HWRS 561b
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Spring 2026

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.

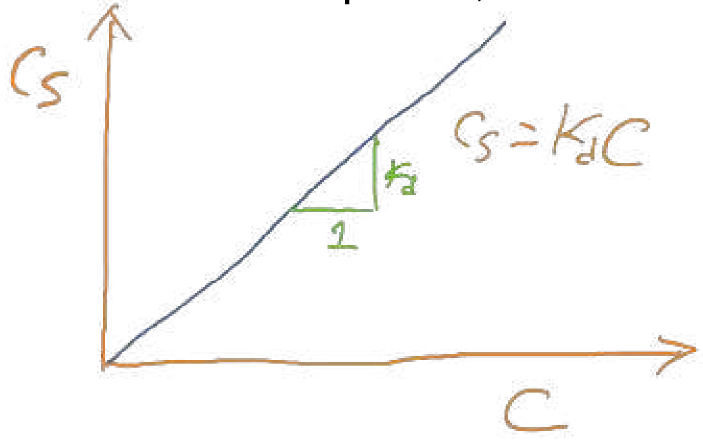
$$C_s = f(C)$$

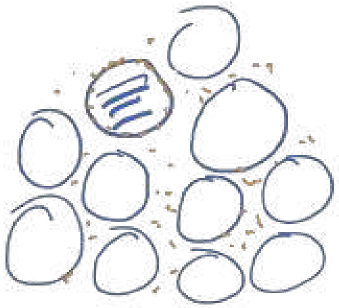
Linear isotherm

L^3/M

$$C_s = K_d C$$

M/M 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)

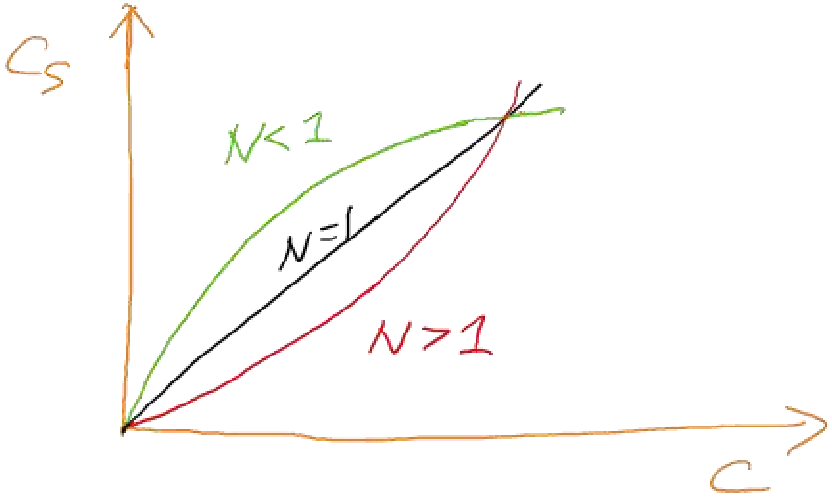
Sorption

Nonlinear isotherm

Freundlich isotherm

$$C_s = K_f C^N$$

K_f and N are fitting parameters to measured isotherms.



