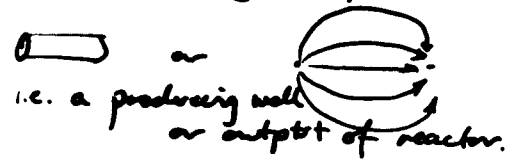
Classic references: Danckwerts

Levenspiel

$$E(t) = \frac{Q_{TOT} \, c(t)}{m_T}$$
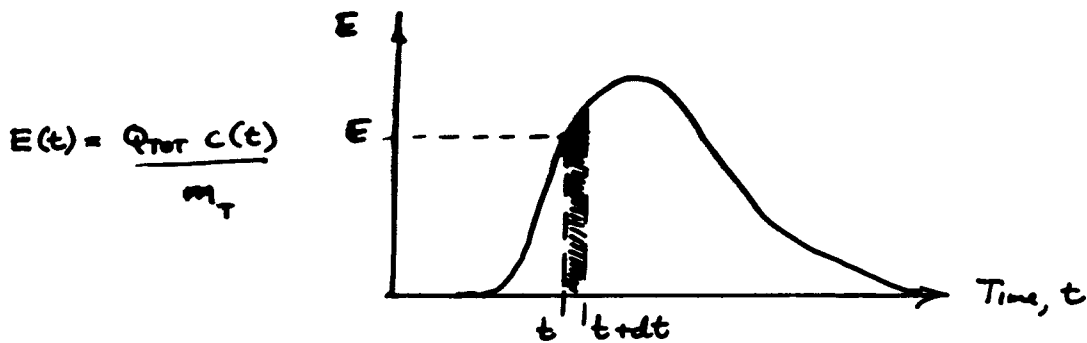
$E(t) \, dt =$ Fraction of fluid at exit stream that possessed a residence time between times t and $t + dt$

Q_{TOT} = Volumetric flow rate

m_T = Total mass injected

$c(t)$ = Concentration at any time

WHAT INFORMATION DO RTDs YIELD

Use $E(\Psi)$: Cumulative produced fluid volume, Ψ,

$$E(\Psi) = E(t)/Q_{TOT}$$

Allows a comparison of tests at various flow rates.

$E(\Psi) = \dfrac{C(t)}{m_T}$

Cumulative volume of fluid, Ψ

$$\Psi = Q_{TOT} \cdot t$$
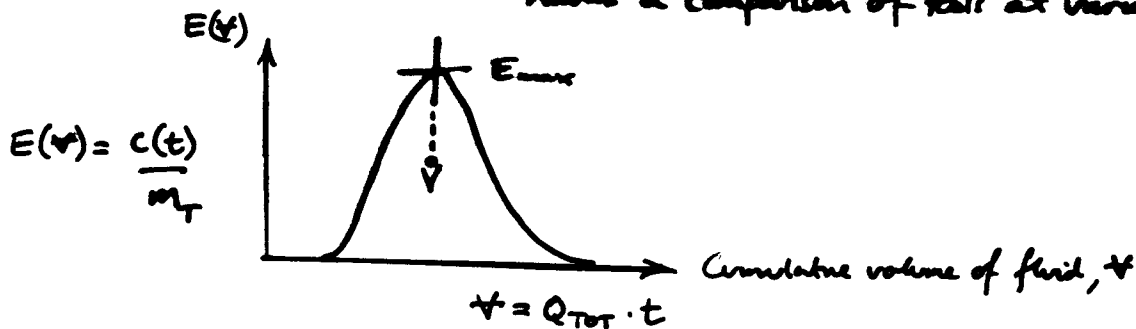
STATISTICAL PARAMETERS

Modal volume, $\overset{\circ}{\Psi}$.
 - Max probability of RTD curve
 - Gives volume of low impedance flow paths (cumulative)

Integral mean volume, $\langle\Psi\rangle$

$$\langle\Psi\rangle = \int_0^\infty \Psi \cdot E(\Psi) \, d\Psi$$

$\langle\Psi\rangle$ = total volume of flow through system – i.e. void volume.

but strongly influenced by tail.
∴ truncate tail.

Moments of distribution – i^{th} moment, $M_i(\bar{\Psi})$ with respect to volume, Ψ, is

$$M_i(\bar{\Psi}) = \int_0^\infty (\Psi - \bar{\Psi})^i \, E(\Psi) \, d\Psi$$

Variance, σ^2, to define the spread of the PDF

$$\sigma^2 = M_2(\langle\Psi\rangle) = \int_0^\infty (\Psi - \langle\Psi\rangle)^2 \, E(\Psi) \, dN$$

But gives more weight to the tail, especially as $i \uparrow$

Width at ½ height, $W_{1/2}$
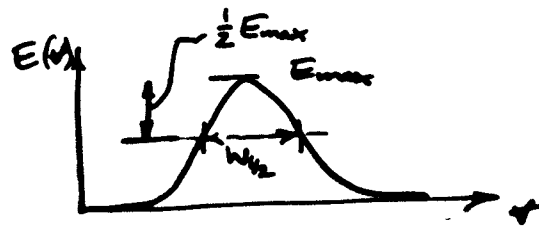
Defines dispersion along flow-path — qualitative.

