

# Physical Nonequilibrium Transport

## Review: Equilibrium Transport Equation

System composed of a liquid phase involving advective and diffusive/dispersive transport, and a solid phase subject to chemical sorption or exchange

$$\theta \frac{\partial c}{\partial t} = -\frac{\partial J_s}{\partial x} - J_a \quad J_s = qc - \theta D \frac{\partial c}{\partial x}$$

$$\rho \frac{\partial s}{\partial t} = J_a$$

Transport equation for the system as a whole

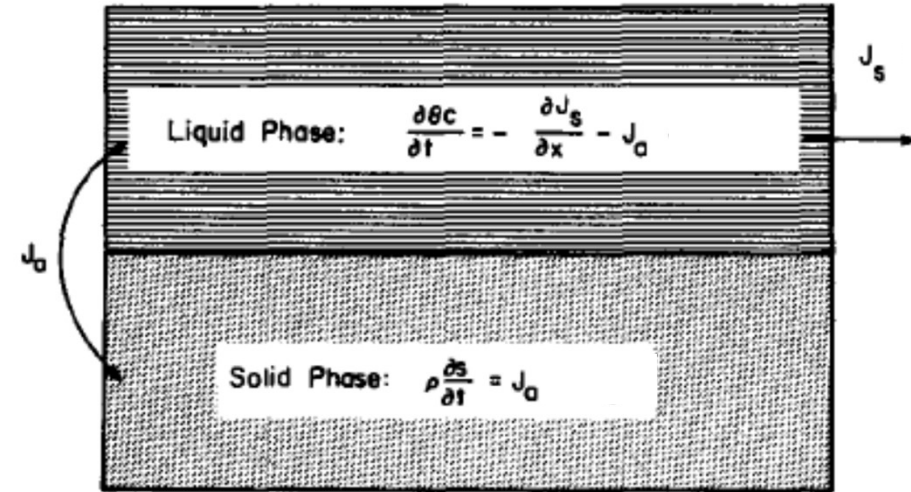
$$\theta \frac{\partial c}{\partial t} + \rho \frac{\partial s}{\partial t} = -q \frac{\partial c}{\partial x} + \theta D \frac{\partial^2 c}{\partial x^2}$$

This equation is valid whether sorption is an equilibrium or kinetic process. If we assume instantaneous sorption such that the solute exchange between the liquid and solid phases occurs at such a rate that at all times the mass fraction  $s$  is uniquely related to the aqueous concentration  $c$ . For example, we can assume a linear isotherm  $s = K_d c$

$$\frac{\partial s}{\partial t} = K_d \frac{\partial c}{\partial t} \longrightarrow \frac{\partial s}{\partial c} = K_d \longrightarrow \theta \frac{\partial c}{\partial t} + \rho \frac{\partial s}{\partial c} \frac{\partial c}{\partial t} = -q \frac{\partial c}{\partial x} + \theta D \frac{\partial^2 c}{\partial x^2} \longrightarrow \theta \frac{\partial c}{\partial t} + \rho K_d \frac{\partial c}{\partial t} = -q \frac{\partial c}{\partial x} + \theta D \frac{\partial^2 c}{\partial x^2}$$

$$\longrightarrow (\theta + \rho K_d) \frac{\partial c}{\partial t} = -q \frac{\partial c}{\partial x} + \theta D \frac{\partial^2 c}{\partial x^2} \longrightarrow \frac{(\theta + \rho K_d)}{\theta} \frac{\partial c}{\partial t} = -v \frac{\partial c}{\partial x} + D \frac{\partial^2 c}{\partial x^2} \longrightarrow \boxed{R \frac{\partial c}{\partial t} = -v \frac{\partial c}{\partial x} + D \frac{\partial^2 c}{\partial x^2} \quad R = 1 + \frac{1}{\theta} \rho K_d}$$

$\theta$  [ $L^3/L^3$  or  $L^0$ ] as the volumetric water content;  $s$  is the sorbed mass fraction [ $M_{\text{solute}}/M_{\text{solid}}$  or  $M^0$ ];  $c$  [ $M/L^3$ ] is the aqueous concentration;  $\rho$  [ $M/L^3$ ] is the soil bulk density;  $J_s$  [ $M/L^2T$ ] is the solute mass flux;  $J_a$  [ $M/L^3T$ ] is the transfer rate from the solution to the sorbed phase (also known as sorption rate);  $K_d$  [ $L^3/M$ ] is the empirical distribution coefficient;  $v=q/\theta$  is the average pore water velocity with volumetric water flux  $q$  [ $L/T$ ]



