

# HWRS 561b: Physical Hydrogeology II

## Solute transport (Part 4)

Agenda:

1. Equilibrium and non-equilibrium sorption
2. Non-conservative solute transport

# Sorption

When solute moves through the pore space, they can interact with the solid through various physical and chemical processes that lead to the solute partition to the solid and leave the aqueous phase. We refer to the net effect of these processes as **sorption**.

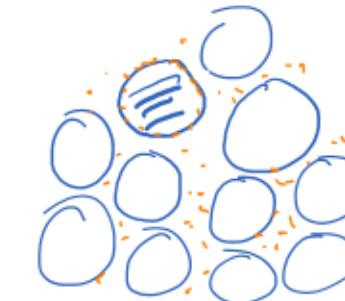
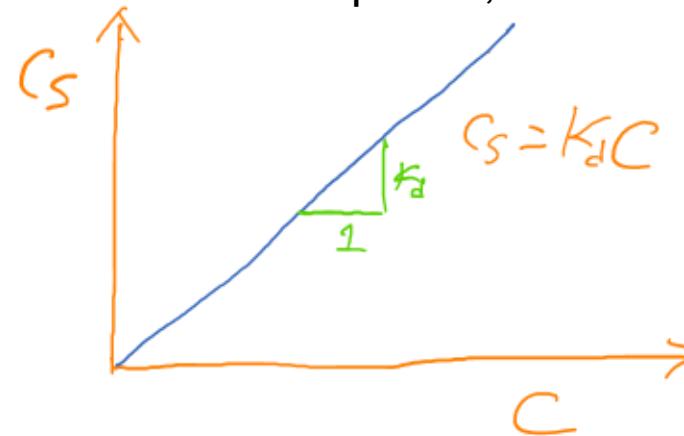
## Equilibrium sorption vs. kinetic sorption

If the sorptive process is rapid compared with the transport, the solute in the aqueous may be assumed in equilibrium condition with the sorbed phase, which is often modeled by an isotherm.

$$C_s = f(C)$$

**Linear isotherm**

$$C_s = K_d C \quad \text{M/L}^3$$



$C_s$  = mass of solute sorbed per dry unit weight of solid (mg/kg)

$C$  = concentration of solute in solution in equilibrium with the mass of solute sorbed onto the solid (mg/L)

$K_d$  = coefficient (L/kg)

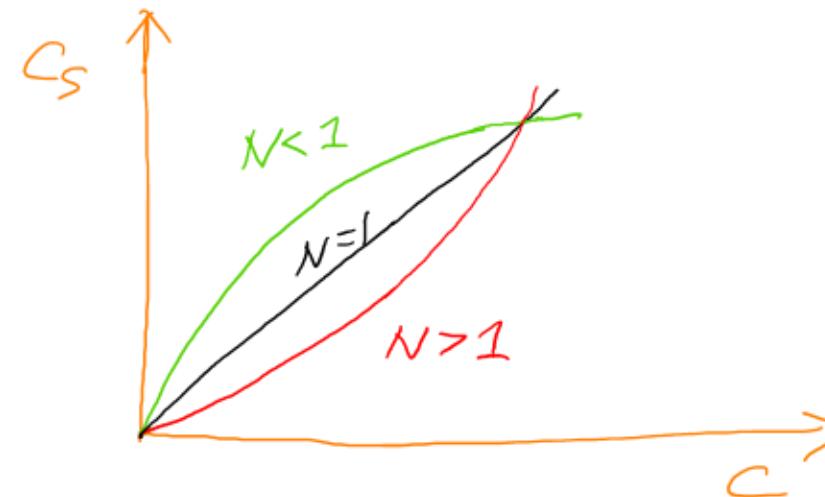
# Sorption

## Nonlinear isotherm

Freundlich isotherm

$$C_s = K_f C^N$$

$K_f$  and  $N$  are fitting parameters to measured isotherms.



