Solute Transport
Theory & Hydrus applications

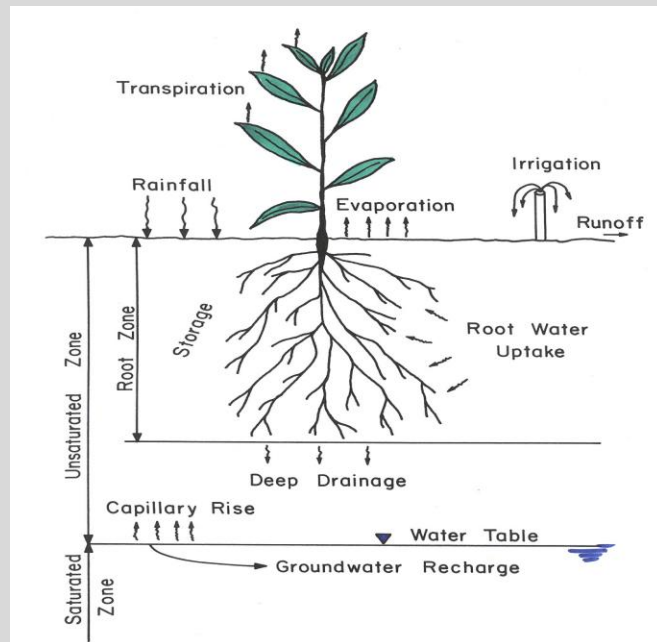## *Rien van Genuchten / Jan Hopmans*
UC Davis

HYD 210

Davis, May - 2011

Outline

◆ **Introduction: Water Flow and Solute Transport**

◆ **Solute Transport**
- – Governing transport equations
- – Advection, diffusion, dispersion, reactions (ADE)
- – Solute Break-Through Curves, Boundary conditions
- – Nonequilibrium transport (chemical, physical)
- – Decay chains

Agricultural Applications

Agricultural and Other Contaminants

- ◆ Fertilizers (nitrogen, phosphorus, potassium)
- ◆ Pesticides (insecticides, fungicides, herbicides)
- ◆ Hormones (estrodial)
- ◆ Pharmaceuticals (antibiotics)
- ◆ Fumigants (methyl bromide)
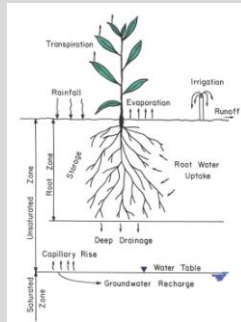
Salinization and reclamation of sodic soils

Other pollutants: Heavy metals, radionuclides, hydrocarbons, and many others
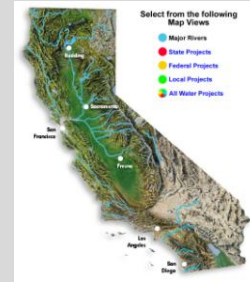
Increasing Spatial and Time Scales

Core or Lab   Plot   Field   Watershed

Water Flow - Richards Equation

Governing flow equation for one-dimensional isothermal flow in a variably saturated isotropic rigid porous medium:

$$\frac{\partial \theta(h)}{\partial t} = -\frac{\partial q}{\partial z} - S(h)$$

$$\hat{v} = \frac{q}{\theta}$$

$$\frac{\partial \theta(h)}{\partial t} = \frac{\partial}{\partial z}\left[K(h)\frac{\partial h}{\partial z} + K(h) \right] - S(h)$$

θ - volumetric water content [$L^3 L^{-3}$]
h - pressure head [L]
K - unsaturated hydraulic conductivity [LT^{-1}]
z - vertical coordinate positive upward [L]
t - time [T]
S - root water uptake [T^{-1}]

Solute Transport
Advection-Dispersion Equation - Simplified

One-dimensional chemical transport during transient flow in a variably-saturated rigid porous medium

$$\frac{\partial(\theta c)}{\partial t} + \frac{\partial(\rho s)}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial c}{\partial z} - qc\right) - r_c$$

c - solution concentration $[ML^{-3}]$
s - adsorbed concentration $[MM^{-1}]$
θ - water content $[L^3 L^{-3}]$
ρ - soil bulk density $[ML^{-3}]$
D - dispersion coefficient $[L^2 T^{-1}]$
q - volumetric flux $[LT^{-1}]$
r_c - rate constant representing reactions $[ML^{-3}T^{-1}]$

HOW DOES IT COME ABOUT ??????

Continuity Equation - Solute

$$\frac{\partial C_T}{\partial t} + \frac{\partial J_c}{\partial z} + r_c = 0$$

C_T total concentration of chemical in all forms, as mass of chemical per soil volume $[M/L^3]$

J_c chemical mass flux (mass of chemical flowing per unit area per unit time) $[M/L^2\,T]$

r_c the rate of loss of mass per unit volume by reactions or other sinks (e.g. plant uptake) $[M/L^3\,T]$

Total Solute Concentration

$$C_T = \rho_b C_a + \theta C_l + a C_g$$

C_a adsorbed concentration (mass per unit mass of dry soil), [M/M]

C_l dissolved concentration (mass per unit volume of soil solution), [M/L^3]

C_g gaseous concentration (mass of chemical vapor per unit volume of soil air), [M/L^3]

ρ_b bulk density of dry soil, [M/L^3]

θ volumetric water content, [L^3/L^3]

a volumetric air content, [L^3/L^3]

Total Flux of Chemical in Soil - J_c

$$J_c = J_l + J_g$$

J_c chemical mass flux (mass of chemical being transported per unit area per unit time) [M/L^2 T]