Modified from van Genuchten and Wagenet [1989]

# Review: Equilibrium Transport Equation

System composed of a liquid phase involving advective and diffusive/dispersive transport, and a solid phase subject to chemical sorption or exchange such that sorption is an equilibrium process. We get the advection dispersion equation (ADE)

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

### Sorption Isotherm

### Retardation factor

$$s(x) = f(c_w(x))$$

$$s(x) = K_d c$$

$$\frac{\partial s}{\partial t} = K_d \frac{\partial c}{\partial t}$$

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

$$s(x) = K c^n$$

$$\frac{\partial s}{\partial t} = K_d n c^{n-1} \frac{\partial c}{\partial t}$$

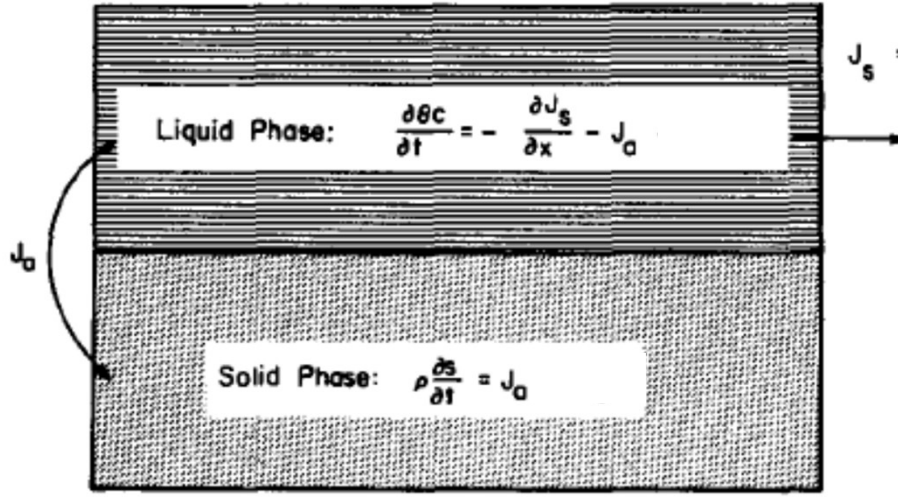
$$R = 1 + \frac{1}{\theta} \rho K n c^{n-1}$$

$$s(x) = \frac{s_{\max} K}{c + K}$$

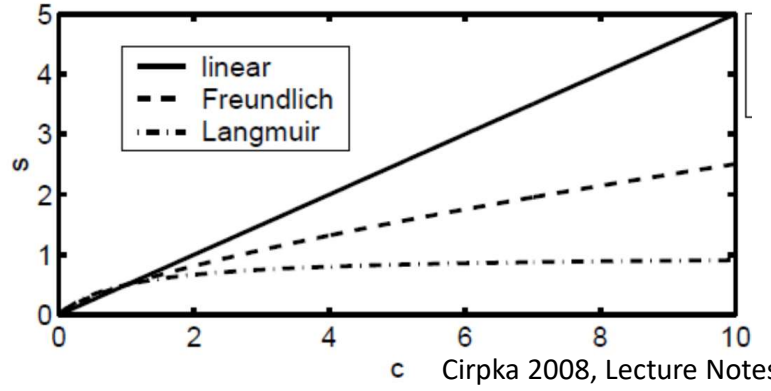
$$\frac{\partial s}{\partial t} = K_d \frac{s_{\max} K}{(c + K)^2} \frac{\partial c}{\partial t}$$

$$R = 1 + \frac{1}{\theta} \rho \frac{s_{\max} K}{(c + K)^2}$$

Equilibrium sorption can be linear or nonlinear. In case of non-linear sorption, the retardation factor depends on the concentration. **What if sorption is a kinetic process, how will the transport equation look like? This will be your homework.**