$W_{1/2}$ is arbitrary — but can be related to dispersion coeff.
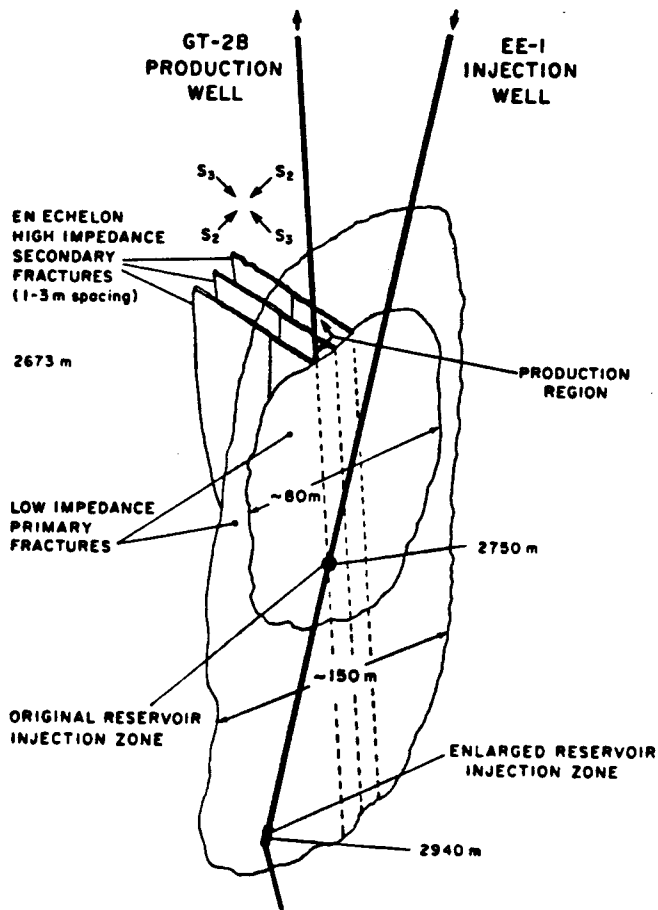
Fig. 3a. Conceptual schematic of the EE-1/GT-2 fracture system (adapted from Tester et al. [1982]). Schematic of the fracture-well bore geometry.
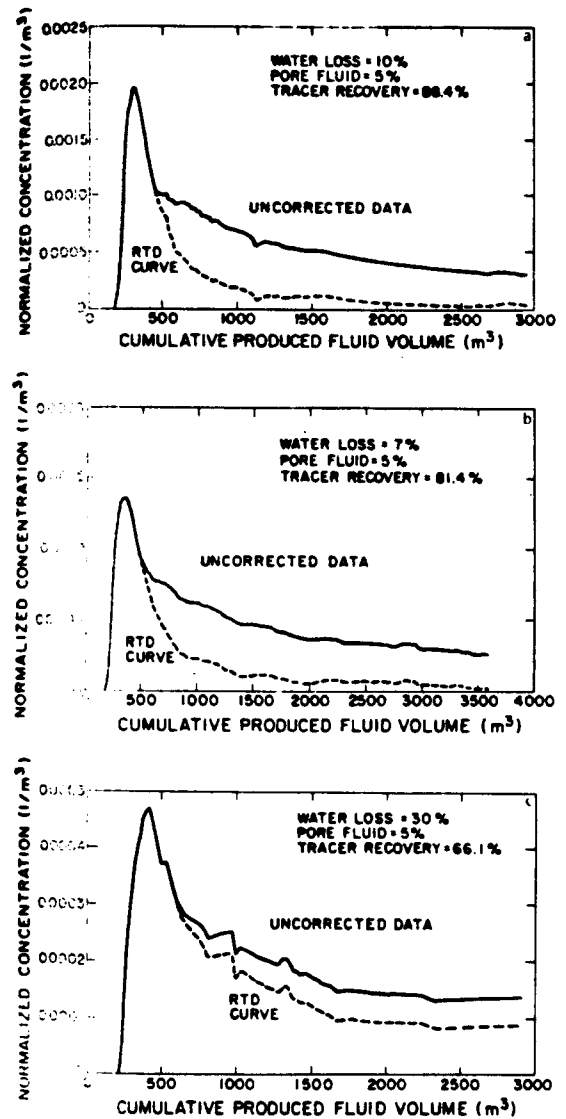
Fig. 4. Fenton Hill [82]Br tracer results, showing uncorrected data and the RTD curve calculated by subtracting the effect of fluid recirculation. Well bore plug flow delay volume of 161 m³ included in the response curves. (a) Experiment 217-A2, May 9, 1980. (b) Experiment 217-A3, September 3, 1980. (c) Experiment 217-A5, December 12, 1980.

TABLE 1. Summary of [82]Br Tracer Tests Conducted on the Fenton Hill Geothermal Reservoir

Date	Experiment	GT-2B Flow Rate, m³/s × 10⁻³	Water Loss, %	Tracer Recovery, %	Modal Volume $\hat{V}$,* m³	Volumetric Width at 1/2 Height, m³	Integral Mean Volume $\langle V \rangle$,*† m³
May 9, 1980	217-A2	5.9	10	88.4	161	227	1311
Sept. 3, 1980	217-A3	5.7	7	81.4	178	323	1845
Dec. 2, 1980	217-A4	5.1	40	···	187	303	···
Dec. 12, 1980	217-A5	8.1	30	66.1	266	479	2173

*Well bore plug flow delay volume of 161 m³ subtracted from measured values.
†Calculated assuming an exponentially decaying tail (see Appendix B for details).

APPROACHES TO REACTIVE TRANSPORT MODELING

1. <u>Pseudo-reactive using linear isotherms</u>
     - Retardation approach → gives chromatographic effect
     - Adsorption of monolayer of components at sorption sites
     - No pore clogging or dissolution
     - Multi-component retardation possible, but no reaction/interaction

2. <u>First order reaction with a single component</u>
     - Reaction rate law defines rate of precipitation/dissolution
     - Dissolution/precipitation may be used to update
          pore volume/surface area/permeability

3. <u>Reaction with multiple reacting components</u>

     - Complex interacting solutes
     - Precipitation/dissolution

General approaches of 2. & 3.
          1. Determine $\partial c/\partial t$ in transport (spatial)
          2. Determine $\partial c/\partial t$ in species due to reaction.