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

Langmuir isotherm

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

a physical meaning of K_l

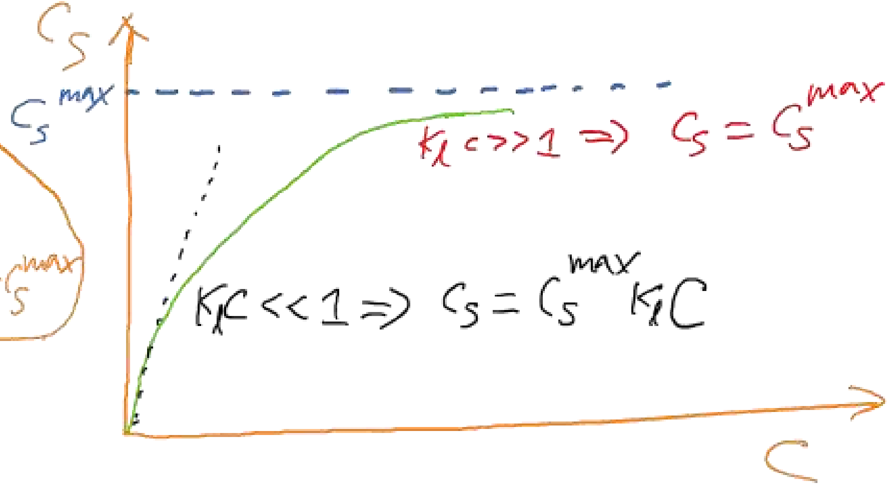
$K_l C = 1$

$C_s = \frac{1}{2} C_s^{max}$

$K_l = \frac{1}{C}$ when $C_s = \frac{1}{2} C_s^{max}$

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

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



ADE with sorption

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

If solid-phase sorption follows a linear isotherm

$$C_s=K_dC$$

We obtain

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

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

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

Define $1+\frac{\rho_bK_d}{\phi}\equiv R$ 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

$$C_s = K_f C^N$$

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

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

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

If solid-phase sorption follows a Langmuir isotherm

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

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

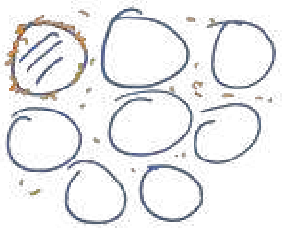
$$R = 1 + \frac{\rho_b}{\phi}\frac{C_s^{max} K_l}{(1+K_l C)^2}$$

Non-equilibrium (kinetic) sorption

Irreversible first-order kinetic sorption model

$$\begin{cases} \frac{\partial C_s}{\partial t} = k_1 C \\ \frac{\partial C}{\partial t} + \frac{\rho_b}{\phi}\frac{\partial C_s}{\partial t} + V\frac{\partial C}{\partial x} - D\frac{\partial^2 C}{\partial x^2} = 0 \end{cases}$$

First-order decay rate constant



Reversible linear kinetic sorption model

Forward rate constant

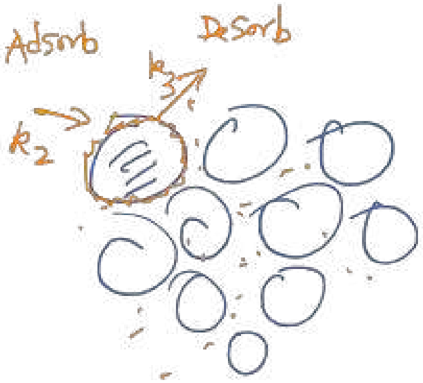
$$\frac{\partial C_s}{\partial t} = k_2 C - k_3 C_s$$

Backward rate constant.

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

First-order rate coefficient

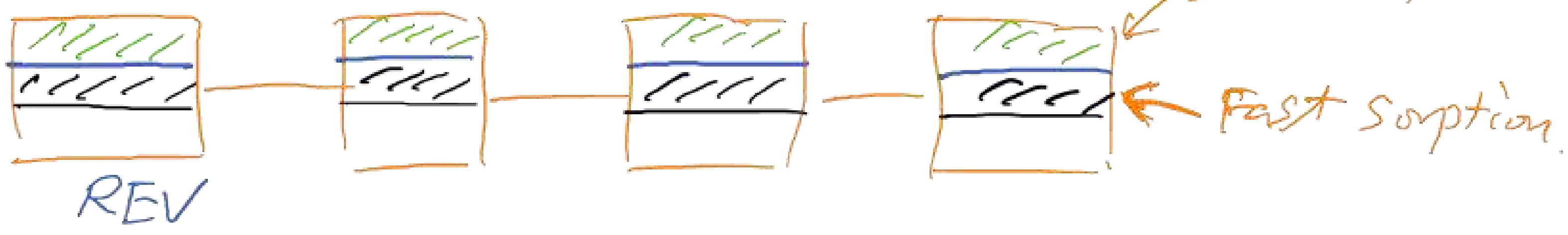
solid-phase adsorption coefficient (equivalent to K_d)



Non-equilibrium (kinetic) sorption

Two-site nonequilibrium sorption model

Model conceptualization



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

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

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

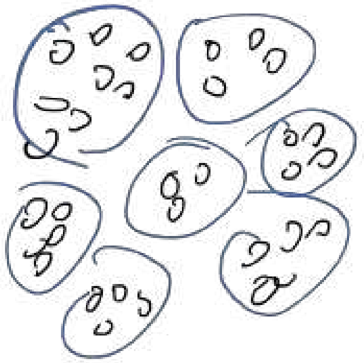
① At equilibrium, $C_{s,2} = (1-F_s) K_d C$

② At early time, when the solute just arrives $C_{s,2}$ is far from equilibrium and increases fast.