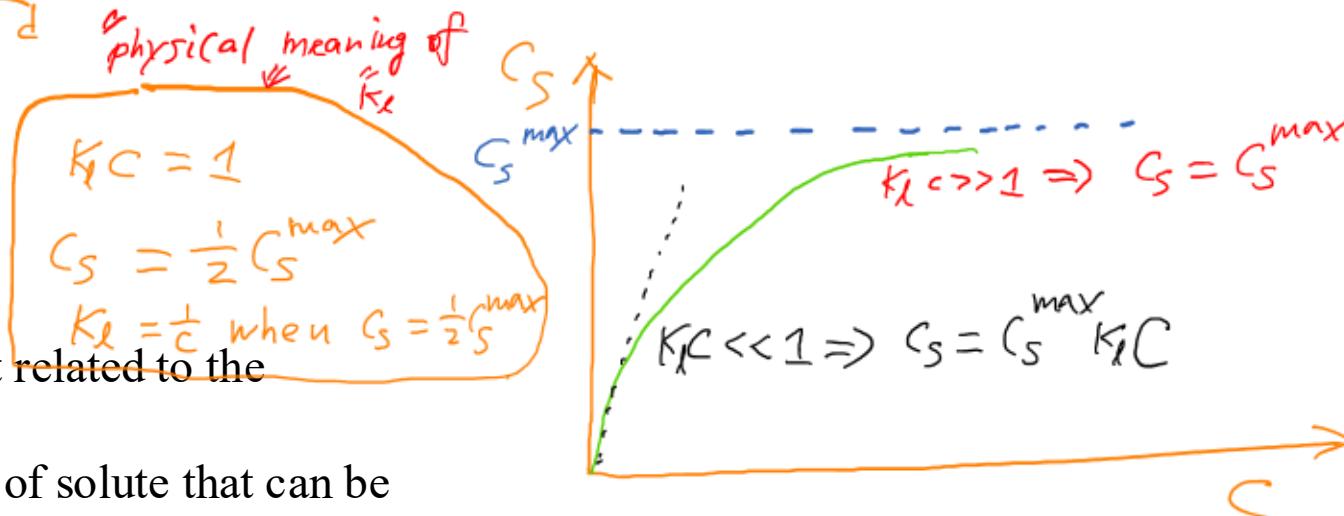
$$C_s = \frac{K_f C^{N-1}}{K_d} C$$

Langmuir isotherm

$$C_s = \frac{C_s^{\max} K_l C}{1 + K_l C}$$

$K_l$  is an adsorption constant related to the binding energy (L/mg)

$\beta$  is the maximum amount of solute that can be absorbed by the solid (mg/kg)



# ADE with sorption

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$$\phi \frac{\partial C}{\partial t} + \rho_b \frac{\partial C_s}{\partial t} + \phi V \frac{\partial C}{\partial x} - \phi D \frac{\partial^2 C}{\partial x^2} = 0$$

If solid-phase sorption follows a linear isotherm

$$C_s = K_d C$$

We obtain

$$\phi \frac{\partial C}{\partial t} + \rho_b K_d \frac{\partial C}{\partial t} + \phi V \frac{\partial C}{\partial x} - \phi D \frac{\partial^2 C}{\partial x^2} = 0$$

$$\Rightarrow \frac{\partial C}{\partial t} + \frac{\rho_b K_d}{\phi} \frac{\partial C}{\partial t} + V \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} = 0$$

$$\Rightarrow \left( 1 + \frac{\rho_b K_d}{\phi} \right) \frac{\partial C}{\partial t} + V \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} = 0$$

Define  $1 + \frac{\rho_b K_d}{\phi} \equiv R$  Retardation factor

$$\Rightarrow R \frac{\partial C}{\partial t} + V \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} = 0$$

# ADE with sorption

If solid-phase sorption follows a Freudlich isotherm

$$C_s = K_f C^N$$

$$\frac{\partial C}{\partial t} + \frac{\rho_b}{\phi} \frac{\partial C}{\partial t} + V \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} = 0$$

$$\Rightarrow \frac{\partial C}{\partial t} + \frac{\rho_b}{\phi} K_f N C^{N-1} \frac{\partial C}{\partial t} + V \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} = 0$$

$$R = H \frac{\rho_b}{\phi} K_f N C^{N-1}$$

If solid-phase sorption follows a Langmuir isotherm

$$C_s = \frac{C_s^{\max} K_l C}{1 + K_l C}$$

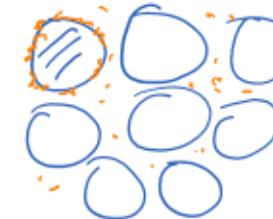
$$\Rightarrow \frac{\partial C}{\partial t} + \frac{\rho_b}{\phi} \frac{C_s^{\max} K_l}{(1 + K_l C)^2} \frac{\partial C}{\partial t} + V \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} = 0$$

$$R = 1 + \frac{\rho_b}{\phi} \frac{C_s^{\max} K_l}{(1 + K_l C)^2}$$

# Non-equilibrium (kinetic) sorption

Irreversible first-order kinetic sorption model

$$\left\{ \begin{array}{l} \frac{\partial C_s}{\partial t} = k_1 C \\ \qquad \text{First-order decay rate constant} \\ \frac{\partial C}{\partial t} + \frac{\rho_b}{\phi} \frac{\partial S}{\partial t} + V \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} = 0 \end{array} \right.$$

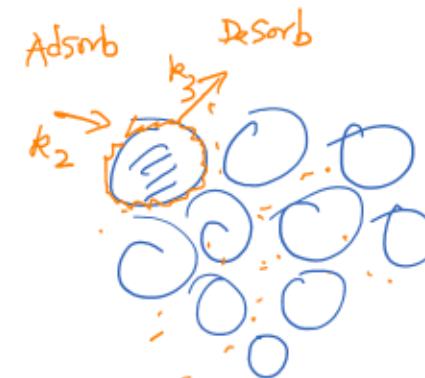


Reversible linear kinetic sorption model

$$\frac{\partial C_s}{\partial t} = k_2 C - k_3 C_s$$

Forward rate constant

Backward rate constant



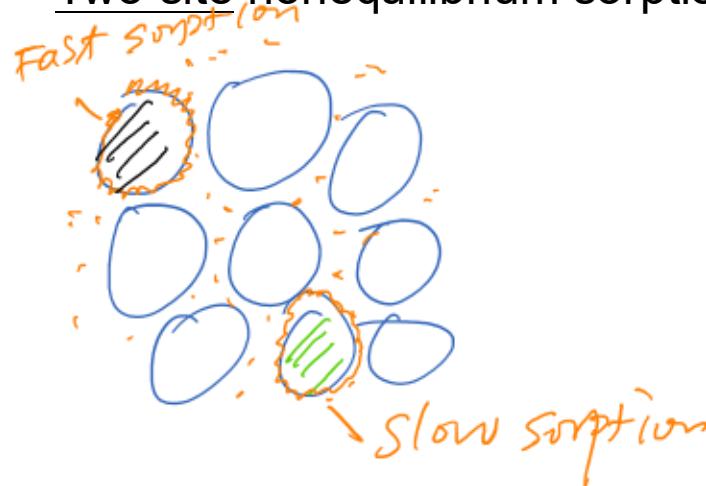
$$\Rightarrow \frac{\partial C_s}{\partial t} = \gamma (k_4 C - C_s)$$