J_l solute liquid flux [M/L^2 T]

J_g flux of chemical vapor [M/L^2 T]

Fick's law for flux in gas phase:
   (Gaseous Diffusion only)

$$J_g = -\xi_g(a) D_g^a \frac{\partial C_g}{\partial z} = -D_g^s \frac{\partial C_g}{\partial z}$$

D_g^a gas diffusion coefficient in air

D_g^s gas diffusion coefficient in soil

ξ_g gaseous tortuosity factor

Total Solute Liquid Flux – J_l [M/L^3 T]

Total Liquid Flux:

$$J_l = J_{lc} + J_{lh} + J_{ld}$$

J_l solute flux [M/L^2 T]
J_{lc} liquid advective flux [M/L^2 T]
J_{lh} hydrodynamic dispersion flux [M/L^2 T]
J_{ld} liquid diffusion flux [M/L^2 T]

Solute Liquid Flux – Diffusion, J_{ld}

Diffusive flux:

$$J_l = J_{lc} + J_{lh} + J_{ld}$$

$$J_{ld} = -\xi_l(\theta) D_l^w \frac{\partial C_l}{\partial z} = -D_l^s \frac{\partial C_l}{\partial z}$$
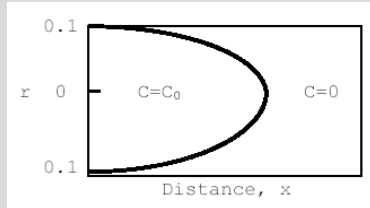
Tortuosity:

$$\xi_l(\theta) = \frac{\theta^{10/3}}{\theta_s^{\,2}}$$

J_{ld} liquid diffusion flux [M/L^2 T]
ξ_l liquid tortuosity factor [-]
D_l^w binary diffusion coefficient of the solute in water [L^2/T]
D_l^s soil liquid diffusion coefficient [L^2/T]
θ_s porosity [-]

Hydrodynamic Dispersion - J$_{lh}$

Fluxes inside a single pore:

Fluxes inside a system of pores:
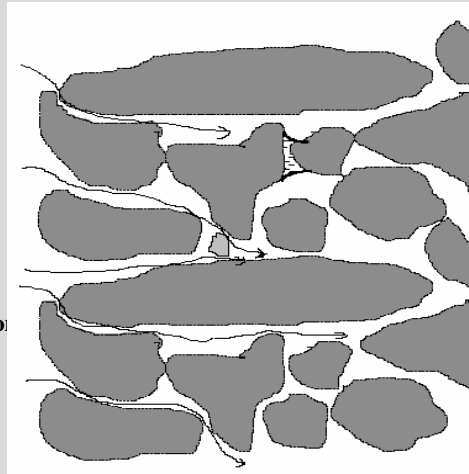

$$v = 2V_0 \left(1 - \frac{r^2}{a^2} \right)$$

V_0 – average flux
a – radius of the pore
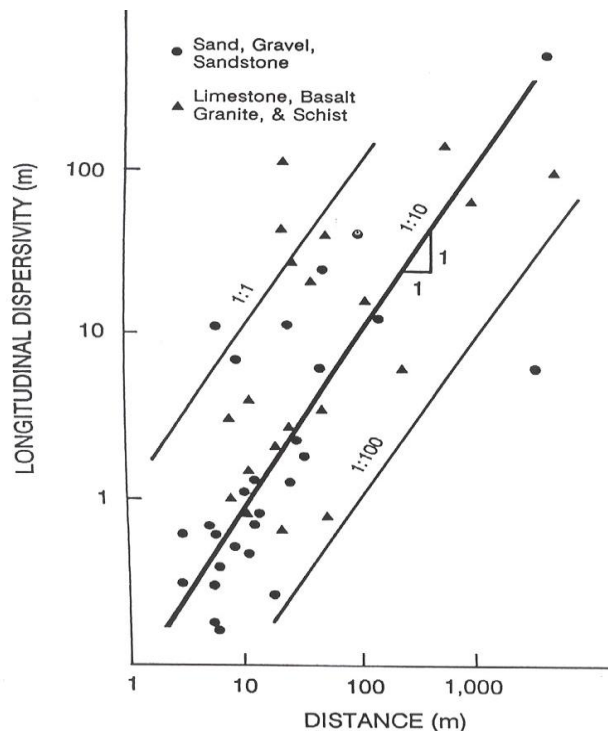
$$J_{lh} = -D_{lh} \frac{\partial C_l}{\partial z}$$
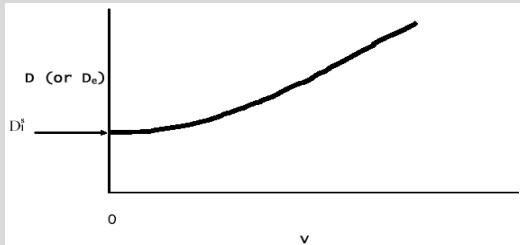
Dispersivity as a function of scale

$D_{hl} = \lambda v$

$\lambda = $ Dispersivity (L)

Total Effective Dispersion Coefficient

Many experiments have shown that D (or D_e) increases with the pore-water velocity, v:

$$D_e = D_{lh} + D_l^s = \lambda V + \frac{\theta^{10/3}}{\phi^2} D_l^w$$

Spreading due to hydrodynamic dispersion is due to complicated flow paths around soil particles, to differences in water velocity within single pores, and to differences in flow velocity between adjacent pores.