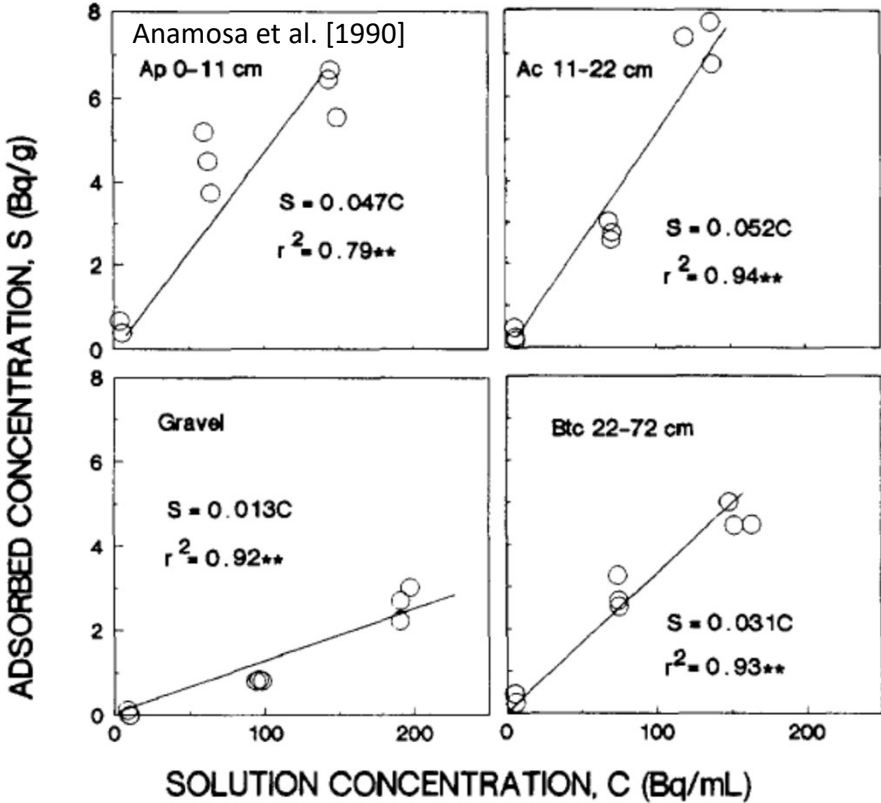
Modified from van Genuchten and Wagenet [1989]



Note that for Langmuir sorption isotherm:  $S_{\max} [M_{\text{solute}}/M_{\text{solid}}]$  is the sorption site density generally reported in mol/kg, and  $K [M/L^3]$  is the half-saturation concentration at which the sorbed mass fraction  $s$  equals exactly 50% of its maximum value.

# Retardation Factor: Measured

Retardation factor R measured using a batch experiment



|                             | $\rho$ | $K_d$ | 1/n   |
|-----------------------------|--------|-------|-------|
| Fine_Ap                     | 0.88   | 0.047 | 1.079 |
| Fine_Ac                     | 1      | 0.052 | 1.099 |
| Fine_Btc                    | 1.46   | 0.031 | 1.086 |
| Gravel_Ap                   | 0.335  | 0.013 | 1.008 |
| Gravel_Ac                   | 0.588  | 0.013 | 1.015 |
| Gravel_Btc                  | 0.72   | 0.013 | 1.018 |
| Mean Retardation Factor [-] |        |       | 1.051 |

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

Using Porosity  $\theta=0.525$  (i.e. the volumetric soil water content) gives  $R=1.05$ .

