# Nonequilibrium Transport

# 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**

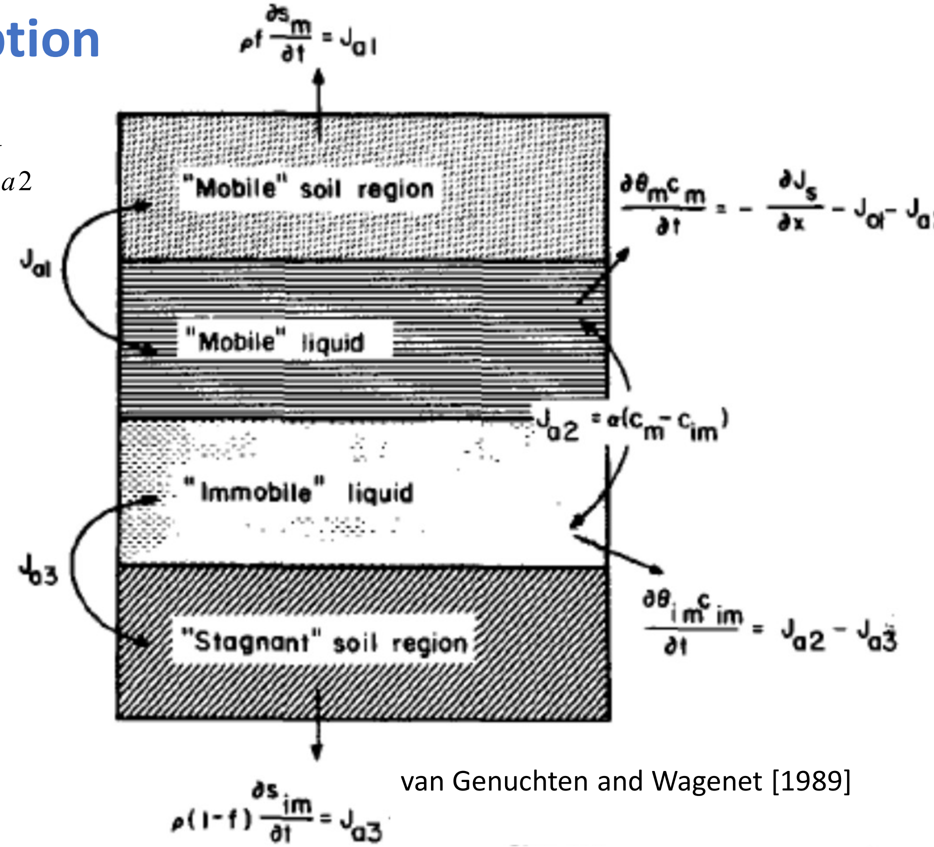
$$\theta_{im} \frac{\partial c_{im}}{\partial t} + (1-f)\rho \frac{\partial s_{im}}{\partial t} = J_{a2}$$

**Transport equations assuming linear equilibrium sorption**

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

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

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




van Genuchten and Wagenet [1989]

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

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

# Dimensionless Transport Equation

## Two-Region Nonequilibrium

This is know as the mobile-immobile (MIM) transport equation

$$(\theta_m + f\rho K_d)\frac{\partial c_m}{\partial t} = -q\frac{\partial c_m}{\partial x} + \theta_m D_m \frac{\partial^2 c}{\partial x^2} - \alpha(c_m - c_{im})$$

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

$$C_1 = \frac{C_m}{C_0} \qquad C_2 = \frac{C_{im}}{C_0}$$

$$T = \frac{vt}{L} \qquad X = \frac{x}{L}$$

$$P = \frac{v_m L}{D_m} = \frac{vL}{D}$$

## Dimensionless Transport Equations:

$$\beta R\frac{\partial C_1}{\partial T} = -\frac{\partial C_1}{\partial X} + \frac{1}{P}\frac{\partial^2 C_1}{\partial X^2} - \omega(C_1 - C_2)$$

$$(1-\beta)R\frac{\partial C_2}{\partial T} = \omega(C_1 - C_2)$$

$$R = \frac{\theta + \rho K_d}{\theta} \qquad \beta = \frac{\theta_m + f\rho_s K_d}{\theta + \rho_s K_d}$$

$$\omega = \frac{\alpha L}{\theta v}$$

<u>For two-sites and two-regions</u>
$\beta$ [-] is the fraction of solute in the mobile region with *f* [-] being the fraction of mobile sorption sites
$\omega$ [-] is a dimensionless mass transfer coefficient with $\alpha$ [1/T] being the mass transfer coefficient between mobile and immobile water