Total Solute Liquid Flux

Advective Flux: $J_{lc} = J_w C_l$

Hydrodynamic Flux: $J_{lh} = -D_{lh} \dfrac{\partial C_l}{\partial z}$

Solute Liquid Flux: $J_l = J_w C_l - D_{lh} \dfrac{\partial C_l}{\partial z} - D_l^s \dfrac{\partial C_l}{\partial z} = J_w C_l - D_e \dfrac{\partial C_l}{\partial z}$

J_l	solute flux [M/L^{2}T]
J_{lc}	liquid advective flux [M/L^{2}T]
J_{lh}	hydrodynamic dispersion flux [M/L^{2}T]
J_{ld}	liquid diffusion flux [M/L^{2}T]
J_w	water flux [L/T]
D_{lh}	hydrodynamic dispersion coefficient [L^2/T]: $D_{lh} = \lambda v$
λ	dispersivity [L]
D_l^s	soil liquid diffusion coefficient [L^2/T]
D_e	effective diffusion-dispersion coefficient [L^2/T]

General Solute Transport Equation

For the most general case where chemicals are present in the dissolved, sorbed and vapor phases, the chemical transport equation is obtained by combining the continuity equation for the total solute with the vapor and liquid flux densities and the reaction term to produce:

$$\frac{\partial C_T}{\partial t} = -\frac{\partial J_c}{\partial z} - r_c$$

$$\frac{\partial}{\partial t}\left(\rho_b C_a + \theta C_l + a C_g\right) =$$

$$= \frac{\partial}{\partial z}\left(\theta D \frac{\partial C_l}{\partial z}\right) + \frac{\partial}{\partial z}\left(D_g^s \frac{\partial C_g}{\partial z}\right) - \frac{\partial}{\partial z}(J_w C_l) - \left(\rho_b r_a + \theta r_l + a r_g\right)$$

Chemical Reactions

$$r_c = \rho_b r_a + \theta r_l + a r_g$$

r_c rate of loss of mass per unit volume by reactions or other sinks (e.g. plant uptake) $[M/L^3/T]$

r_a reactions in the sorbed phase per unit mass of soil $[M/M\,T]$

r_l reactions in the liquid phase per unit volume of water $[M/L^3\,T]$

r_g reactions in the gaseous phase per unit volume of air $[M/L^3\,T]$

Advection-Dispersion Equation (ADE)

When the vapor phase is negligible, C_g and r_g are zero, and the ADE becomes:

$$\frac{\partial}{\partial t}\left(\theta C + \rho_b C_a\right) = \frac{\partial}{\partial z}\left(\theta D \frac{\partial C_l}{\partial z}\right) - \frac{\partial}{\partial z}\left(J_w C_l\right) - \left(\theta r_l + \rho_b r_a\right)$$

For linear (first-order) decay such that $r = \mu c$:

$$\frac{\partial\left(\theta C_l + \rho C_a\right)}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial C_l}{\partial z}\right) - \frac{\partial}{\partial z}\left(J_w C_l\right) - \theta \mu_l C_l - \rho \mu_a C_a$$

μ: First-order transformation rate constant (1/T)
Can be related to half-life ($T_{1/2}$):

$$\mu = \frac{\ln(2)}{T_{1/2}}$$

One-Dimensional Equilibrium Transport

General Transport Equation; no production/decay

$$\frac{\partial(\theta c + \rho s)}{\partial t} = \frac{\partial}{\partial x}(\theta D \frac{\partial c}{\partial x}) - \frac{\partial qc}{\partial x}$$

Equilibrium Sorption ($s = k\, c$)

$$\frac{\partial(\theta R c)}{\partial t} = \frac{\partial}{\partial x}(\theta D \frac{\partial c}{\partial x}) - \frac{\partial qc}{\partial x}$$

$$R = 1 + \frac{\rho k}{\theta}$$

(Retardation Factor)

Steady-State Flow (homogeneous system; constant q, θ)

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

$$v = \frac{q}{\theta}$$

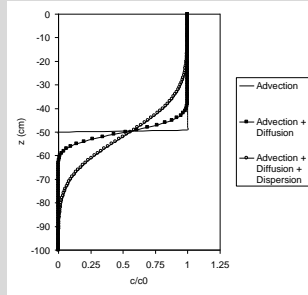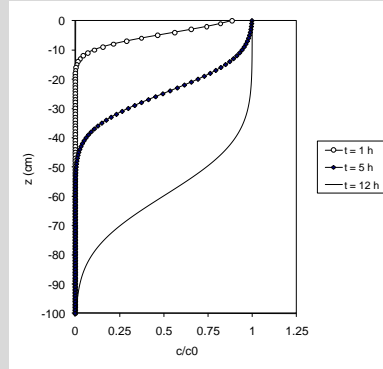# Effects of diffusion and advection on transport of solute

Figure 6.5 Effect of hydrodynamic dispersion and diffusion in dispersing a solute front at $t = 10$ h with a mean pore water velocity of 5 cm h^{-1}.
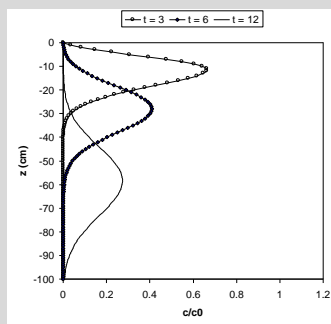

Pulse input of solute in soil column (v = 5 cm/hr)

Figure 6.14 Relative concentrations as a function of depth for times of 3, 6, and 12 h predicted by Equation 6.32 for a pulse input with $v = 5$ cm h^{-1} for $D_e = 10$ cm^2 h^{-1}.
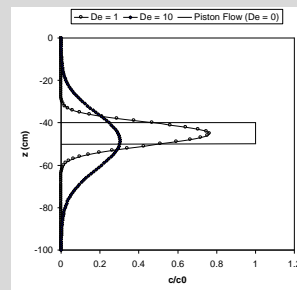

Figure 6.12 Relative concentrations as a function of depth predicted by Equation 6.32 after 10 h for a pulse input of 2 h duration with $v = 5$ cm h^{-1} and for $D_e = 1$ and 10 cm^2 h^{-1} compared to piston flow.