First-order rate coefficient

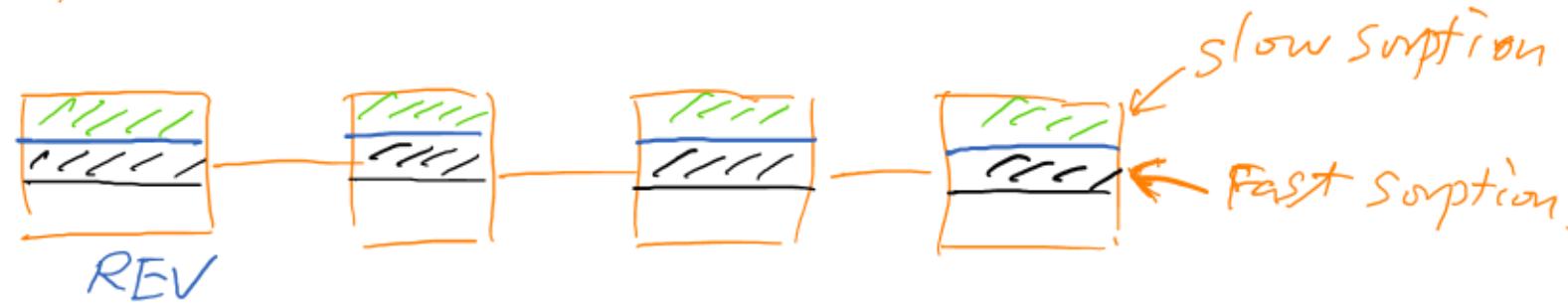
Solid-phase adsorption coefficient (equivalent to  $K_d$ )

# Non-equilibrium (kinetic) sorption

Two-site nonequilibrium sorption model



Model conceptualization



$$C_{s,1} = F_s K_d C$$

$$\frac{\partial C_{s,2}}{\partial t} = \alpha_s [(1-F_s)K_d C - C_{s,2}]$$

- ① At equilibrium,  $C_{s,2} = (1-F_s)K_d C$
- ② At early time, when the solute just arrives

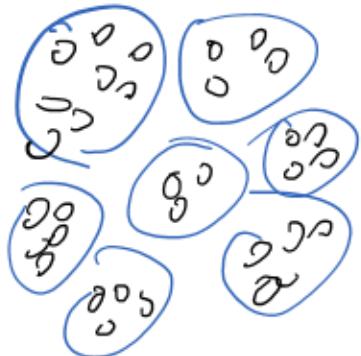
$$\Rightarrow \frac{\partial C}{\partial t} + \frac{\rho_b}{\phi} \frac{\partial [C_{s,1} + C_{s,2}]}{\partial t} + V \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} \Rightarrow$$

- ③ At late time,  $C_{s,2}$  approaches  $C_{s,2}$ .

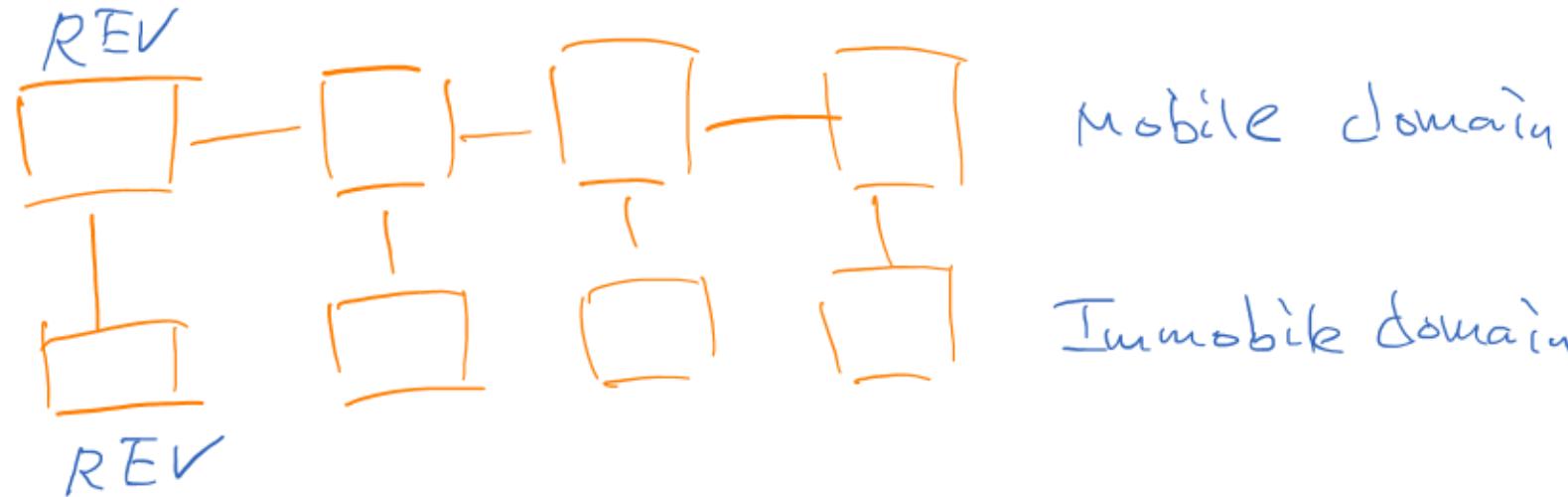
$C_{s,2}$  is far from equilibrium and increases fast.