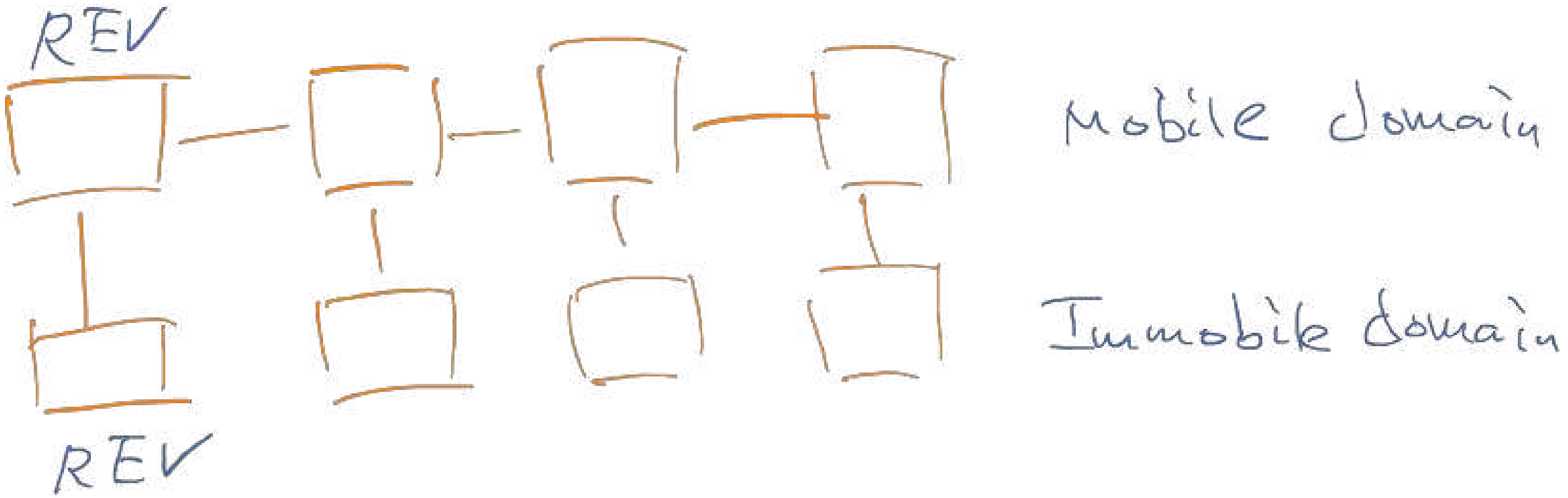
③ At late time, $C_{s,2}$ approaches $C_{s,2}$.

Non-equilibrium (kinetic) sorption

Two-domain nonequilibrium sorption model



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



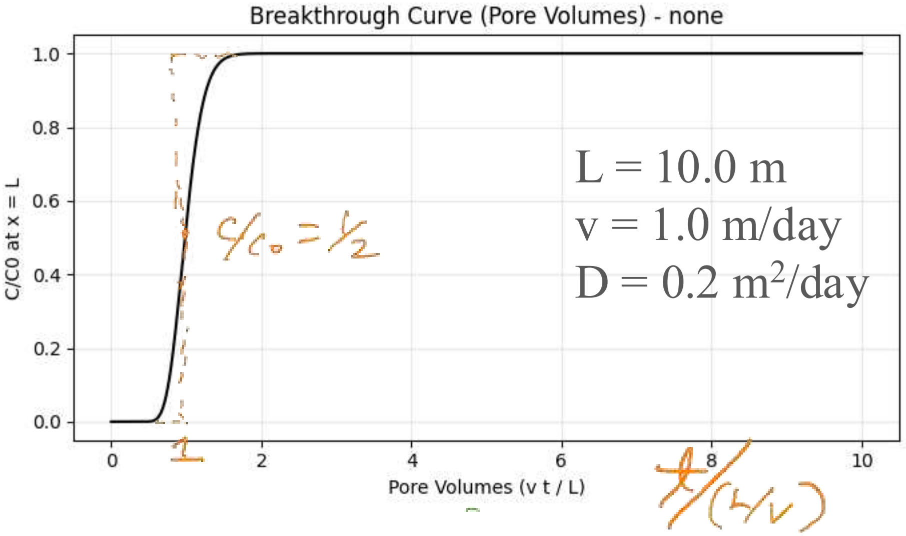
$$\theta_m \frac{\partial C_m}{\partial t} + \rho_b \frac{\partial C_{s,m}}{\partial t} + \theta_m V \frac{\partial C_m}{\partial x} - \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} = \alpha_{im,m} (C_{im} - C_m)$$ Mobile domain