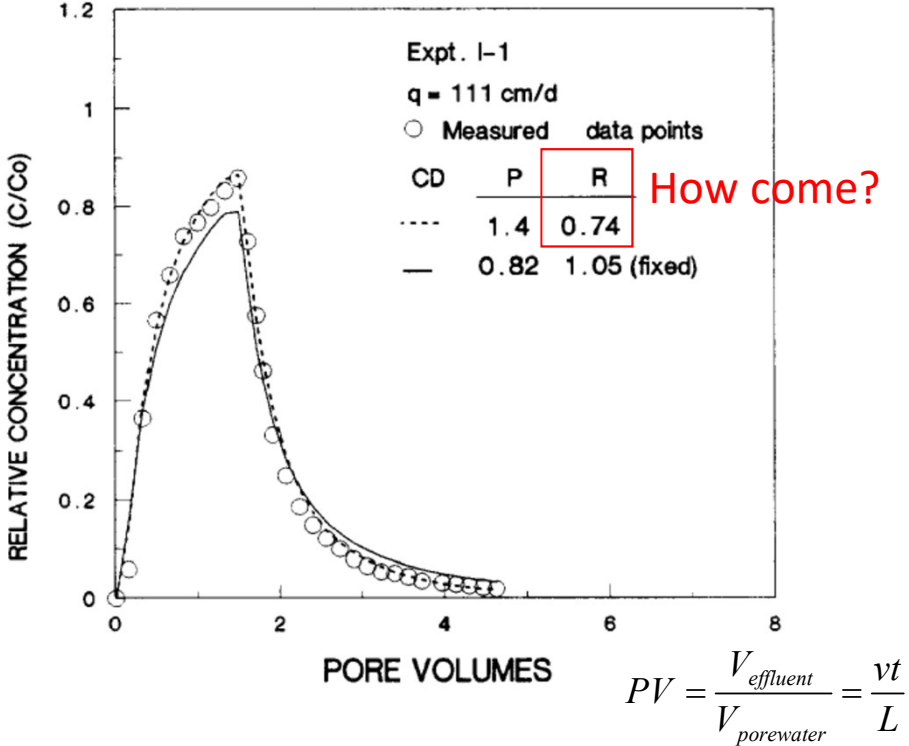
Using Linear sorption isotherm, Anamosa et al. [1990] found that tritium will slightly sorb with retardation factor  $R=1.05$ .

## Breakthrough Curves

- Breakthrough curves are curves of concentrations measured at an observation point downstream from a source plotted against time.
- A breakthrough curve records the concentrations measured at this point (usually the column outlet) over time.
- We usually do not plot observed concentration  $C$  [ $M/L^3$ ] versus time. Rather we plot a relative concentration  $C/C_0$  [-] in which  $C_0$  [ $M/L^3$ ] is the input concentration.
- Instead of time  $t$  [T] we use pore volume  $PV$  [-]. A pore volume in a column is the volume of water that will completely fill all of the voids in the column.
- The shape of the breakthrough curve depends on type of solute input (continuous or pulse) and the type of transport and transformation processes that the solute experiences as it travels through the porous medium from its release point until the observation point.

# Retardation Factor: Estimated

However, Anamosa et al. [1990] fitted a breakthrough curve to a tritium  $^3\text{H}_2\text{O}$  transport column experiment with retardation factor  $R=0.74$  ?!



Experimental estimate :  $R=1.05$   
 Calibration estimate:  $R=0.74$

When we use correct parameter  $R=1.05$  we get somehow a late arriving (solid line) and poor fitting.

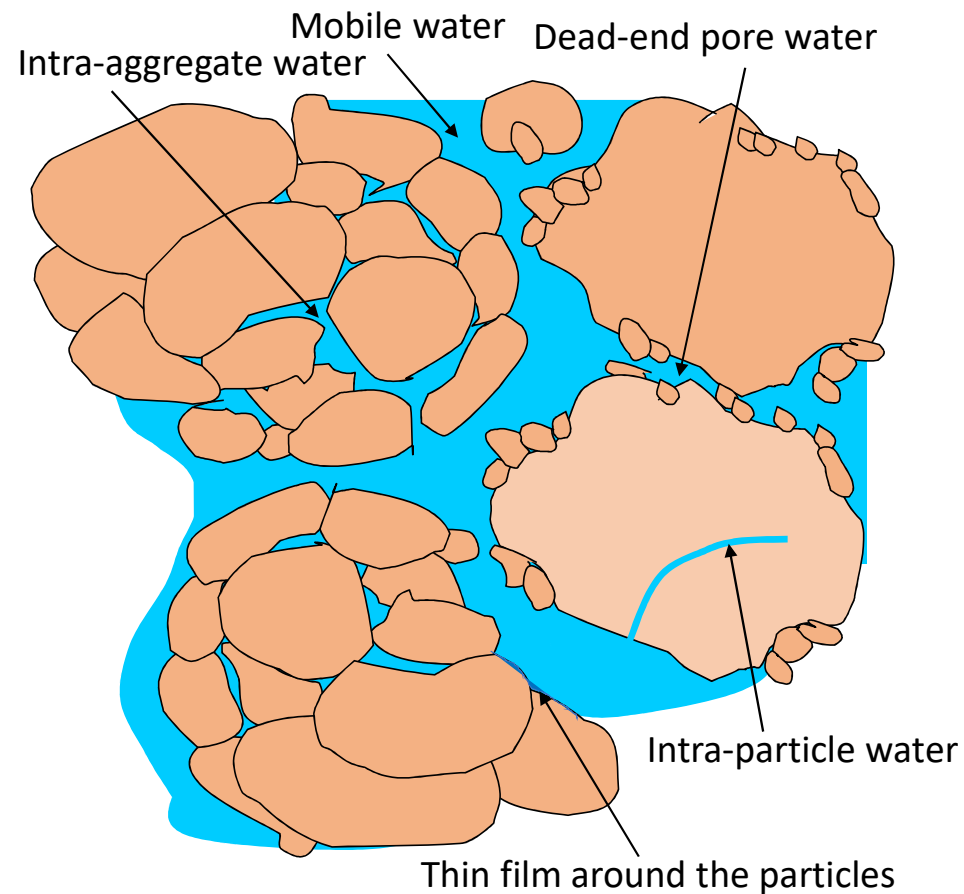
Why the advection dispersion equation (ADE) cannot fit the measurements?