# Non-equilibrium (kinetic) sorption

Two-domain nonequilibrium sorption model



[NOTE: This is just one physical example.  
There are others]



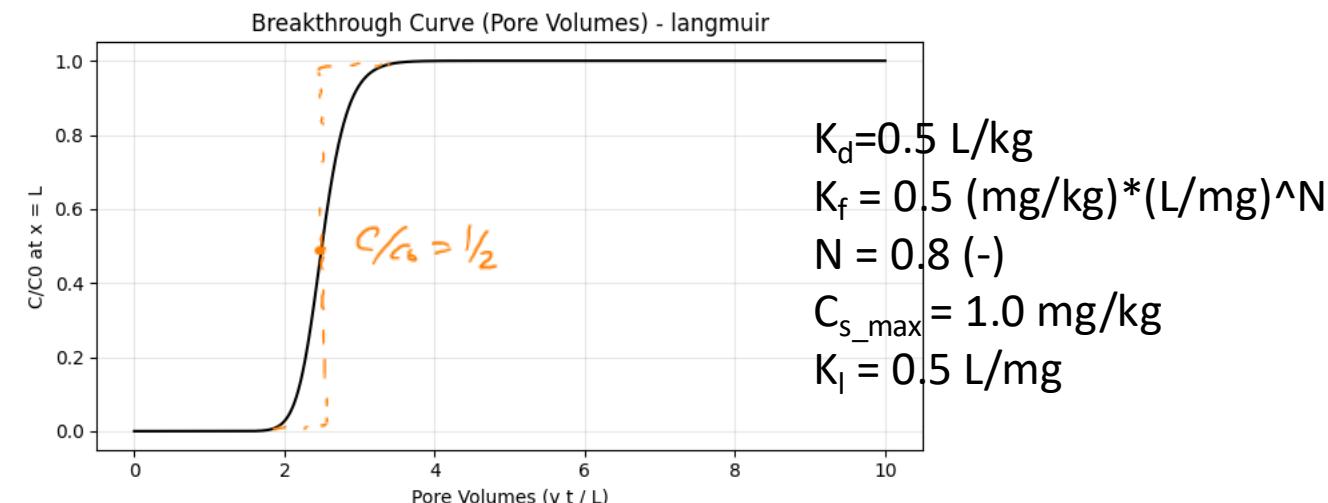
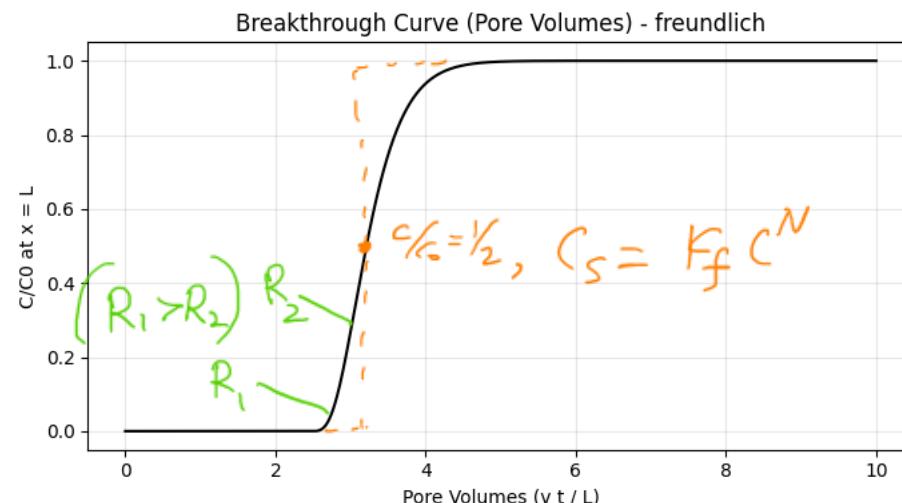
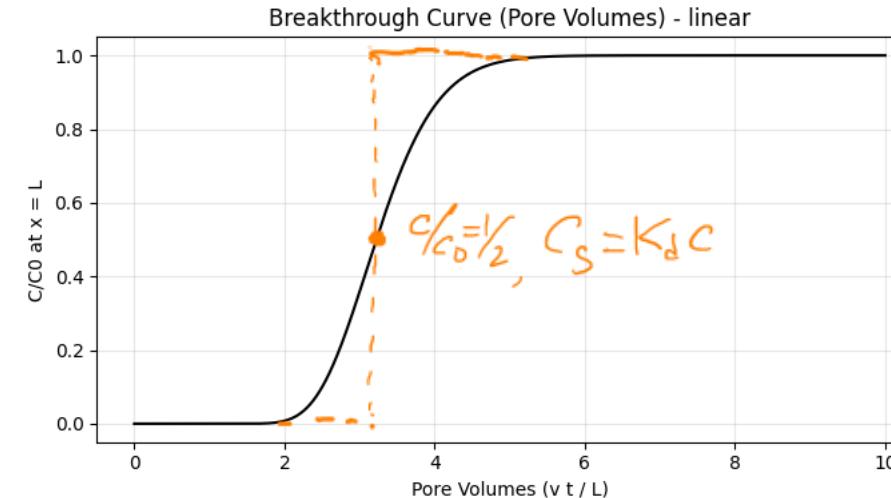
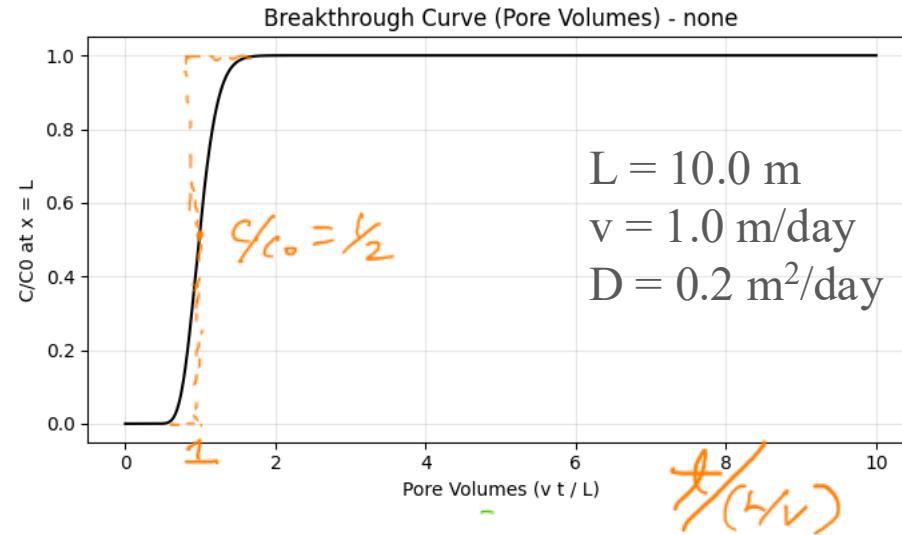
$$\theta_m \frac{\partial C_m}{\partial t} + \rho_b \frac{\partial C_{s,m}}{\partial t} + \theta_m V \frac{\partial C_m}{\partial x} - \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} = J_{im,m} (C_{im} - C_m) \quad \text{Mobile domain}$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} + \rho_b \frac{\partial C_{s,im}}{\partial t} + \cancel{\theta_{im} V \frac{\partial C_{im}}{\partial x}} - \cancel{\theta_{im} D_m \frac{\partial^2 C_{im}}{\partial x^2}} = J_{im,m} (C_m - C_{im}) \quad \text{Immobile domain}$$