Effects of solute retardation on transport of solute
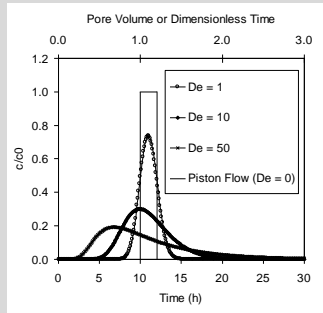

Figure 6.15 BTCs at a depth of 50 cm predicted by Equation 6.32 for a pulse input with $v = 5$ cm h^{-1} for $D_e = 1$, 10, and 50 cm^2 h^{-1} compared to piston flow plotted as a function of time (bottom axis) and as a function of pore volume or dimensionless time (top axis).

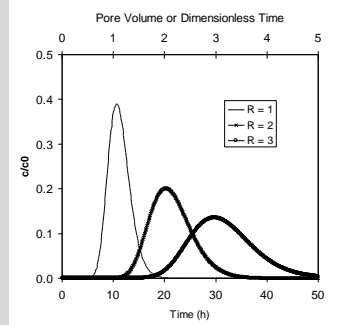Figure 6.19 BTCs for a depth of 50 cm for a pulse input of 2 h duration with $v = 5$ cm h^{-1}, $D_e = 5$ cm^2 h^{-1}, and $R = 1$, 2, and 3 using Equation 6.42 and Equation 6.32 as a function of time (bottom axis) and pore volume or dimensionless time (top axis).

Effects of solute decay on transport

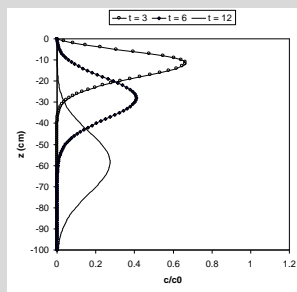Figure 6.14 Relative concentrations as a function of depth for times of 3, 6, and 12 h predicted by Equation 6.32 for a pulse input with $v = 5$ cm h^{-1} for $D_e = 10$ cm^2 h^{-1}.
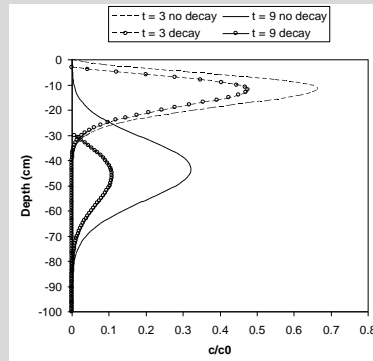

Figure 6.22 Relative concentration as a function of depth with and without decay for a pulse input after 3 and 9 h ($\mu = 0.1$ h^{-1}, $t_0 = 2$ h, $v = 5$ cm h^{-1}, $D_e = 10$ cm^2 h^{-1}, $R = 1$).

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   – **Nonequilibrium transport (chemical, physical)**
   – **Decay chains**

Soil Column Breakthrough Experiment
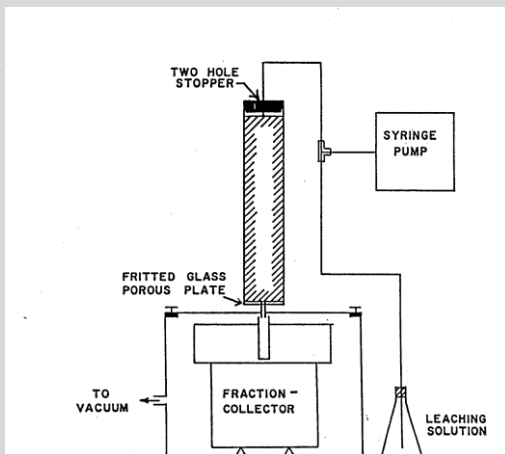
A plot of outflow concentration versus time is called an effluent curve, an outflow curve, or a **"breakthrough" curve** (representing the solute breaking through at the outflow end).
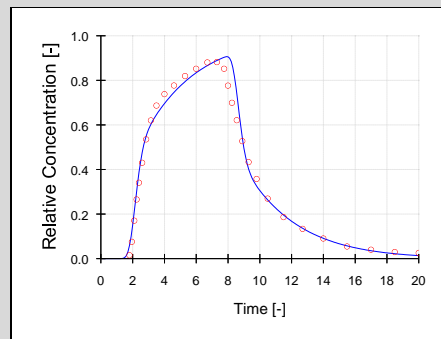
No sorption (tritium) versus sorption (Cr^6)

Bulls Eye
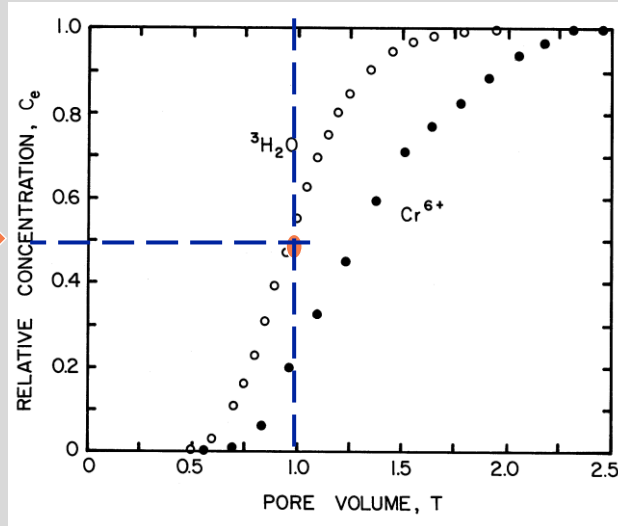
Schematic of Transport Experiment