$$\theta_{im} \frac{\partial C_{im}}{\partial t} + \rho_b \frac{\partial C_{s,im}}{\partial t} \boxed{\xcancel{+ \theta_{im} V \frac{\partial C_{im}}{\partial x} - \theta_{im} D_m \frac{\partial^2 C_{im}}{\partial x^2}}} = \alpha_{im,m} (C_m - C_{im})$$ Immobile domain

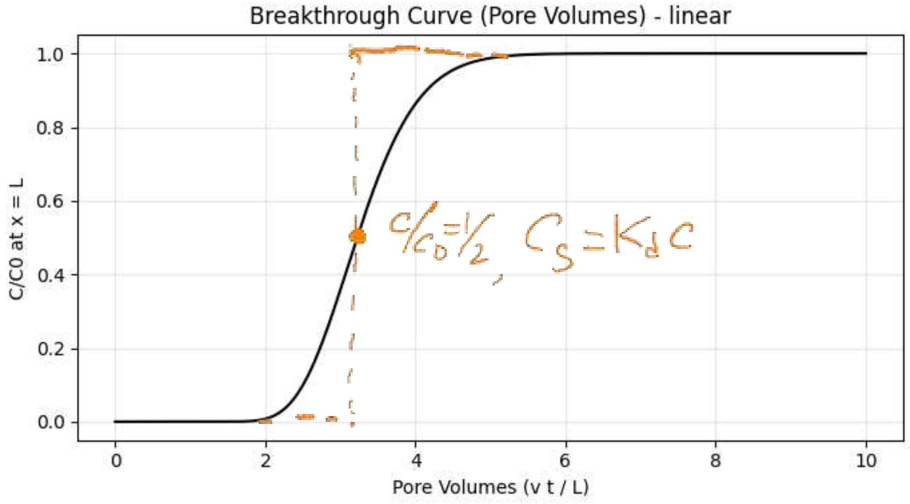
$$C_{s,m} = F_m K_d C_m , \quad C_{s,im} = (1 - F_m) K_d C_{im}$$

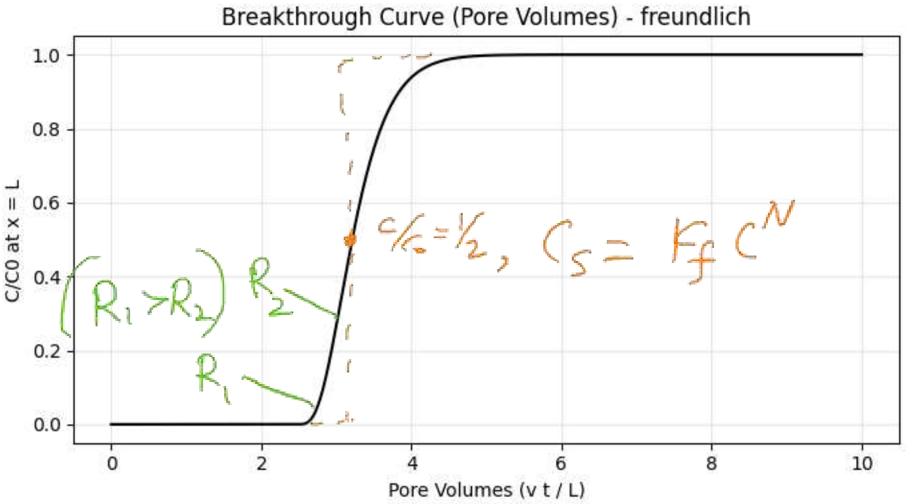
Solute transport under different isotherms