$$C_{s,m} = F_m K_d C_m, \quad C_{s,im} = (1-F_m) K_d C_{im}$$

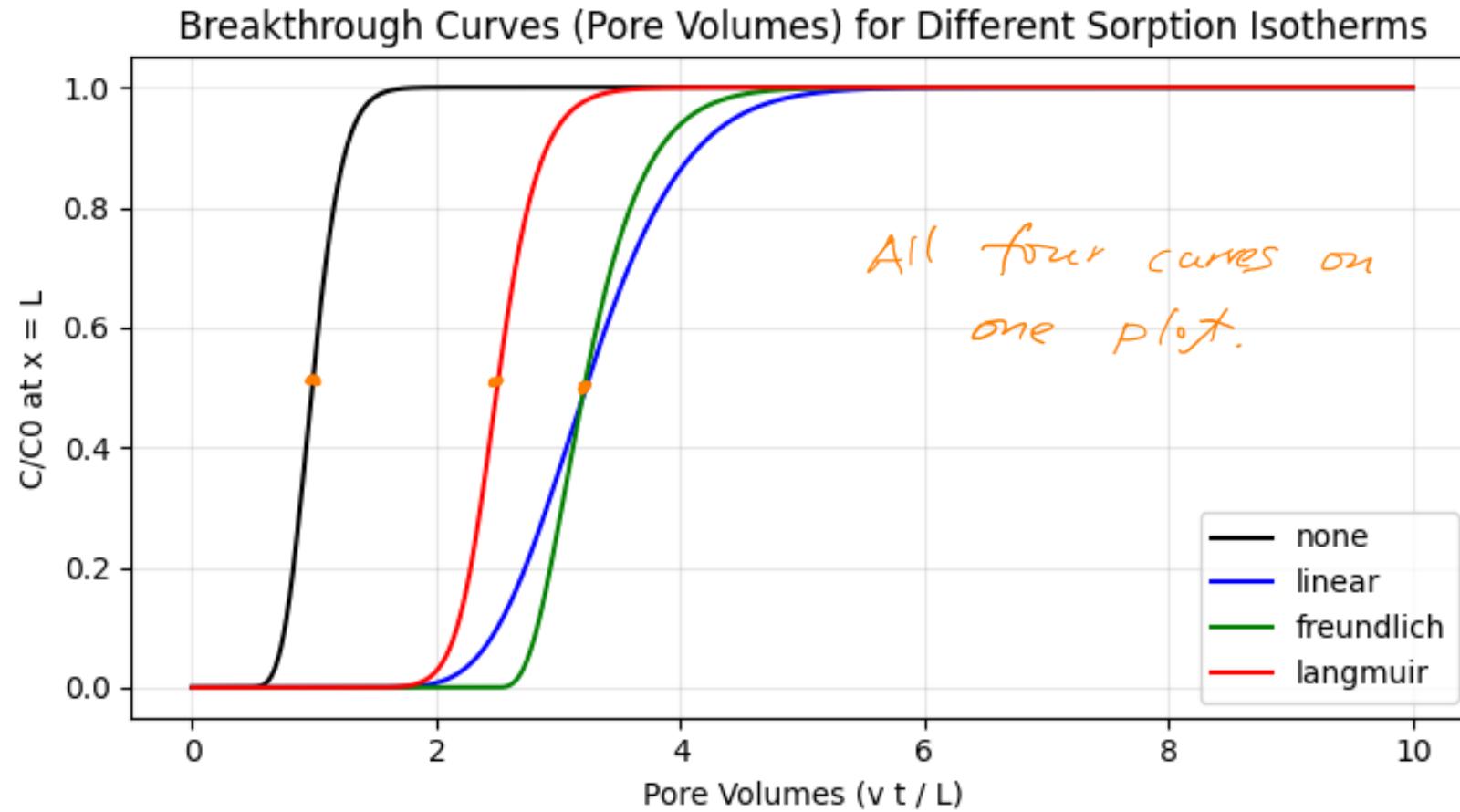
# Solute transport under different isotherms