PSEUDO-REACTIVE SYSTEM — "RETARDATION" APPROACH

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - \frac{v_d}{n}\frac{\partial c}{\partial x} - \frac{\rho_b}{n}\frac{\partial c^*}{\partial t}$$

concentration on mineral surfaces

Linear isotherm:

(Aqueous) c

K_d

c^* (solid)
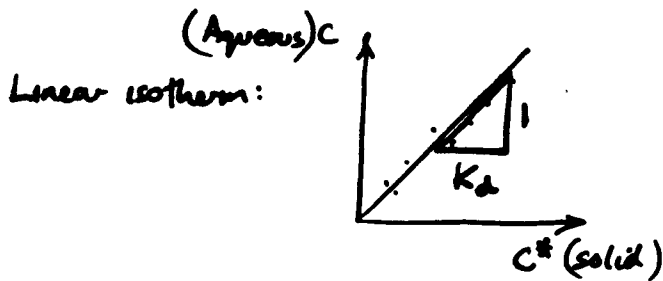
$$\frac{\partial c^*}{\partial t} = \frac{\partial c^*}{\partial c}\frac{\partial c}{\partial t} \Rightarrow K_d\frac{\partial c}{\partial t}$$

Replacing $\frac{\rho_b}{n}\frac{\partial c^*}{\partial t}$ yields a modified transport equation

$$\left(1 + \frac{\rho_b}{n}K_d\right)\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - \frac{v_x}{n}\frac{\partial c}{\partial x}$$

R = retardation coefficient

$$\frac{\partial c}{\partial t} = \frac{D}{R}\frac{\partial^2 c}{\partial x^2} - \frac{v_x}{Rn}\frac{\partial c}{\partial x}$$

c/c_0

Retarded at time, t.

Unretarded $R=1$ at time, t

$\frac{1}{2}$

0

x

$l = \frac{v}{n}\cdot t$

$l = \frac{v}{Rn}t$

FIRST ORDER REACTION — SINGLE COMPONENT

Dissolution/Precipitation of Quartz

$$H_4SiO_4 (aq) = SiO_2 (q) + 2H_2O (l) \qquad (1) \qquad \text{Stochiometric reaction}$$

$$\left(\frac{\partial c}{\partial t}\right)_{Rxn} = -k(c - c_{eq}) \qquad (2) \qquad \text{Rate law}$$

equilibrium concentration — no precip./dissol.

Transport Equation (one component) for fluid phase.

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - \frac{V_x}{n}\frac{\partial c}{\partial x} + \left(\frac{\partial c}{\partial t}\right)_{Rxn}$$

Translate to FE statement:

$$\int_V \underline{b}^T \underline{b}\, dV\, \underline{\dot{c}} + D\int_V \underline{a}^T \underline{a}\, dV\, \underline{c} + \frac{V_x}{n}\int_V \underline{b}^T \underline{a}\, dV\, \underline{c} - k_1 \int \underline{b}^T \underline{b}\, dV (\underline{c} - \underline{c_{eq}}) = \underline{q}$$

$$\underline{K}_0\, \underline{\dot{c}} + D\underline{K}_{II}\underline{c} + \frac{V_x}{n}\underline{K}_I\underline{c} - k_1\underline{K}_0(\underline{c} - \underline{c_{eq}}) = \underline{q}$$

Separate terms for solution (implicit time stepping ($\lambda=1$)):

$$\left[\frac{1}{\Delta t}\underline{K}_0 + D\underline{K}_{II} + \frac{V_x}{n}\underline{K}_I - k_1\underline{K}_0\right]\underline{c}^{t+\Delta t} = \underline{q}^{t+\Delta t} + \frac{1}{\Delta t}\underline{K}_0\underline{c}^t$$

Mass   + Diffusion + Advection   + Dissol./Precip $-k_1\underline{K}_0\, \underline{c}^t_{eq}$
Accumulation

Solve for $\underline{c}$ with time
These are fluid concentrations of any species (quartz)
Similar to retardation approach.

Reaction with Multiple Reacting Components

See for example: Steefel & MacQuarrie in "Reactive Transport in Porous Media"
Ed Lichtner, P.C, Steefel, C.I. and Oelkers, E.H.
Mineralogical Soc. of Amer. 1996.

Basic Approach

1. Write a single equation for each species considered, as:
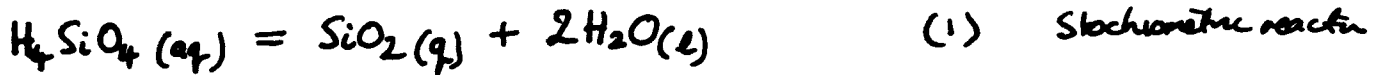
$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} - \frac{v_x}{n} \frac{\partial c_i}{\partial x} + R_i c_i$$

Reaction rate: $R_i c_i = \frac{\partial c_i}{\partial t} = -k_i(c - c_{eq})$

$\sim \frac{\partial c_i}{\partial t} = -k_i[c]$

Components are not necessarily independent

2. Solve sequentially as:

    1. Solve transport equation $\longrightarrow$ Evaluate $\underline{c}_i$ @ all nodes with $R_i = 0$

    2. ~~Evaluate~~ reaction term $\qquad \frac{\partial \underline{c}_i}{\partial t} = -k_i(\underline{c}_i - \underline{c}_{eq_i})$

$$\underline{c}_i^{\,n+1} \quad \underline{c}_i^{\,n} + \Delta t \left(\frac{\partial \underline{c}_i}{\partial t}\right)_{R+N}$$

— Repeat Step ①

FIRST-ORDER REACTION — SINGLE COMPONENT

Dissolution/Precipitation of quartz: $H_4SiO_4(aq) = SiO_{2(s)} + 2H_2O_{(l)}$ (1)