## Dimensionless Transport Equation

The dimensionless mobile-immobile (MIM) transport equation

$$\beta R\frac{\partial C_1}{\partial T} = -\frac{\partial C_1}{\partial X} + \frac{1}{P}\frac{\partial^2 C_1}{\partial X^2} - \omega(C_1 - C_2) \qquad (1-\beta)R\frac{\partial C_2}{\partial T} = \omega(C_1 - C_2)$$

$$C_1 = \frac{C_m}{C_0} \qquad C_2 = \frac{C_{im}}{C_0} \qquad T = \frac{vt}{L} \qquad X = \frac{x}{L} \qquad P = \frac{v_m L}{D_m} = \frac{vL}{D} \qquad R = \frac{\theta + \rho K_d}{\theta}$$

$$\omega = \frac{\alpha L}{\theta v} \qquad \beta = \frac{\theta_m + f\rho_s K_d}{\theta + \rho_s K_d}$$

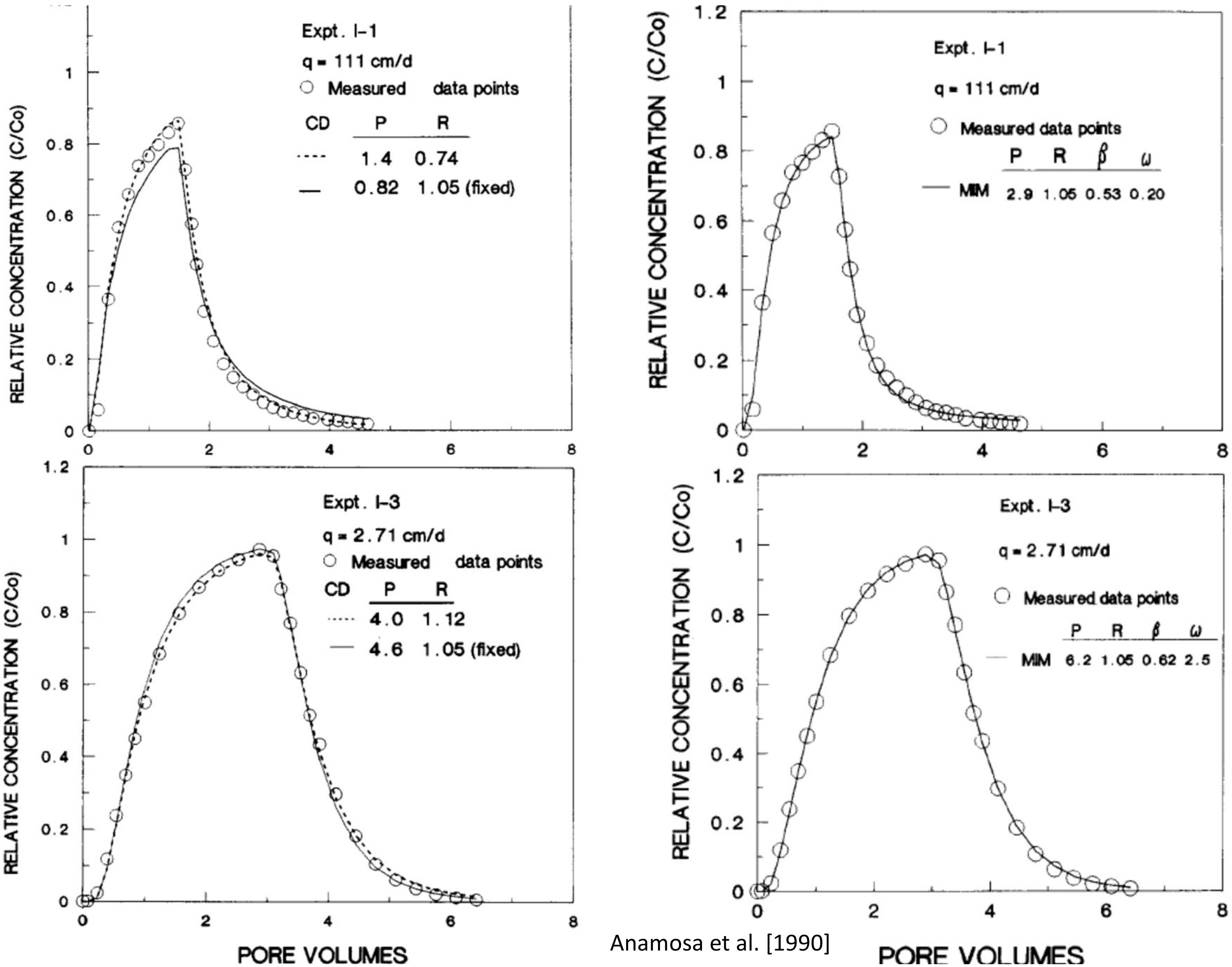
**Physical nonequilibrium transport:** $C_1$ and $C_2$ are relative concentrations in the mobile and immobile regions; β [-] mobile-immobile water partition coefficient (a function of the fraction of solute present in the mobile region under equilibrium conditions) with $\Theta_m$ as the mobile pore water content and *f* as the fraction of sorption sites that equilibrates with solute in mobile water; ω [-] dimensionless mass transfer coefficient between mobile-immobile water with mass transfer coefficient α [1/T] between mobile and immobile water; $K_d$ [$L^3/M$] is a partitioning coefficient.