$$PV = \frac{V_{effluent}}{V_{porewater}} = \frac{vt}{L}$$

Note that Anamosa et al. [1990] calls our transport equation convection dispersion (CD) equation, but we call it ADE. The dimensionless Peclet number  $P=vL/D$  is the characteristic time of advection over the characteristic time of dispersion (in which  $L$  in this case is the column length). In this problem  $L=71.6$  cm,  $\Theta=0.525$  and the dimensionless pulse duration is 1.43.

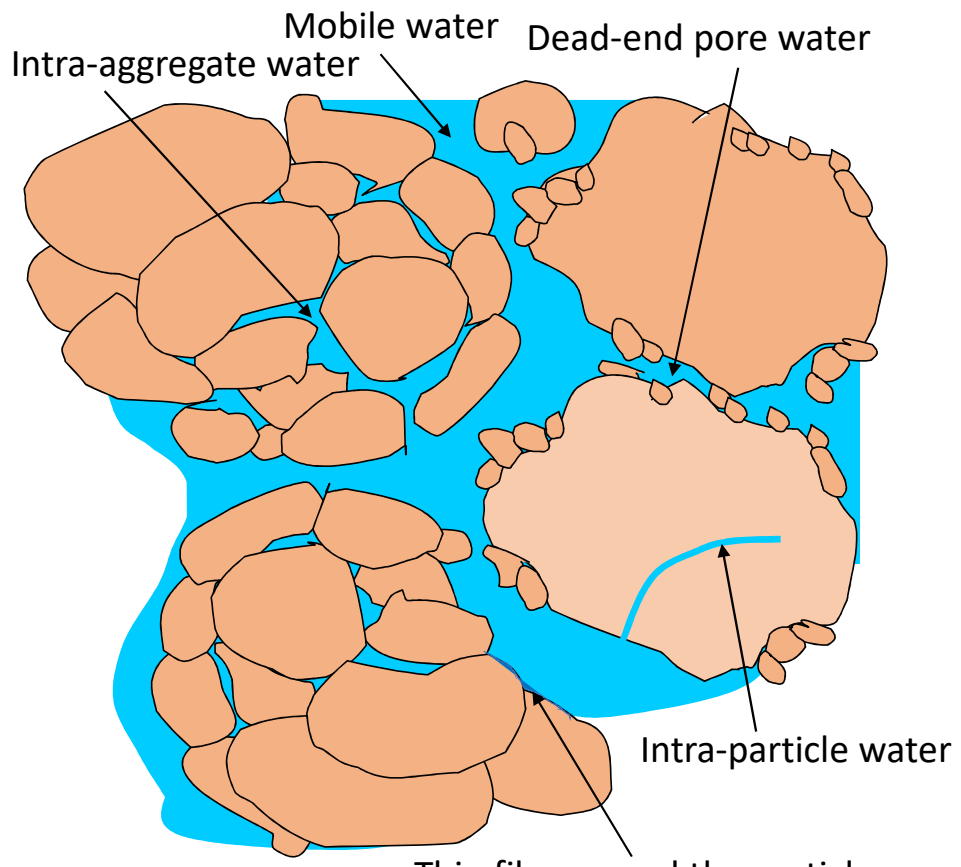
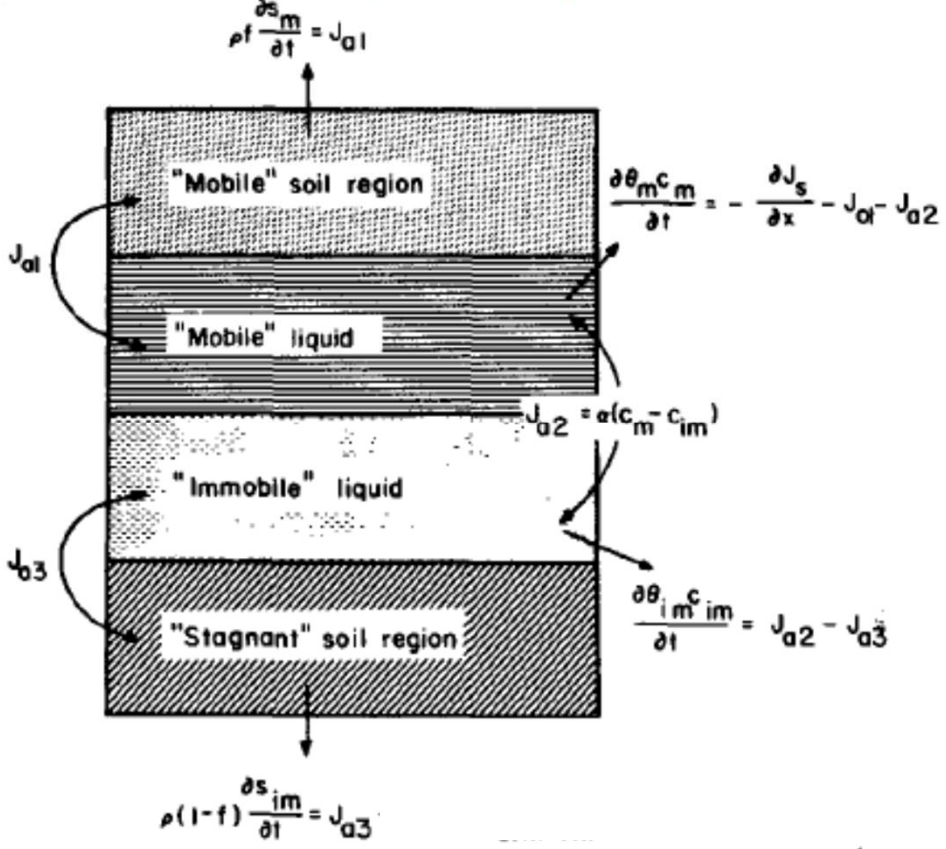
## Nonequilibrium Transport: Physical Nonequilibrium

- Stagnant water (e.g. dead-end pore water, intra-aggregate water, intra-particle water, thin liquid films around particles, etc.)
- Partitions pore space water into mobile (flowing/moving) and immobile (non-flowing/stagnant) regions.
- **Two-Region Nonequilibrium Transport:** Pore-water velocity distribution is bimodal such that advective- dispersive transport is happening in only a fraction of the liquid-filled pores (mobile water) and the remainder of the pores have stagnant water (immobile water). In literature they also refer to this a dual-domain, dual-porosity or mobile-immobile transport.



Modified from Srivastava 2014

# Nonequilibrium Transport: Physical Nonequilibrium



- "Mobile" soil region refers to the solid phase assigned to "mobile" liquid region (flowing water).
- "Immobile" soil region refers to the solid phase assigned to "immobile" liquid region (stagnant water).

Modified from Srivastava 2014



## Two-Region Nonequilibrium Transport with Sorption

Transport equations for:

"Mobile" liquid region  $\theta_m \frac{\partial c_m}{\partial t} = -q \frac{\partial c_m}{\partial x} + \theta_m D_m \frac{\partial^2 c_m}{\partial x^2} - J_{a1} - J_{a2}$

"Mobile" solid region  $f \rho \frac{\partial s_m}{\partial t} = J_{a1}$

"Immobile" liquid region  $\theta_{im} \frac{\partial c_{im}}{\partial t} + f \rho \frac{\partial s_{im}}{\partial t} = J_{a2} - J_{a3}$