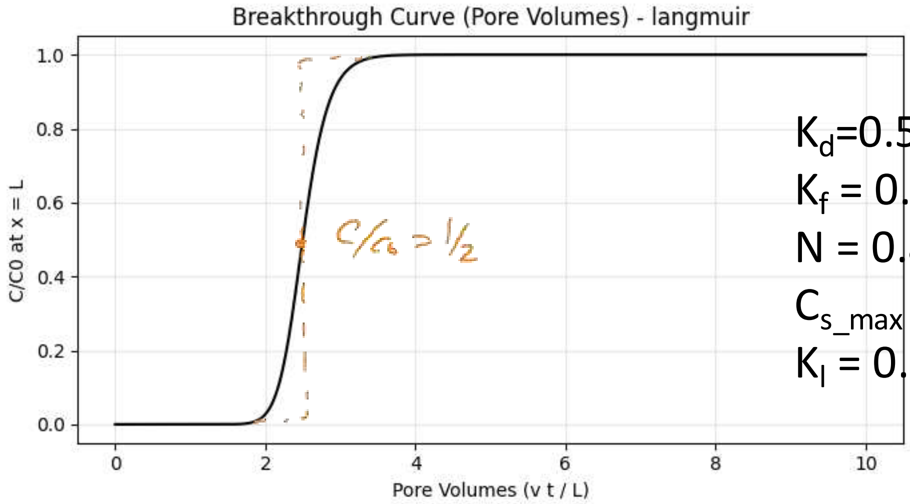
Continuous injection at a constant concentration (numerical solutions)