Breakthrough curves are often expressed in Pore Volumes, *T* (dimensionless time) and relative concentration (dimensionless)

$$T = \frac{\text{Volume Effluent}}{\text{Total Volume Solution in Column}}$$

$$T = \frac{qAt}{\theta AL} = \frac{qt}{\theta L} = \frac{vt}{L}$$

Effect of Dispersion

The effect of dispersion on the breakthrough curve is to cause some early and late arrival of solute with respect to the breakthrough time. This deviation is due to diffusion and small-scale convection ahead of and behind the front moving at velocity *V* and becomes more pronounced as *D* becomes larger.

Outflow concentration versus time for a step change in solute input at t = O. Column length is 50 cm and water velocity V = 2 cm h^{-1}. Curves are for different values of D in cm^{2}h^{-1}.
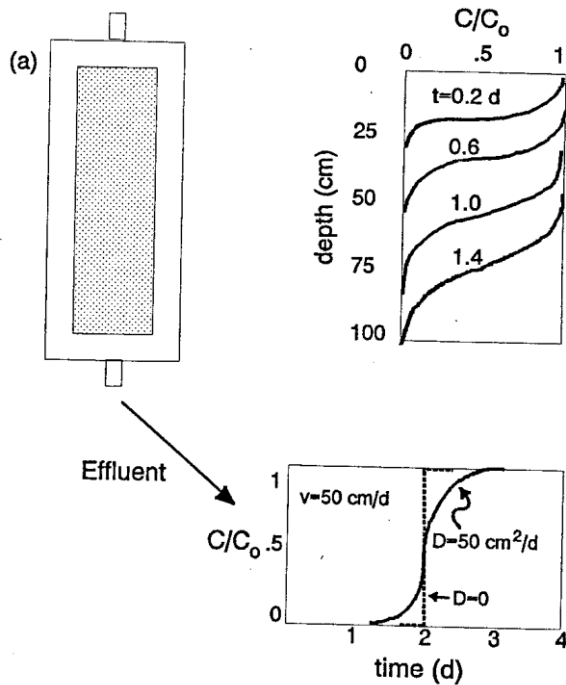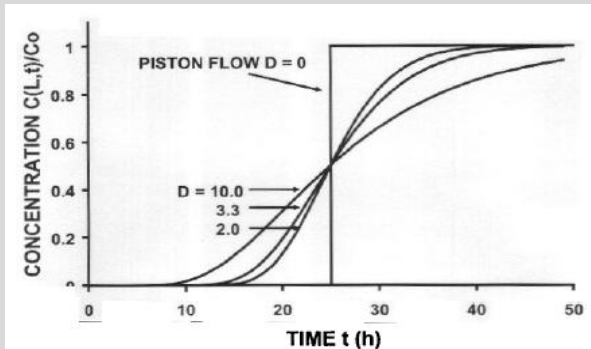
D = 0 => **Piston Flow**

$$C(L,t) = \frac{C_0}{2}\left[erfc\left(\frac{L-Vt}{\sqrt{4Dt}}\right) + \exp\left(\frac{VL}{D}\right) erfc\left(\frac{L+Vt}{\sqrt{4Dt}}\right)\right]$$

$$erfc(x) = \frac{2}{\sqrt{\pi}}\int_x^\infty \exp(-\xi^2)d\xi$$

Effect of Dispersion

Note that as *D* becomes larger,the pulse spreads out more and the pulse height decreases.

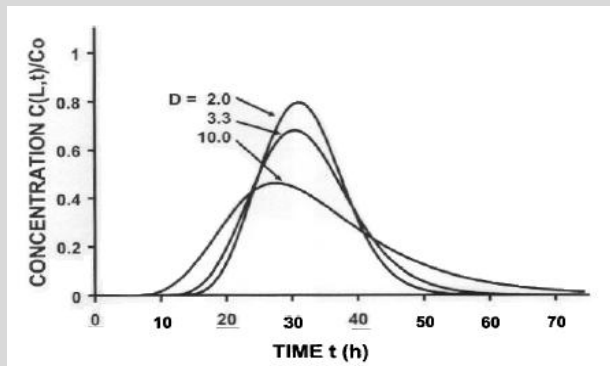Outflow concentration versus time for a narrow pulse of solute input at t = O. Column length is 50 cm and water velocity V = 2 cm h^{-1}. Curves are for different values of D in cm^{2}h^{-1}. (M_0 – solute mass)

$$C(L,t) = \frac{M_0 L}{2J_w\sqrt{2Dt^3}} erfc\left[-\frac{(L-Vt)^2}{2Dt}\right]$$

Effect of Sorption
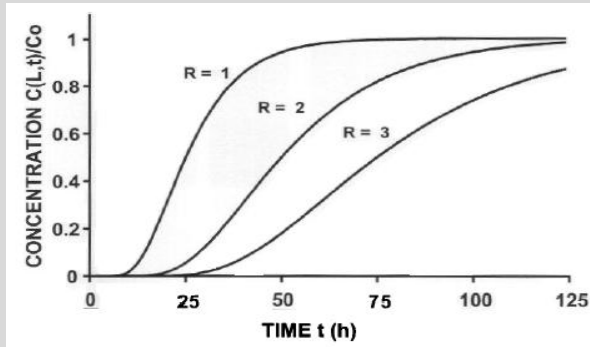
The breakthrough times increase as *R* increases, and the apparent amount of solute spreading of the outflow curves increases with *R* as well.