$$R\frac{\partial C}{\partial T} = -\frac{\partial C}{\partial X} + \frac{1}{P}\frac{\partial^2 C}{\partial X^2} \qquad \beta R\frac{\partial C}{\partial T} = -\frac{\partial C}{\partial X} + \frac{1}{P}\frac{\partial^2 C}{\partial X^2}$$

$$R_m = 1 + \frac{1}{\theta_m}\rho K_d \qquad \phi_m = \theta_m / \theta$$

$$\beta = \frac{\phi_m R_m}{R} \qquad \phi_{im} = \theta_{im} / \theta$$

**Equilibrium transport:** With β=1 ($\Theta_m$=$\Theta$ and thus *f=1*) we get the dimensionless ADE equation. This is a special case from ω=0 in which MIM becomes an equilibrium model with βΘ representing the effective water content.




Anamosa et al. [1990]

Note that MIM refers to the mobile-immobile transport equation and CD refers to the Advection dispersion equation

For the fast flux q=111 cm/d and slow flux q=2.71 cm/d the dimensionless pulse durations are 1.43 and 2.84, respectively; the column length is 71.6 cm; the water content is 0.526; the measured retardation factor is 1.05; the estimated mobile water fraction is about 0.53 [Anamosa et al. [1990] .

$$J_{a2} = \alpha (c_m - c_{im})$$

$$\omega = \frac{\alpha L}{\theta v}$$

Parameter estimation four experiments of Anamosa et al. (1990)

| | | λ (cm) | θ | β | ω | RMSE | $R^2$ | $\lvert\rho\rvert_{max}$ |
|---|---|---|---|---|---|---|---|---|
| Expt. I-1 | CDE1 | 86.60 ± 6.62 | | | | 0.044 | 0.979 | |
| q = 111 | CDE2 | 36.39 ± 3.47 | 0.373 ± 0.013 | | | 0.026 | 0.993 | 0.874 |
| | MIM | 25.00 ± 2.19 | | 0.536 ± 0.017 | 0.193 ± 0.020 | 0.013 | 0.998 | 0.937 |
| Expt. I-3 | CDE1 | 15.63 ± 0.71 | | | | 0.023 | 0.996 | |
| q = 2.71 | CDE2 | 16.74 ± 0.42 | 0.560 ± 0.005 | | | 0.013 | 0.999 | 0.385 |
| | MIM | 4.58 ± 3.26 | | 0.373 ± 0.089 | 2.988 ± 0.339 | 0.012 | 0.999 | 0.942 |
| Expt. II-1 | CDE1 | 21.09 ± 0.64 | | | | 0.016 | 0.998 | |
| q = 2.69 | CDE2 | 22.00 ± 0.51 | 0.551 ± 0.005 | | | 0.012 | 0.999 | 0.396 |
| | MIM | 9.89 ± 3.16 | | 0.600 ± 0.089 | 1.195 ± 0.211 | 0.013 | 0.999 | 0.972 |
| Expt. II-2 | CDE1 | 100.03 ± 5.21 | | | | 0.034 | 0.989 | |
| q = 36.7 | CDE2 | 92.74 ± 4.67 | 0.438 ± 0.021 | | | 0.029 | 0.992 | 0.387 |
| | MIM | 27.45 ± 2.75 | | 0.467 ± 0.019 | 0.280 ± 0.020 | 0.013 | 0.998 | 0.945 |