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ Stochiometric

Rate law: $\left(\dfrac{\partial c}{\partial t}\right)_{Rxn} = -k\,(c - c_{eq})$ $\qquad\qquad\qquad\qquad$ (2)

$$\frac{\partial c}{\partial t} = -k(c-c_{eq})$$

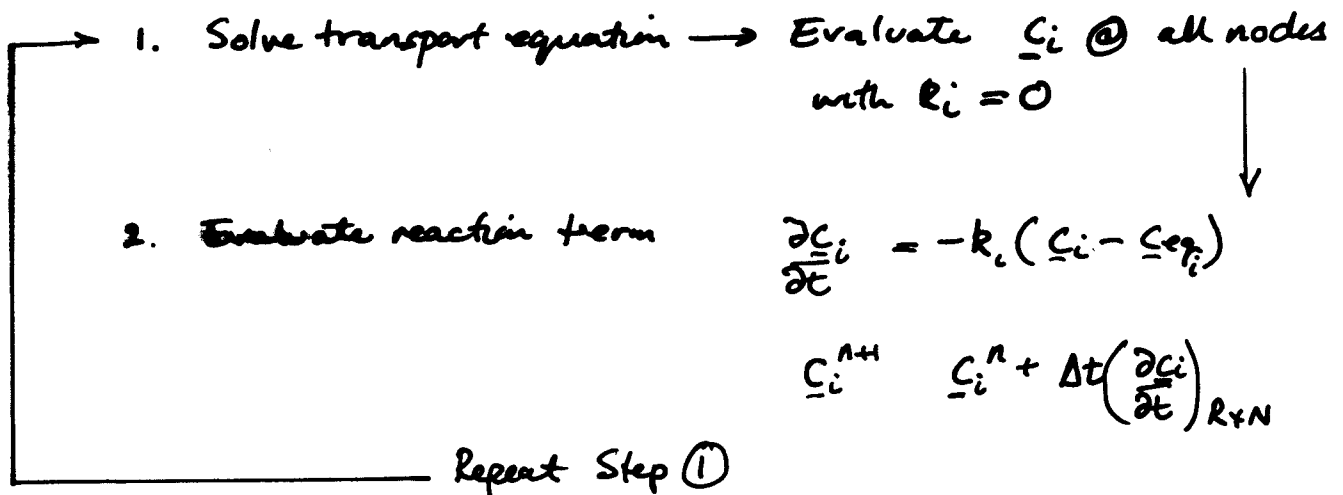Transport Equation: $\dfrac{\partial c}{\partial t} = D\dfrac{\partial^2 c}{\partial x^2} - \dfrac{v_x}{n}\dfrac{\partial c}{\partial x} + \dfrac{\partial c}{\partial t}\Big|_{Rxn}$

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - \frac{v_x}{n}\frac{\partial c}{\partial x} - k(c-c_{eq}) \quad \begin{cases} Pe = \dfrac{v\ell}{D} \\[2mm] Da = \dfrac{k\ell^2}{D} \end{cases}$$

Divide by D and multiply by ℓ^2

$$\frac{\ell^2}{D}\frac{\partial c}{\partial t} = \frac{\ell^2 \partial^2 c}{\partial x^2} - \frac{\ell^2 v_x}{Dn}\frac{\partial c}{\partial x} - \frac{\ell^2 k}{D}(c - c_{eq})$$

Define $t_D = tD/\ell^2$; Pe ; Da ; $x_D = x/\ell$

$$\frac{\partial c}{\partial t_D} = \frac{\partial^2 c}{\partial x_D^2} - \frac{Pe}{n}\frac{\partial c}{\partial x_D} - Da\,(c - c_{eq})$$

FIRST ORDER REACTION — SINGLE COMPONENT

Dissolution / Precipitation of Quartz

$$H_4SiO_4 \; (aq) = SiO_2 \; (q) + 2H_2O \; (l) \qquad (1) \qquad \text{Stoichiometric reaction}$$

$$\left(\frac{\partial c}{\partial t}\right)_{Rxn} = -k(c - c_{eq}) \qquad (2) \qquad \text{Rate law}$$

equilibrium concentration — no precip./dissol.

Transport Equation (one component) for fluid phase.

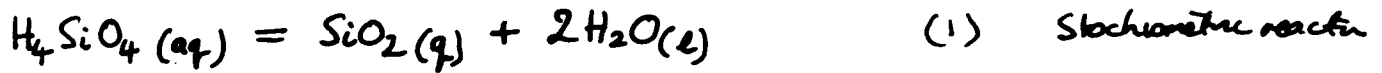$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - \frac{V_x}{n} \frac{\partial c}{\partial x} + \left(\frac{\partial c}{\partial t}\right)_{Rxn}$$

Translate to FE statement:

$$\int_V \underline{b}^T \underline{b} \, dV \, \underline{\dot{c}} + D \int_V \underline{a}^T \underline{a} \, dV \, \underline{c} + \frac{V_x}{n} \int_V \underline{b}^T \underline{a} \, dV \, \underline{c} - k_1 \int \underline{b}^T \underline{b} \, dV (\underline{c} - \underline{c}_{eq}) = \underline{q}$$

$$\underline{K}_0 \, \underline{\dot{c}} + D \, \underline{K}_{II} \underline{c} + \frac{V_x}{n} \underline{K}_I \underline{c} - k_1 \underline{K}_0 (\underline{c} - \underline{c}_{eq}) = \underline{q}$$

Separate terms for solution (implicit time stepping ($\lambda = 1$)):

$$\left[\frac{1}{\Delta t} \underline{K}_0 + D \underline{K}_{II} + \frac{V_x}{n} \underline{K}_I - k_1 \underline{K}_0 \right] \underline{c}^{t+\Delta t} = \underline{q}^{t+\Delta t} + \frac{1}{\Delta t} \underline{K}_0 \underline{c}^t$$

Mass   + Diffusion + Advection   + Dissol./Precip $- k_1 \underline{K}_0 \, \underline{c}_{eq}^t$
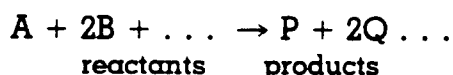Accumulation

Solve for $\underline{c}$ with time
These are fluid concentration of any species (quartz)
Similar to retardation approach.