Continuous injection at a constant concentration (numerical solutions)



# Solute transport under different isotherms

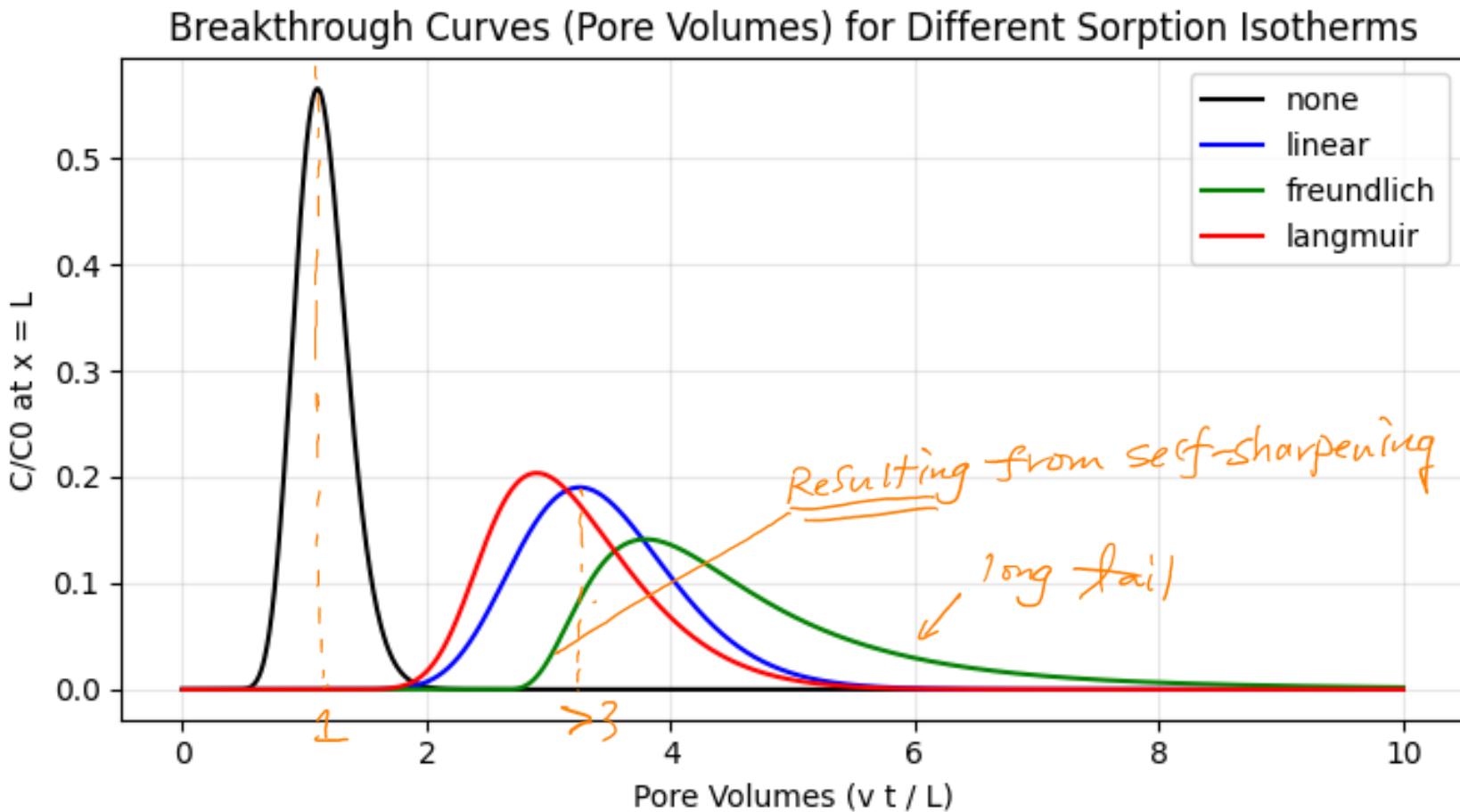
Continuous injection at a constant concentration (numerical solutions)



$$\begin{aligned}L &= 10.0 \text{ m} \\v &= 1.0 \text{ m/day} \\D &= 0.2 \text{ m}^2/\text{day}\end{aligned}$$

# Solute transport under different isotherms

Pulse injection at a constant concentration (numerical solutions)



$L = 10.0 \text{ m}$   
 $v = 1.0 \text{ m/day}$   
 $D = 0.2 \text{ m}^2/\text{day}$   
Pulse duration = 3 days

# Solute transport under different isotherms

Under a Freundlich isotherm with  $N < 1$  and a Langmuir isotherm, the concentration-dependent retardation causes self-sharpening of the leading edge and rarefaction of the trailing edge in breakthrough curves.