(Tang et al. 2009)

**Note:**

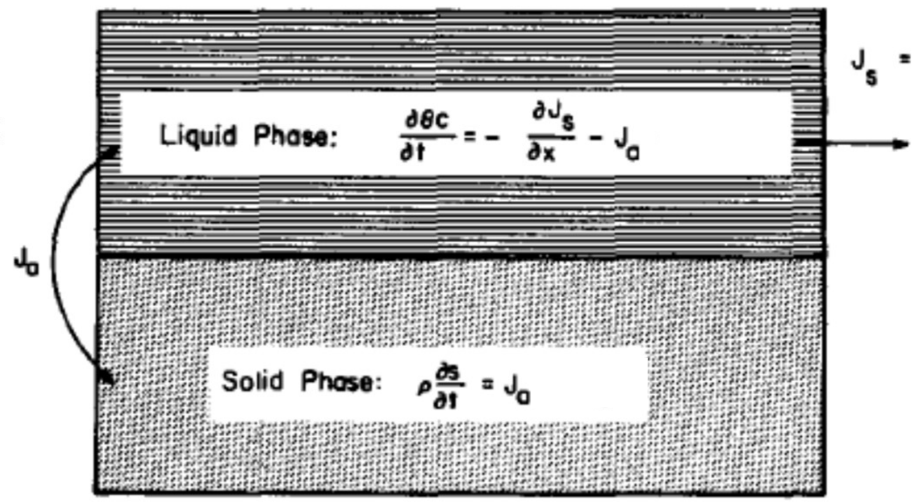
- At slow flux q [m/d] we get higher estimates for the dimensionless mass transfer coefficient ω [-] as the dual domain functions more like a single domain with porosity approaching the total porosity of the medium. For more information the reader is referred Figure 3.26 in Zheng and Bennett (2002) and the discussion thereof.
- For conventional advection dispersion equation (CDE1/CDE2) the dispersivity λ [cm] is estimated at a large values, while for the dual-domain mass transfer model the dispersivity can be set at a smaller values to account for molecular diffusion and microscopic dispersion, since much of the macroscopic dispersion is represented through the mass transfer between mobile and immobile domain (Jury et al., 1991; Zheng and Bennett, 2002).

# Homework: One-Site Nonequilibrium Transport

A 1D system composed of a liquid phase involving advective and diffusive/dispersive transport, and a solid phase subject to chemical sorption or exchange. Assuming linear kinetic sorption, the sorption rate Ja from the solution to the sorbed phase is given by

$$J_a = \alpha\rho(Kc - s)$$

Such that s is the sorbed mass fraction [$M_{solute}/M_{solid}$ or M°]; ρ [$M/L^3$] the soil bulk density; Ja [$M/L^3T$] is the transfer rate from the solution t the sorbed phase; K [$L^3/M$] is the empirical distribution coefficient; α [1/T] is a first-order kinetic rate coefficient.




van Genuchten and Wagenet [1989]

(1) Drive the transport equation for non-equilibrium sorption as defined above. Try to use the notation of v=q/ Θ [L/T] as the average pore water velocity with volumetric water flux q [L/T] , *Θ* as the volumetric water content [$L^3/L^3$ or L°], D as the dispersion coefficient [$L^2/T$].

(2) Check Toride et al. (1995, Table 3.1) for the dimensionless non-equilibrium sorption transport equation. It looks exactly the same as dimensionless mobile immobile transport equation except that the dimensionless parameters (e.g. ω, β, etc.) of the two equations are different. Comment on the physical meaning of the dimensionless mass transfer coefficient ω [-] for the two equations.

(3) Explain the difference between (i) equilibrium linear sorption and equilibrium nonlinear sorption? and (ii) equilibrium sorption and kinetic (nonequilibrium chemical) sorption?

# Reference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