2.4. THE RATE LAW

We can show experimentally that for the general irreversible reaction

$$A + 2B + \ldots \rightarrow P + 2Q \ldots$$
$$\text{reactants} \quad \text{products}$$

we can write the rate law,

$$\frac{d[A]}{dt} = -k[A]^a[B]^b[P]^p[Q]^q \ldots \tag{2-1}$$

where

$$\frac{d[A]}{dt} = \text{time rate of change in molar concentration of species A,}$$

$$k = \text{reaction rate constant, and}$$

$$a, b, p, q, \ldots = \text{constants}$$

In this book, [ ] is used to signify concentration in moles/liter. We may use concentration units other than moles/liter in the rate law but in doing so we should use the same concentration unit for each species and realize that both the numerical value and units of the reaction rate constant will differ from those found when molecular concentrations are used.

Using our knowledge of the stoichiometry of the reaction, that is, the relative number of moles of species reacting and the relative number of moles of products being formed as the reaction proceeds, we can state that

$$\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt} \ldots = \frac{-d[P]}{dt} = \frac{-1}{2}\frac{d[Q]}{dt} \ldots \tag{2-2}$$

because 1 mole of A reacts for every 2 moles of B that react, and so forth, and 1 mole of P is formed for every mole of A that reacts, and so forth. We can determine the *reaction order* from the rate law. The *overall* reaction order is

$$a + b + p + q \ldots \tag{2-3}$$

while the order *with respect to* A is a, the order with respect to B is b, and so forth. If the reaction is irreversible, then $p, q, \ldots$, the exponents of the product concentration, are usually zero. For example, if

$$\frac{d[A]}{dt} = -k[A][B]^2$$

then we would say that the reaction was first order with respect to A, second order with respect to B, and third order overall. It is important to note that reaction order is generally not determined by the stoichiometry of the overall reaction. Laboratory experimentation is necessary to determine the order.

The following example illustrates several points that are important for a good understanding of the rate law.

Integrated forms of the **rate law are very** useful for analyzing rate data to determine reaction rate constants and reaction order. Let us first consider the irreversible reaction

$$A \rightarrow products$$

which has the rate law

$$\frac{d[A]}{dt} = -k[A]^n$$

To determine the behavior of [A] as a function of time, we must integrate the rate expression with respect to time. We will do this for several values of the reaction order, n. When $n = 0$, the reaction is zero order, and

$$\frac{d[A]}{dt} = -k[A]^0 = -k \tag{2-4}$$

Upon integrating, we obtain

$$[A] = [A]_0 - kt \tag{2-5}$$

where $[A]_0 =$ the concentration of A at $t = 0$, that is, the initial concentration of A. The *half-life*, $t_{1/2}$, or time for 50 percent of the initial concentration to react can be obtained from Eq. 2-5 by setting $[A] = 0.5 [A]_0$ when $t = t_{1/2}$. Then

$$t_{1/2} = \frac{0.5[A]_0}{k}$$

When $n = 1$, the reaction is *first order*, both with respect to A and overall, and we can write,

$$\frac{d[A]}{dt} = -k[A] \tag{2-6}$$

Rearranging Eq. 2-6 and solving the integral,

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -\int_0^t k \, dt$$

we find

$$\ln [A] = \ln [A]_0 - kt \tag{2-7}$$

or

$$[A] = [A]_0 e^{-kt} \tag{2-8}$$

Examination of Eq. 2-7 suggests that the rate constant k may be determined experimentally from a plot of ln [A] versus t, which has a slope of $-k$. Also, from Eq. 2-8, when $[A] = 0.5 [A]_0$, we find the half-life to be

$$t_{1/2} = \frac{0.693}{k}$$

If the reaction is greater than first order, then we can write

$$\frac{d[A]}{dt} = -k[A]^n \tag{2-9}$$

Reaction with Multiple Reacting Components

See for example: Steefel & Mac Quarrie in "Reactive Transport in Porous Media"
Ed Lichtner, P.C, Steefel, C.I. and Oelkers, E.H.
Mineralogical Soc. of Amer. 1996.

Basic Approach

1. Write a single equation for each species considered, as:

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} - \frac{v_x}{n} \frac{\partial c_i}{\partial x} + R_i c_i$$

Reaction rate: $R_i c_i = \frac{\partial c_i}{\partial t} = -k_i(c - c_{eq})$

$\sim \frac{\partial c_i}{\partial t} = -k_i[c]$

Components are not necessarily independent

2. Solve sequentially as:

1. Solve transport equation $\longrightarrow$ Evaluate $\underline{c}_i$ @ all nodes with $R_i = 0$

2. Evaluate reaction term

$$\frac{\partial \underline{c}_i}{\partial t} = -k_i(\underline{c}_i - \underline{c}_{eq_i})$$

$$\underline{c}_i^{n+1} \quad \underline{c}_i^n + \Delta t \left(\frac{\partial \underline{c}_i}{\partial t}\right)_{R+N}$$