K_d is the distribution or partition coefficient. For linear isotherm:

$$C_a = K_d C_l$$

$$R = 1 + \frac{\rho_b K_d}{\theta}$$

Outflow concentration versus time of chemicals with different retardation factors for a step change of solute input at *t* = 0. Column length is 50 cm and water velocity *V* = 2 cm h^{-1}. Curves are for different values of *R (K_d)*.

Effect of Sorption of solute to soil

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

$$C_a = K_d C_l$$

$$R = 1 + \frac{\rho_b K_d}{\theta}$$

$$\frac{\partial c}{\partial t} = D_R \frac{\partial^2 c}{\partial z^2} - \overline{v}_R \frac{\partial c}{\partial z}$$

$$\overline{v}_R = \overline{v} / R$$ **where**
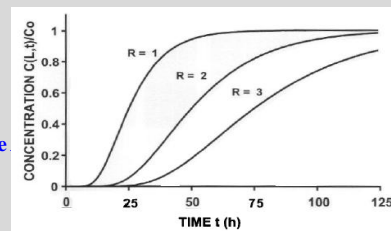
Sorption

Adsorption isotherms:

Linear:

Freundlich:

Langmuir:

k or K_d **– distribution coefficient**
[L³/M], [m³/kg, cm³/g]

Figure 7.4 Different shapes of adsorption isotherm.

One-Dimensional Equilibrium Transport

General Transport Equation; no production/decay

$$\frac{\partial(\theta c + \rho s)}{\partial t} = \frac{\partial}{\partial x}(\theta D \frac{\partial c}{\partial x}) - \frac{\partial qc}{\partial x}$$

Equilibrium Sorption (*s=k c*)

$$\frac{\partial(\theta R c)}{\partial t} = \frac{\partial}{\partial x}(\theta D \frac{\partial c}{\partial x}) - \frac{\partial qc}{\partial x}$$

$$R = 1 + \frac{\rho k)}{\theta}$$

(Retardation Factor)

Steady-State Flow (homogeneous system; constant *q, θ*)

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

Initial and Boundary Conditions

Initial Condition: $c(x,0)=C_i$

Inlet Boundary Conditions, at $x=0$:

$$c(0,t) = C_0 \qquad (-D\frac{\partial c}{\partial x} + v\,c)|_{x=0+} = v\,C_0$$

Outlet Boundary Condition: Finite ($x=L$) or semi-infinite ($x \to \infty$) system

$$\frac{\partial c}{\partial x}(L,t) = 0 \qquad \frac{\partial c}{\partial x}(\infty,t) = 0$$

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One-Site Chemical Nonequilibrium

$$\frac{\partial(\theta c)}{\partial t} = \frac{\partial}{\partial z}(\theta D \frac{\partial c}{\partial z} - qc) - \alpha\rho(kc - s)$$

$$\frac{\partial s}{\partial t} = \alpha(kc - s)$$

Effect of Nonequilibrium Sorption

When the time of contact is short compared to the time required for sorption, the assumption of instantaneous equilibrium between the adsorbed and dissolved chemical concentrations is not valid.

$$\rho_b \frac{\partial C_a}{\partial t} + \theta \frac{\partial C_l}{\partial t} = D_e \frac{\partial^2 C_l}{\partial z^2} - J_w \frac{\partial C_l}{\partial z}$$

$$\rho_b \frac{\partial C_a}{\partial t} = \alpha(K_d C_l - C_a)$$

α - a rate parameter that expresses the rate of mass transfer of chemical between the phases. Note that the rate of change of mass in the sorbed phase is assumed to be proportional to the deviation from equilibrium.

Outflow concentration versus pore volume for a chemical with a retardation factor $R = 2$ as a function of the rate parameter α.

For large values of α, the sorption process reaches equilibrium during the time of contact, and the equilibrium sorption model may be used. When the rate parameter approaches zero, sorption is largely blocked, and the chemical moves like a mobile tracer. For intermediate values of α, breakthrough begins earlier than with equilibrium sorption, and the outflow curve has a long tail.

Effect of Soil Structure

Aggregated soils have a continuous network of large pores through which water can flow rapidly, and a set of finer pores within the aggregates where water is present but largely stagnant. Soils with a massive structure may have fracture planes that channel virtually all of the water in the medium. In contrast, soils that have been packed uniformly have a distribution of pore sizes, and most of the water is either moving or in close contact with moving water. For such media, the uniform CDE generally provides a good description of the transport process.
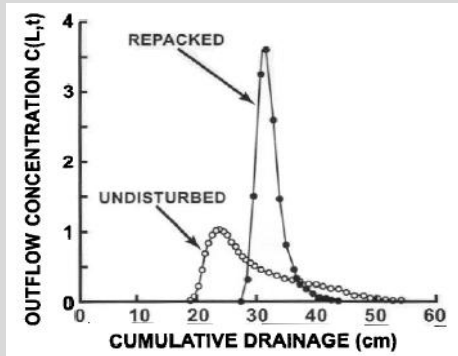
Chloride arrives after less drainage in the undisturbed soil column than in the repacked one and has substantial delay in the arrival of the final portion of the applied pulse at the outflow end. For soils of this type, some of the solute can be transported much more rapidly than one would expect based on the total volumetric water content and the piston flow model.