L = 10.0 m
v = 1.0 m/day
D = 0.2 m^2/day



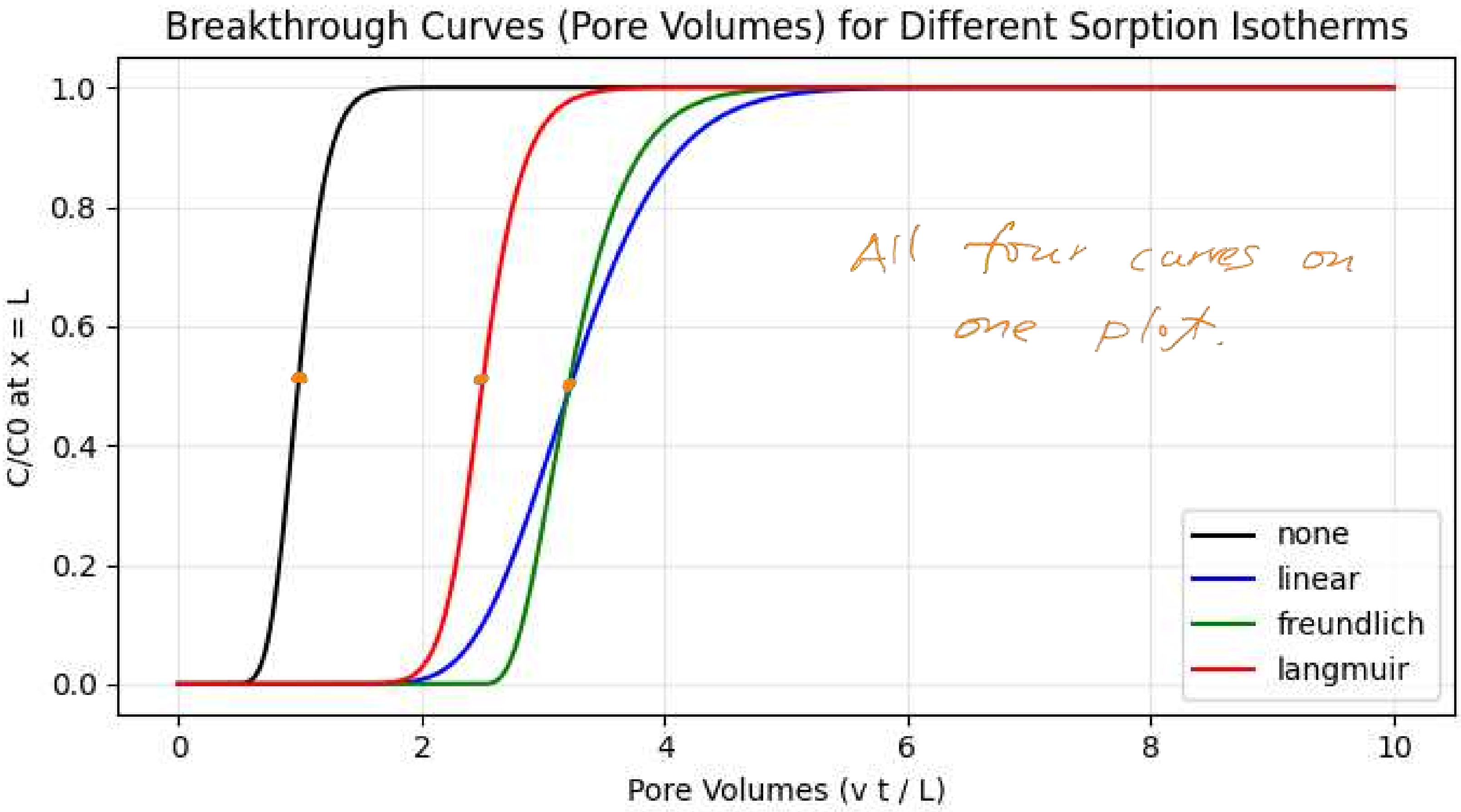




K_d=0.5 L/kg
K_f = 0.5 (mg/kg)*(L/mg)^N
N = 0.8 (-)
C_{s_max} = 1.0 mg/kg
K_l = 0.5 L/mg

Solute transport under different isotherms

Continuous injection at a constant concentration (numerical solutions)