Freundlich isotherm

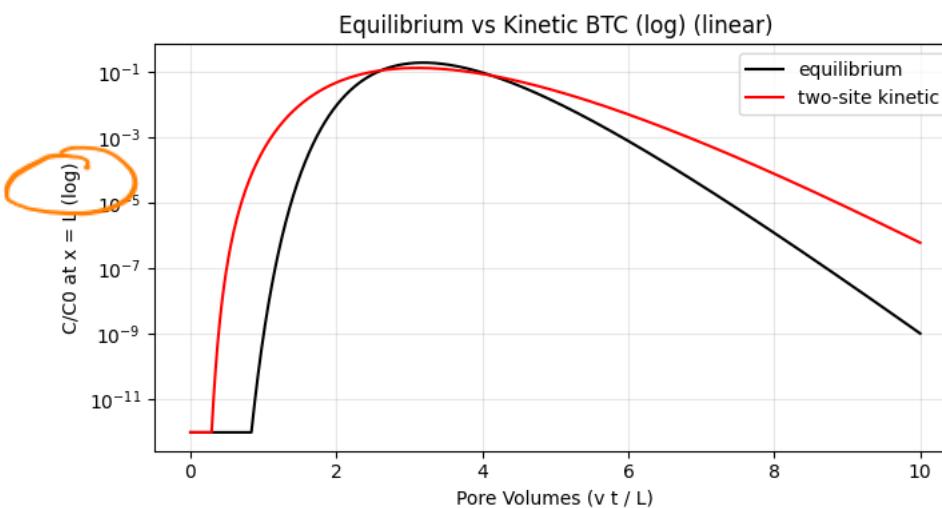
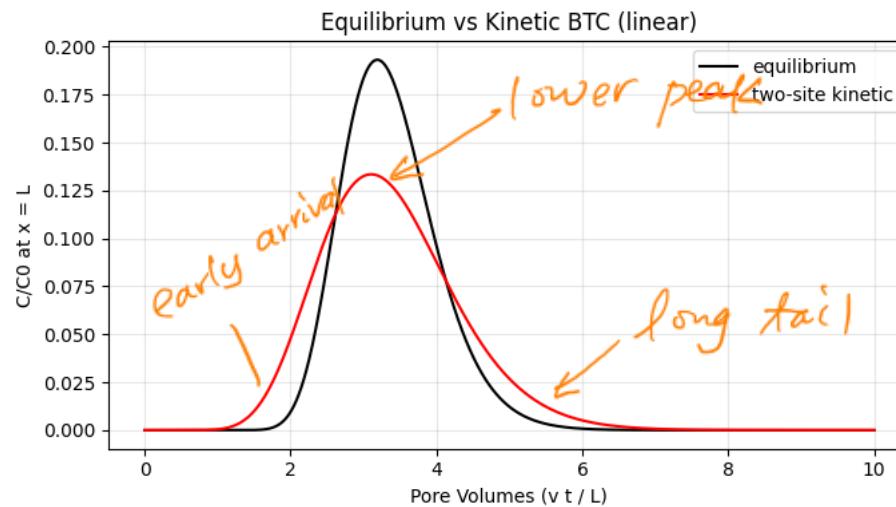
$$R = \frac{P_b}{\phi} k_f N C^{N-1}$$

Langmuir isotherm

$$R = 1 + \frac{P_b}{\phi} \frac{C_s^{\max} K_e}{(1+K_e C)^2}$$

In both cases, the retardation factor increases with decreasing concentration. Behind the front is higher  $C$ , smaller  $R$ , faster velocity; ahead of the front is lower  $C$ , larger  $R$ , and slower velocity.

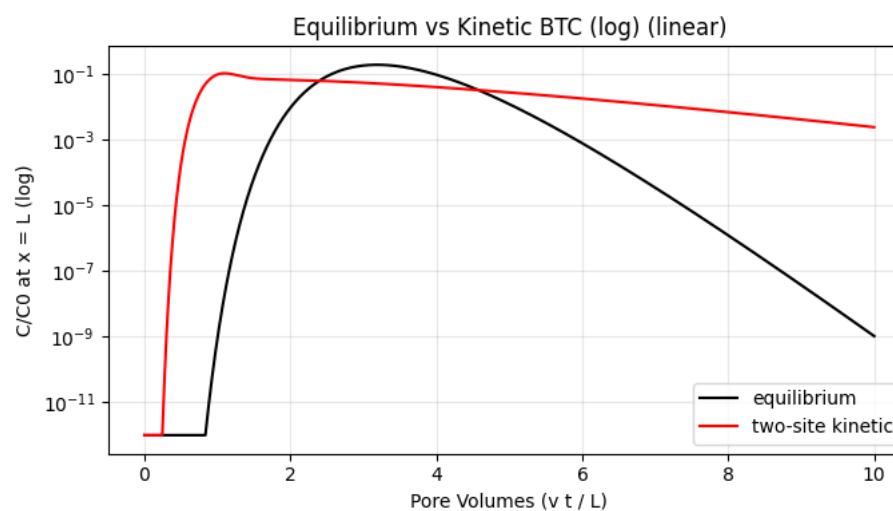
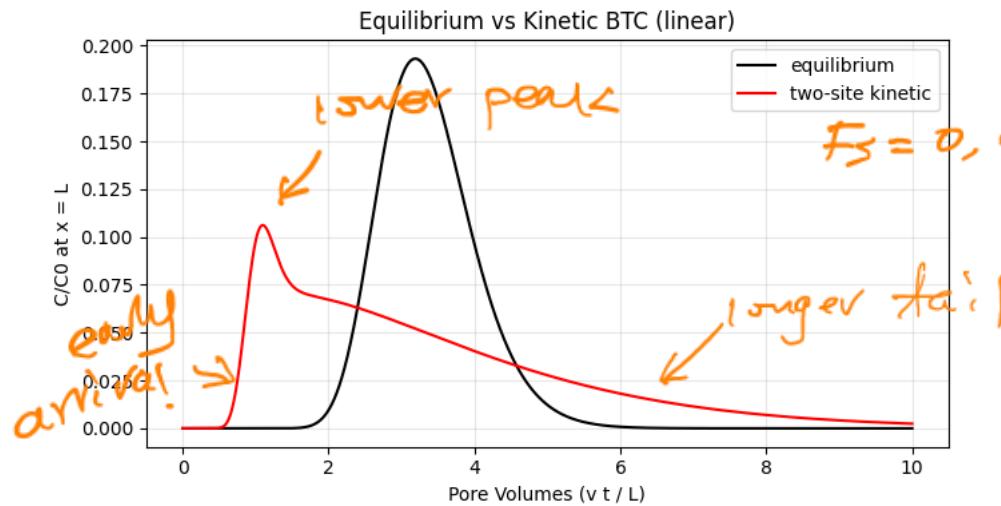
# Solute transport under kinetic sorption