Repeat Step ①
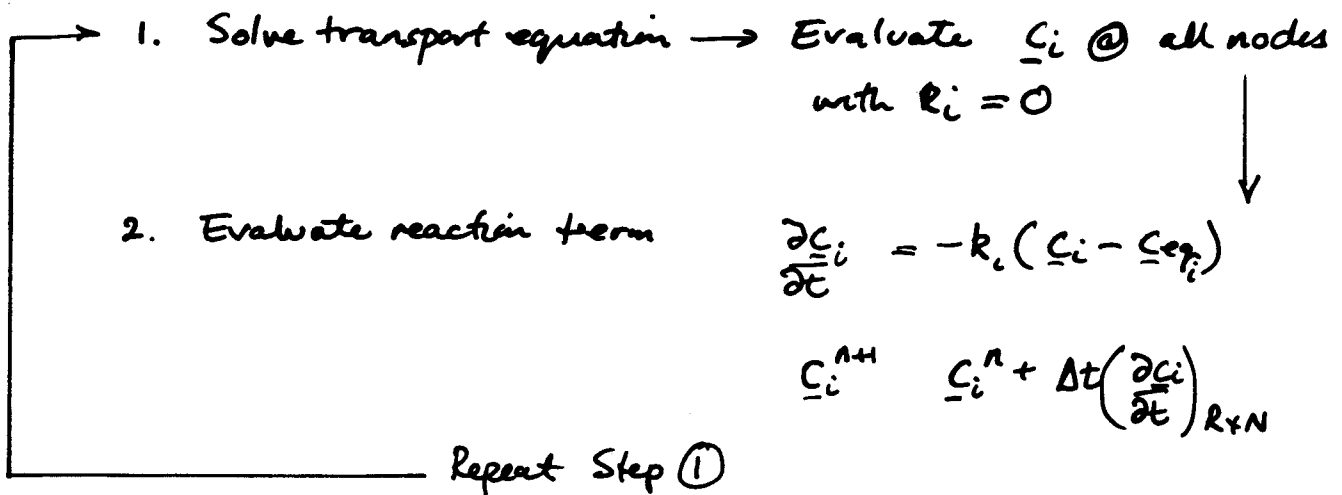
Reaction Rates

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (c_i \mathbf{u}) - \nabla \cdot (D_i \nabla c_i) = R_i \tag{1}$$

For the reaction:

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C \tag{2}$$

$$\begin{aligned} \text{Forward rate} \quad &= \quad k_1[A][B] \\ \text{Reverse rate} \quad &= \quad k_2[C] \end{aligned} \tag{3}$$

At equilibrium: $\qquad$ Forward rate = Reverse rate

$$k_1[A][B] = k_2[C] \tag{4}$$

$$\therefore \quad [A][B] = \frac{k_2}{k_1}[C] \tag{5}$$

For closed system and one mole each of [A] and of [B], with $k_1 = 1$ and $k_2 = 10$, then:

$$\frac{[A][B]}{[C]} = \frac{(1-X)^2}{X} = \frac{10}{1} \tag{6}$$

And $(1-X) = [A] = [B] = 0.916$ and X=[C] = 0.0839.

Implementation:

$$\begin{aligned} R_A \quad &= \quad -k_1[A][B] \quad + \quad k_2[C] \\ R_B \quad &= \quad -k_1[A][B] \quad + \quad k_2[C] \\ R_C \quad &= \quad +k_1[A][B] \quad - \quad k_2[C] \end{aligned} \tag{7}$$

Generalized:

$$R_i = -k_i^f \prod_{j=1}^{N} [c_j^f]^{\alpha_j^r} + k_i^r \prod_{j=1}^{N} [c_j^r]^{\alpha_j^r} \tag{8}$$

Heats of reaction:

$$H_i = R_i \Delta H_i \tag{9}$$

And heat balance requires:

$$\rho c \frac{\partial T}{\partial t} + \nabla \cdot (T\mathbf{u}) - \nabla \cdot (\lambda \nabla T) = H_i \tag{10}$$

REACTION ALGORITHMS FOR MULTICOMPONENT SYSTEMS

Mathematical descriptions of reaction systems

The multicomponent, multi-species systems typical of those which occur in porous media require some special treatment, both because they involve multiple unknowns and because they are usually nonlinear. The mathematical description used, however, will depend on what form the reactions in the system are assumed to take. It is instructive to derive a general approach to handle multicomponent, multi-species reactive systems. Formulations for arbitrarily complex reaction systems characterized by both equilibrium and non-equilibrium reactions have been presented by Lichtner (1985), Lichtner (this volume), Friedly and Rubin (1992), Sevougian et al. (1993), and Chilakapati (1995). A clear discussion of one possible way of doing so is given by Chilakapati (1995). His approach begins with the most general case, a set of ordinary differential equations for each species in the system and reactions between the species described by kinetic rate laws. A system containing N_{tot} species and N_r reactions can be expressed as
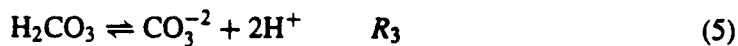
$$\mathbf{I} \cdot \frac{d\mathbf{C}}{dt} = \nu \cdot \mathbf{R}. \tag{1}$$

The raised dot indicates matrix multiplication. $\mathbf{I}$ is the identity matrix of dimension $N_{tot} \times N_{tot}$, $\mathbf{C}$ is the vector of solute concentrations of length N_{tot}, ν is a matrix of dimension $N_{tot} \times N_r$, and $\mathbf{R}$ is a vector of length N_r. For example, the matrix ν and the vector $\mathbf{R}$ have the form

$$\nu = \begin{bmatrix} \nu_{1,1} & \nu_{1,2} & \cdots & \nu_{1,N_r} \\ \nu_{2,1} & \nu_{2,2} & \cdots & \nu_{2,N_r} \\ \vdots & \cdots & \cdots & \vdots \\ \nu_{N_{tot},1} & \nu_{N_{tot},2} & \cdots & \nu_{N_{tot},N_r} \end{bmatrix} \qquad \mathbf{R} = \begin{bmatrix} R_1 \\ R_2 \\ \cdots \\ R_{N_r} \end{bmatrix}. \tag{2}$$

The multiplication of the identity matrix by the derivatives of the individual species concentrations results in an ODE of similar form for each of the species in the system.