Mobile-Immobile Water Model

The mobile-immobile water model (MIM) divides the wetted pore space into two regions: a mobile water content (θ_m through which water is flowing and an immobile water content (θ_{im} = θ - θ_m) which contains stagnant water. For this system, the solute concentration is divided into an average concentration C_m in the mobile region and a second concentration C_{im} in the immobile region. The solute is transported by a convection-dispersion process in the mobile region while mass is exchanged with the immobile region by a rate-limited diffusion process. For an inert, nonreactive solute:

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = D_e \frac{\partial^2 C_m}{\partial z^2} - J_w \frac{\partial C_m}{\partial z}$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha(C_m - C_{im})$$

α - rate coefficient.

The rate of change of solute stored in the immobile region is proportional to the difference in concentration between the two regions. Thus, when solute is added to the soil as a pulse, it will first diffuse from the mobile to the stagnant region and then return to the mobile region after the pulse has passed through the system.

Mobile-Immobile Water Model

Effect of mobile/immobile water ratio

Effect of mobile/immobile water ratio
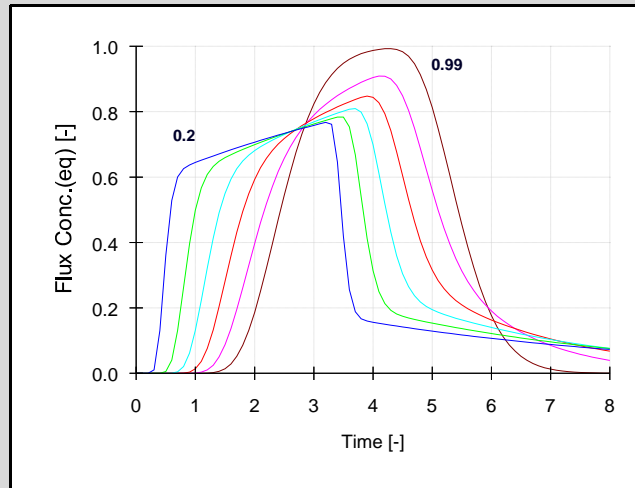
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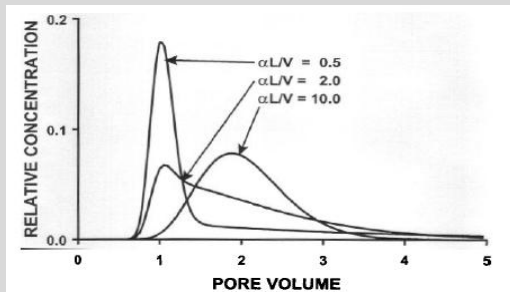- **Nonequilibrium transport (chemical, physical)**
- **Decay chains**
- **Parameter estimation**

General structure of system of solutes:

Products

$\mu_{g,1}$ $\mu_{w,1}$ $\mu_{s,1}$

Products

$\mu_{g,2}$ $\mu_{w,2}$ $\mu_{s,2}$

A

g_1 c_1 s_1

$k_{g,1}$ $k_{s,1}$

$\mu_{w,1} \rightarrow$

$\mu_{s,1} \rightarrow$

$\mu_{g,1} \rightarrow$

B

g_2 c_2 s_2

$k_{g,2}$ $k_{s,2}$

$\mu_{w,2} \rightarrow$

$\mu_{s,2} \rightarrow$

$\mu_{g,2} \rightarrow$

C ...

$\gamma_{g,1}$ $\gamma_{w,1}$ $\gamma_{s,1}$

Products

$\gamma_{g,2}$ $\gamma_{w,2}$ $\gamma_{s,2}$

Products

Example sequential first-order chains:

◆ **Radionuclides** [van Genuchten, 1985]

^{238}Pu $\longrightarrow$ ^{234}U $\longrightarrow$ ^{230}Th $\longrightarrow$ ^{226}Ra

c_1 s_1 $\qquad$ c_2 s_2 $\qquad$ c_3 s_3 $\qquad$ c_4 s_4

◆ **Nitrogen** [Tillotson et al., 1980]

$g2$

N_2

$(NH_2)_2CO \longrightarrow NH_4^+ \longrightarrow NO_2^- \longrightarrow NO_3^-$

c_1 s_1 $\qquad$ c_2 s_2 $\qquad$ c_3 $\qquad$ c_4 $\qquad$ N_2O
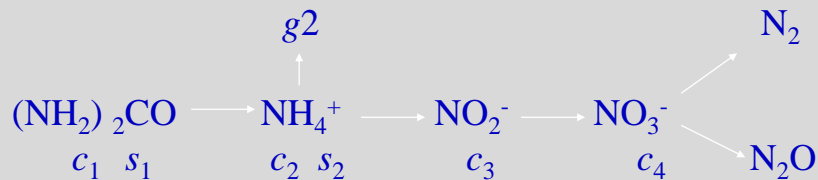
Governing Solute Transport Equations