"Immobile" solid region  $(1-f) \rho \frac{\partial s_{im}}{\partial t} = J_{a3}$

Transport equation for mobile region

$$\theta_m \frac{\partial c_m}{\partial t} + f \rho \frac{\partial s_m}{\partial t} = -q \frac{\partial c_m}{\partial x} + \theta_m D_m \frac{\partial^2 c_m}{\partial x^2} - J_{a2}$$

Transport equation for immobile region

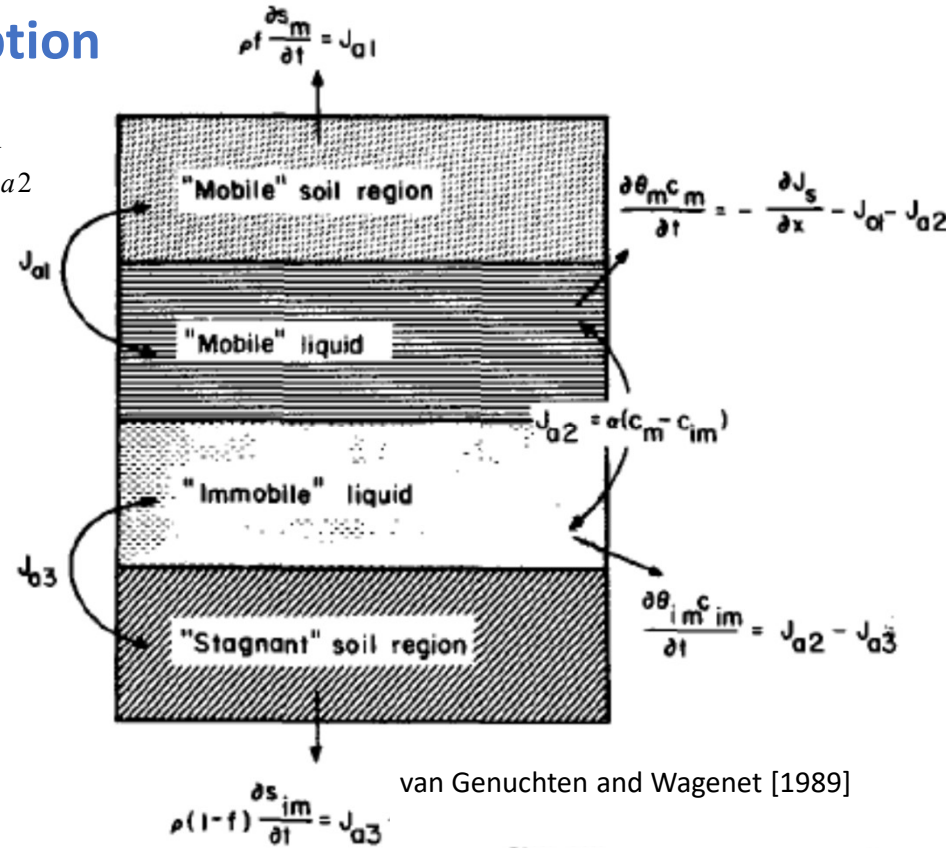
$$\theta_{im} \frac{\partial c_{im}}{\partial t} + (1-f) \rho \frac{\partial s_{im}}{\partial t} = J_{a2}$$

Transport equations assuming linear equilibrium sorption

$$s_m = K_d c_m \quad s_{im} = K_d c_{im}$$

$$(\theta_m + f \rho K_d) \frac{\partial c_m}{\partial t} = -q \frac{\partial c_m}{\partial x} + \theta_m D_m \frac{\partial^2 c_m}{\partial x^2} - J_{a2}$$

$$[\theta_{im} + (1-f) \rho K_d] \frac{\partial c_{im}}{\partial t} = J_{a2} \quad J_{a2} = \alpha (c_m - c_{im})$$



van Genuchten and Wagenet [1989]

$$s = f s_m + (1-f) s_{im} \quad \theta = \theta_{im} + \theta_m$$

$f$  [-] is mass fraction of solid phase assigned to mobile region;  $\alpha$  [1/T] is a first order mass transfer coefficient describing the rate of transfer between the mobile and immobile liquid phases.

## Analytical Solutions

- CXTFIT [Toride et al. 1995]
- STANMOD Model van Genuchten, et al. 2012]
- CXTFIT/Excel [Tang, et al., 2010]