As an example, consider an aqueous system consisting of Ca^{+2}, H^+, OH^-, CO_3^{-2}, HCO_3^-, H_2CO_3, and $CaCO_3(s)$ (calcite). We ignore H_2O for the sake of conciseness. In addition, we assume that the following reactions occur, without yet specifying whether they are to be considered equilibrium or kinetically-controlled reactions,

$$CaCO_3 \rightleftharpoons Ca^{+2} + CO_3^{-2} \qquad R_1 \tag{3}$$

$$HCO_3^- \rightleftharpoons CO_3^{-2} + H^+ \qquad R_2 \tag{4}$$

$$H_2CO_3 \rightleftharpoons CO_3^{-2} + 2H^+ \qquad R_3 \tag{5}$$

$$H^+ + OH^- \rightleftharpoons H_2O \qquad R_4. \tag{6}$$

In the above equations R_i symbolizes the rate expression for reaction i. We also make no assumptions at this stage about whether the set of reactions included are linearly independent (although the reactions listed above are). We have shown the reactions to be reversible here (thus the symbol $\rightleftharpoons$) but the results below apply whether the reactions are irreversible or reversible since at this stage, one can think of the reaction rates as simply time-dependent expressions of the mole balances inherent in a balanced chemical reaction. The reversibility or lack thereof only determines whether the sign of the reaction rate can change. The term *reversible* is generally used by thermodynamicists to refer to equilibrium reactions (Lichtner, this volume), although we prefer to use it to refer to reactions which are sufficiently close to equilibrium that the backward reaction is important. It is quite possible in a steady-state flow system, for example, for backward reactions to be important and yet not to be at equilibrium (e.g. Nagy et

al., 1991; Nagy and Lasaga, 1992; Burch et al., 1993). According to this definition, the term *irreversible* is used for those reactions which proceed in only one direction (i.e. those that can be represented with a unidirectional arrow, $\longrightarrow$).

For our example aqueous system, the rates for the individual species can be written

$$\frac{d[\text{H}_2\text{CO}_3]}{dt} = -R_3 \tag{7}$$

$$\frac{d[\text{HCO}_3^-]}{dt} = -R_2 \tag{8}$$

$$\frac{d[\text{CaCO}_3]}{dt} = -R_1 \tag{9}$$

$$\frac{d[\text{OH}^-]}{dt} = -R_4 \tag{10}$$

$$\frac{d[\text{H}^+]}{dt} = R_2 + 2R_3 - R_4 \tag{11}$$

$$\frac{d[\text{Ca}^{+2}]}{dt} = R_1 \tag{12}$$

$$\frac{d[\text{CO}_3^{-2}]}{dt} = R_1 + R_2 + R_3. \tag{13}$$

In matrix form the system of equations becomes

$$
\begin{bmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
\frac{d[\text{H}_2\text{CO}_3]}{dt} \\
\frac{d[\text{HCO}_3^-]}{dt} \\
\frac{d[\text{CaCO}_3]}{dt} \\
\frac{d[\text{OH}^-]}{dt} \\
\frac{d[\text{H}^+]}{dt} \\
\frac{d[\text{Ca}^{+2}]}{dt} \\
\frac{d[\text{CO}_3^{-2}]}{dt}
\end{bmatrix}
=
\begin{bmatrix}
0 & 0 & -1 & 0 \\
0 & -1 & 0 & 0 \\
-1 & 0 & 0 & 0 \\
0 & 0 & 0 & -1 \\
0 & 1 & 2 & -1 \\
1 & 0 & 0 & 0 \\
1 & 1 & 1 & 0
\end{bmatrix}
\begin{bmatrix}
R_1 \\
R_2 \\
R_3 \\
R_4
\end{bmatrix}
\tag{14}
$$

As written in Equation (14), the stoichiometric reaction matrix, v, is referred to as being in *canonical* form (Smith and Missen, 1982; Lichtner, 1985; Lichtner, this volume). The system of equations is partitioned into the first four rows where the associated species (H_2CO_3, HCO_3^-, $\text{CaCO}_3(\text{s})$, and OH^-) are involved in only one reaction while in the remaining three rows the species are involved in multiple reactions. The first four species are referred to as secondary or non-component species, while the last three are the primary or component species (Lichtner, this volume). These are also referred to as *basis* species because they form a basis which spans the concentration space. In this example, we have written all of the carbonate reactions using the species CO_3^{-2} precisely so as to restrict all of the other carbonate species to involvement in a single reaction. This is an essential first step in obtaining either the canonical formulation (Lichtner, 1985; Lichtner, this volume) or to writing the reactions in *tableaux* form (Morel and Hering, 1993), both of which assume that one is dealing with a set of linearly independent reactions, but it is not essential for what follows below. The procedure will also work if, for example, the formation of H_2CO_3 involved H^+ and HCO_3^- rather than 2 H^+ and CO_3^{-2}, although we will not obtain the conserved quantities (total H^-, total CO_3^{-2}, etc.) found in the tableaux method without additional manipulations.