$$\frac{\partial(\theta c)}{\partial t} + \frac{\partial(\rho s)}{\partial t} = \frac{\partial}{\partial z}(\theta D \frac{\partial c}{\partial z} - qc) - \phi$$
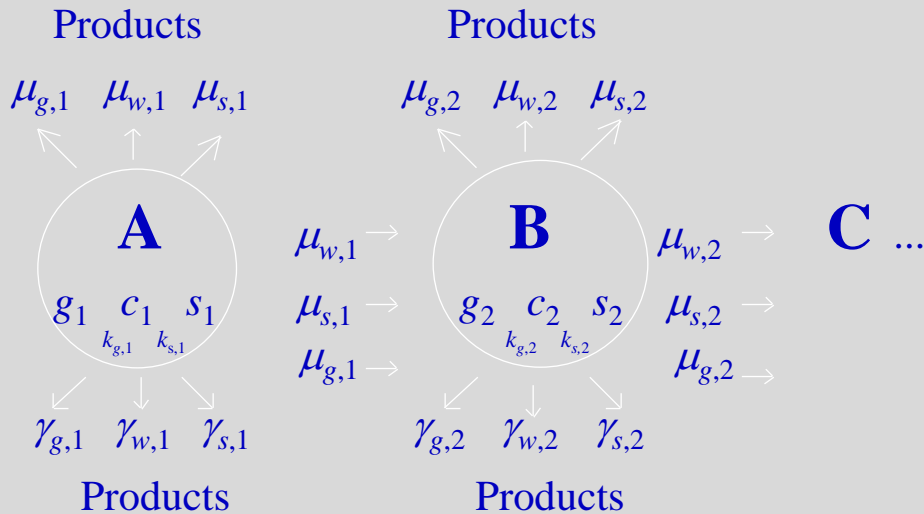
$$\frac{\partial \theta c_k}{\partial t} + \frac{\partial \rho s_k}{\partial t} + \frac{\partial a g_k}{\partial t} = \frac{\partial}{\partial z}(\theta D_k^w \frac{\partial c_k}{\partial z}) + \frac{\partial}{\partial z}(a D_k^g \frac{\partial g_k}{\partial z}) - \frac{\partial q c_k}{\partial z} -$$

$$-(\mu_{w,k} + \mu_{w,k}^{'})\theta c_k - (\mu_{s,k} + \mu_{s,k}^{'})\rho s_k - (\mu_{g,k} + \mu_{g,k}^{'})a g_k + \mu_{w,k-1}^{'}\theta c_{k-1} +$$

$$-\mu_{s,k-1}^{'}\rho s_{k-1} - \mu_{g,k-1}^{'}a g_{k-1} + \gamma_{w,k}\theta + \gamma_{s,k}\rho + \gamma_{g,k}a - Sc_{r,k} \qquad k\varepsilon(2, n_s)$$

w, s, g   **subscripts corresponding with the liquid, solid and gaseous phases, respectively**

c, s, g   **concentration in liquid, solid, and gaseous phase, respectively**

Governing Solute Transport Equations

q_i	volumetric flux [LT^{-1}]
ρ	soil bulk density [ML^{-3}]
a	air content [L^{3}L^{-3}]
S	sink term in the water flow equation [T^{-1}]
c_r	concentration of the sink term [ML^{-3}]
D^w, D^g	dispersion coefficients for the liquid and gaseous phase [L^{2}T^{-1}], respectively
k	subscript representing the kth chain number
μ_w, μ_s, μ_g	first-order rate constants for solutes in the liquid, solid, and gaseous phases [T^{-1}], respectively
γ_w, γ_s, γ_g	zero-order rate constants for the liquid [ML^{-3}T^{-1}], solid [T^{-1}], and gaseous phases [ML^{-3}T^{-1}], respectively
μ_w', μ_s', μ_g'	first-order rate constants for solutes in the liquid, solid and gaseous phases [T^{-1}], respectively; these rate constants provide connections between the individual chain species.
n_s	number of solutes involved in the chain reaction

Outline

◆ **Introduction: Water Flow and Solute Transport**

◆ **Solute Transport**
- –   **Governing transport equations**
- –   **Advection, diffusion, dispersion, reactions (ADE)**
- –   **Solute Break-Through Curves, Boundary conditions**
- –   **Nonequilibrium transport (chemical, physical)**
- –   **Decay chains**
- –   **Parameter estimation**

Parameter Estimation with HYDRUS

Parameter Estimation:
- **- Soil hydraulic parameters**
- **- Solute transport and reaction parameters**
- **- Heat transport parameters**

Sequence:
- **- Independently**
- **- Simultaneously**
- **- Sequentially**

Method:
- **- Marquardt-Levenberg optimization**

Objective Function for Inverse Problems

$$\Phi(\mathbf{b}, \mathbf{q}, \mathbf{p}) = \sum_{j=1}^{m_q} v_j \sum_{i=1}^{n_{qj}} w_{i,j}[q_j^*(x, t_i) - q_j(x, t_i, \mathbf{b})]^2 +$$

$$\sum_{j=1}^{m_p} \overline{v_j} \sum_{i=1}^{n_{pj}} \overline{w}_{i,j}[p_j^*(\theta_i) - p_j(\theta_i, \mathbf{b})]^2 +$$

$$\sum_{j=1}^{n_b} \hat{v}_j[b_j^* - b_j]^2$$

1st term: deviations between measured and calculated space-time variables

2nd term: differences between independently measured, p_j^*, and predicted , p_j, soil hydraulic properties

3rd term: penalty function for deviations between prior knowledge of the soil hydraulic parameters, b_j^*, and their final estimates, b_j.

Formulation of the Inverse Problem

When the covariance matrix *V* is diagonal and all elements of matrix V_β are equal to zero , i.e., the measurement errors are noncorrelated and no prior information about the optimized parameters exists, the problem simplifies into the **weighted least-squares problem**

$$\Phi(\beta) = \sum_{i=1}^{n} w_i \left[C_i^* - C_i(\beta) \right]^2$$

w_i - **weight of a particular measured point**

Parameter Estimation