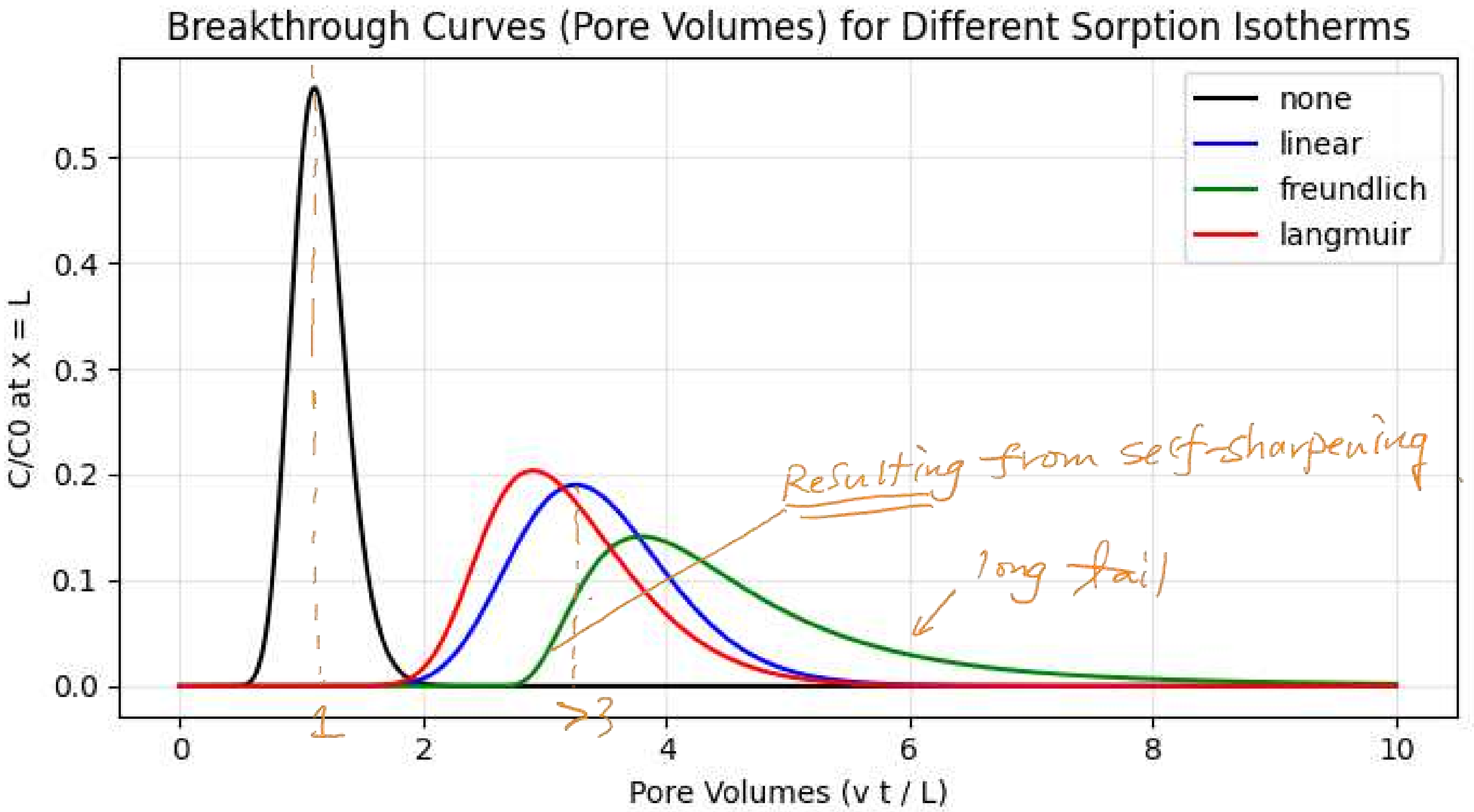


All four curves on one plot.

L = 10.0 m
v = 1.0 m/day
D = 0.2 m^2/day

Solute transport under different isotherms

Pulse injection at a constant concentration (numerical solutions)



Resulting from self-sharpening

long tail

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

Solute transport under different isotherms

Under a Freundlich isotherm with $\mathrm{N} < 1$ 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

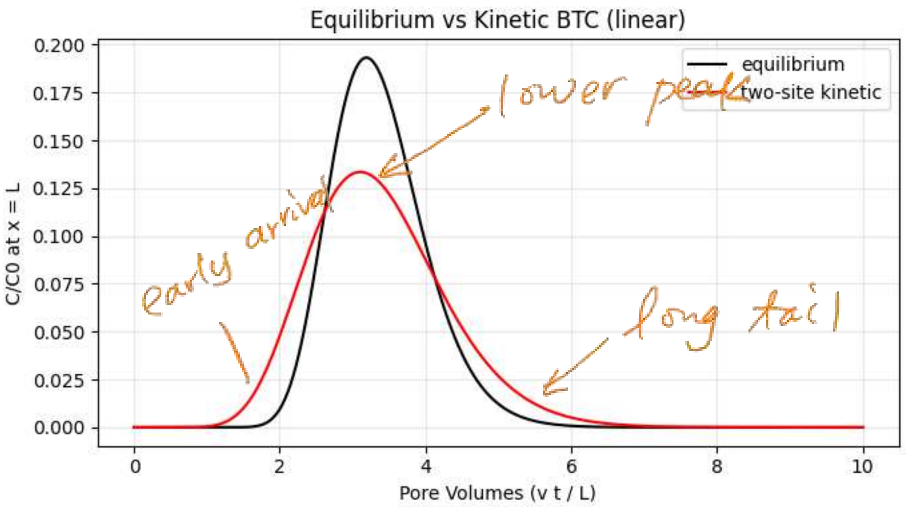
$$R = 1 + \frac{\rho_b}{\phi} K_f N C^{N-1}$$