The system of ODEs could be solved directly in the form of Equation (14) if the reactions are all described with kinetic rate laws. Alternatively, one can apply a Gauss-Jordan elimination

process to the matrix v and simultaneously to the identity matrix I until there are no pivots left (Chilakapati, 1995). The resulting transformed set of ODEs is now

$$M \cdot \frac{dC}{dt} = v^* \cdot R \tag{15}$$

which partitions the system of equations into N_r ODEs associated with reactions and N_c conservation laws with zero right-hand sides (i.e. no associated reactions). The number of conservation laws or mole balance equations is equal to

$$N_c = N_{tot} - \text{rank of } v = N_{tot} - N_r. \tag{16}$$

N_r, therefore, refers to the number of *linearly independent* reactions between the species in the system. For the sake of clarity, we make the first N_r rows of the matrix M the ODEs with associated reactions and the next N_c rows the conservation equations, so that the left hand of Equation (15) takes the form

$$\begin{bmatrix} M_{1,1} & \cdots & M_{1,N_r+N_c} \\ \vdots & \cdots & \vdots \\ M_{N_r,1} & \cdots & M_{N_r,N_r+N_c} \\ M_{N_r+1,1} & \cdots & M_{N_r+1,N_r} \\ \vdots & \cdots & \vdots \\ M_{N_r+N_c,1} & \cdots & M_{N_r+N_c,N_r+N_c} \end{bmatrix} \begin{bmatrix} \frac{dC_1}{dt} \\ \vdots \\ \frac{dC_{N_r}}{dt} \\ \vdots \\ \frac{dC_{N_r+N_c}}{dt} \end{bmatrix} \tag{17}$$

In our example, the Gauss-Jordan elimination is carried out on the the matrix v on the right hand side of Equation (14) and the same row transformations are applied to the identity matrix, I, yielding

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 2 & 1 & 0 & -1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 1 & 0 \\ 1 & 1 & 1 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \frac{d[H_2CO_3]}{dt} \\ \frac{d[HCO_3^-]}{dt} \\ \frac{d[CaCO_3]}{dt} \\ \frac{d[OH^-]}{dt} \\ \frac{d[H^+]}{dt} \\ \frac{d[Ca^{+2}]}{dt} \\ \frac{d[CO_3^{-2}]}{dt} \end{bmatrix} = \begin{bmatrix} 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} R_1 \\ R_2 \\ R_3 \\ R_4 \end{bmatrix} \tag{18}$$

The stoichiometric reaction matrix, v^*, now consists of a nonsingular 4 by 4 matrix (N_r by N_r) and three rows of zeros corresponding to the N_c conservation equations. Writing out the ODEs in Equation (18), we find

$$\frac{d[H_2CO_3]}{dt} = -R_3 \tag{19}$$

$$\frac{d[HCO_3^-]}{dt} = -R_2 \tag{20}$$

$$\frac{d[CaCO_3]}{dt} = -R_1 \tag{21}$$

$$\frac{d[OH^-]}{dt} = -R_4 \tag{22}$$

Soln - us

$$M \cdot \frac{dc}{dt} = v^* \cdot R$$

Premultiply by $\underline{M}^{-1}$

$$\underline{M}^{-1}\underline{M} \cdot \frac{dc}{dt} = \underline{M}^{-1}\underline{v}^* \cdot \underline{R}$$

$$\frac{dc}{dt} = \underline{M}^{-1}\underline{v}^* \cdot \underline{R} \longrightarrow \text{Add in to transport equation}$$

$$\text{as } \left(\frac{dc}{dt}\right)_{R+N}.$$

Table 1. Tableaux for carbonate system, neglecting H_2O as a species and component.

		Components		
		H^+	Ca^{+2}	CO_3^{-2}
Species	H_2CO_3	2		1
	HCO_3^-	1		1
	$CaCO_3$		1	1
	OH^-	-1		
	H^+	1		
	Ca^{+2}		1	
	CO_3^{-2}			1

and

$$\frac{d}{dt}\left([H^+] + 2[H_2CO_3] + [HCO_3^-] - [OH^-]\right) = 0 \tag{23}$$

$$\frac{d}{dt}\left([Ca^{+2}] + [CaCO_3]\right) = 0 \tag{24}$$

$$\frac{d}{dt}\left([CO_3^{-2}] + [H_2CO_3] + [HCO_3^-] + [CaCO_3]\right) = 0. \tag{25}$$

From the example, it is apparent that we have eliminated the reactions in the equations originally corresponding to the species H^+, Ca^{+2}, and CO_3^{-2} by making use of the relations in the first four equations. The last three equations are mole balances for *total* H^+, Ca^{+2}, and CO_3^{-2}

$$TOTH^+ = [H^+] - [OH^-] + [HCO_3^-] + 2[H_2CO_3] \tag{26}$$

$$TOTCa^{+2} = [Ca^{+2}] + [CaCO_3] \tag{27}$$

$$TOTCO_3^{-2} = [CO_3^{-2}] + [H_2CO_3] + [HCO_3^-] + [CaCO_3]. \tag{28}$$

Note that the canonical form of the stoichiometric reaction matrix is identical to the *tableaux* form popularized by Morel and coworkers (Morel and Hering, 1993; Dzombak and Morel, 1990). By transposing the last three rows of the matrix M in Equation (17), we can write the matrix in tableaux form (Table 1).

The procedure has yielded expressions for the total concentrations of the N_c *primary* or *component* species. A more general form is given by

$$TOT_j = C_j + \sum_{i=1}^{N_r} v_{i,j} X_i \tag{29}$$

where C_j and X_i refer to the concentration of the primary and secondary species respectively. Note that the number of secondary species is equal to N_r, the number of linearly independent reactions in the system (i.e. the rank of the matrix v). Equation (27) and Equation (28) are recognizable as the total concentrations of calcium and carbonate respectively. The total concentration of H^+ is written in exactly the same form as the other equations, although its physical meaning is less clear because it may take on negative values due to the negative stoichiometric coefficients in the expression. The mole balance equation for total H^+ is just the *proton condition* equation referred to in many aquatic chemistry textbooks. Oxidation-reduction reactions are also easily handled with this method. If the redox reactions are written as whole cell reactions, there is no need in any application not involving an electrical current

(see Lichtner, this volume) to introduce the electron as an unknown. Writing the reactions as whole cell reactions allows redox reactions to be treated exactly like any other reaction.