$L = 10.0 \text{ m}$   
 $v = 1.0 \text{ m/day}$   
 $D = 0.2 \text{ m}^2/\text{day}$   
Pulse duration = 3 days

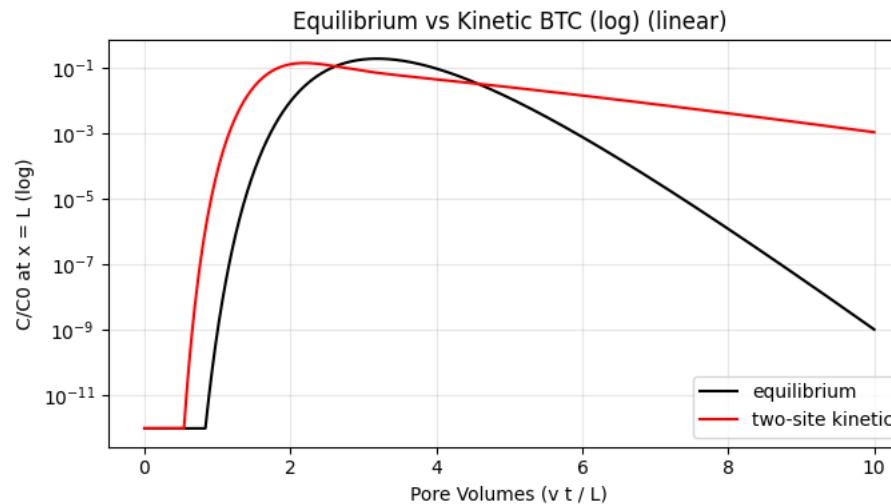
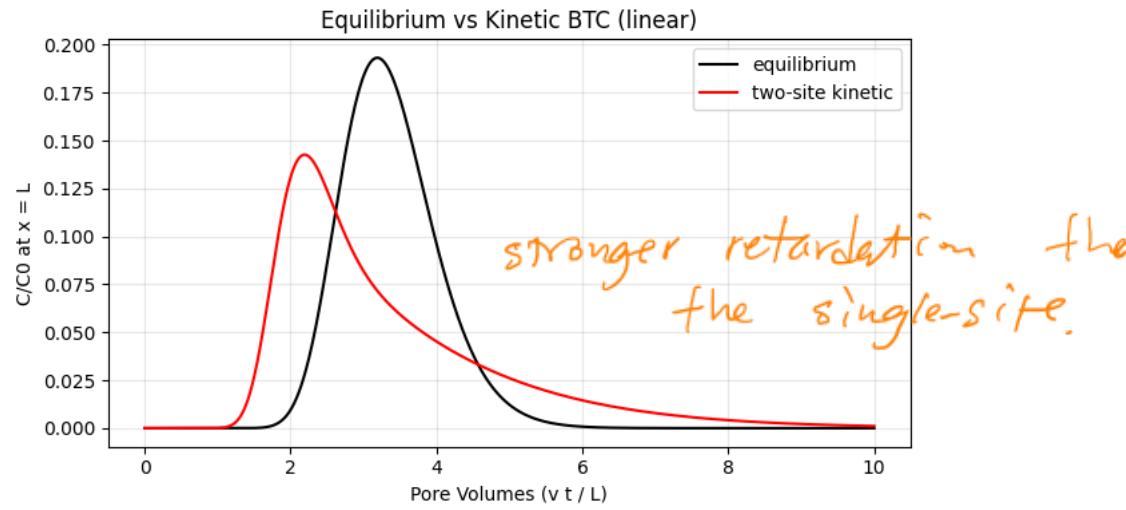
$F_s = 0$   
 $\alpha_s = 1/\text{day}$

# Solute transport under kinetic sorption



$L = 10.0 \text{ m}$   
 $v = 1.0 \text{ m/day}$   
 $D = 0.2 \text{ m}^2/\text{day}$   
Pulse duration = 3 days  
 $F_s = 0$  *single-site*  
 $\alpha_s = 0.1/\text{day}$

# Solute transport under kinetic sorption



$L = 10.0 \text{ m}$   
 $v = 1.0 \text{ m/day}$   
 $D = 0.2 \text{ m}^2/\text{day}$   
Pulse duration = 3 days  
 $F_s = 0.5$   
 $\alpha_s = 0.1/\text{day}$