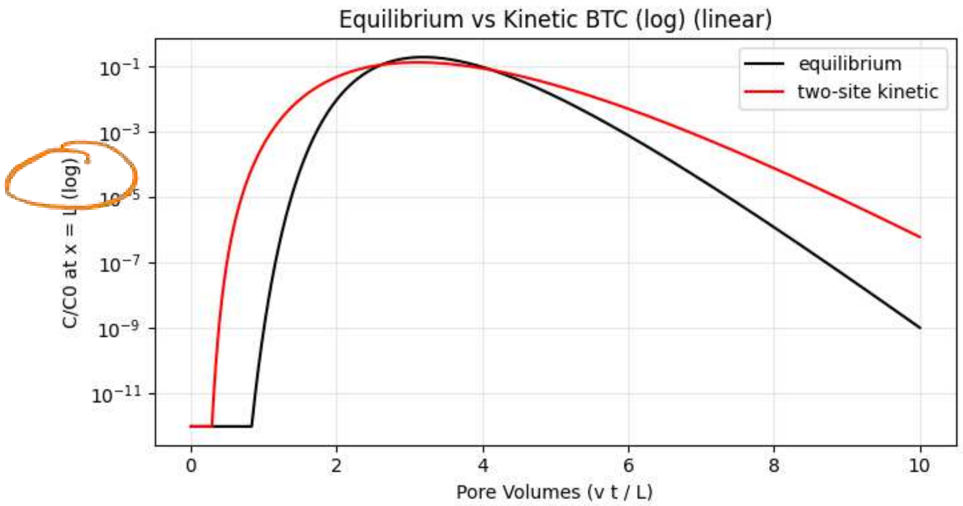
Langmuir isotherm

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

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.

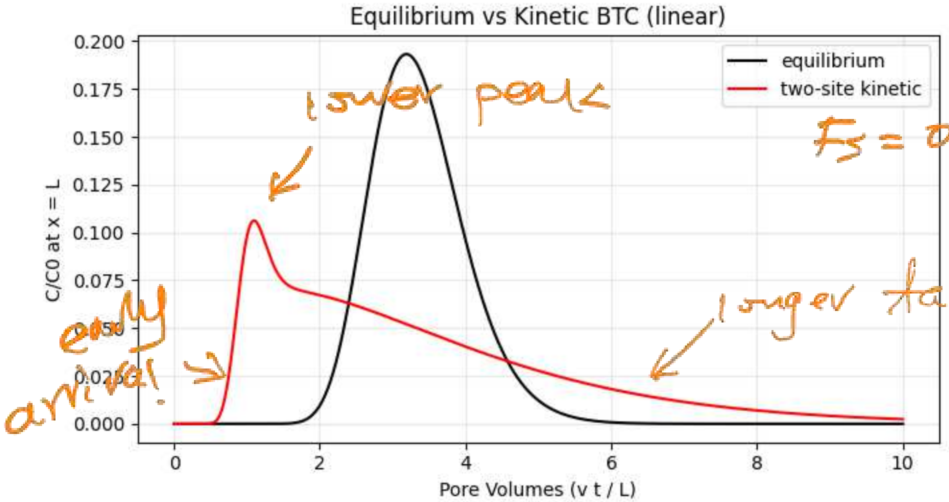
Solute transport under kinetic sorption



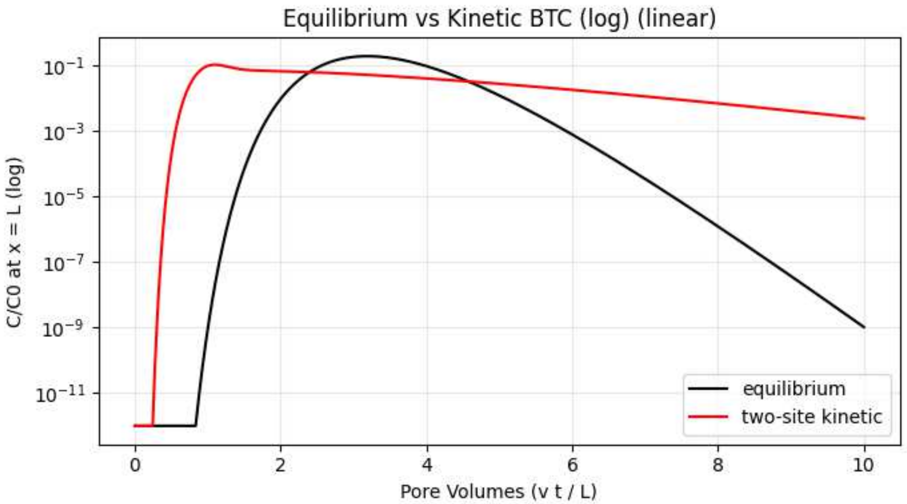


L = 10.0 m
v = 1.0 m/day
D = 0.2 m^2/day
Pulse duration = 3 days
Fs = 0
alpha_s = 1/day

Solute transport under kinetic sorption

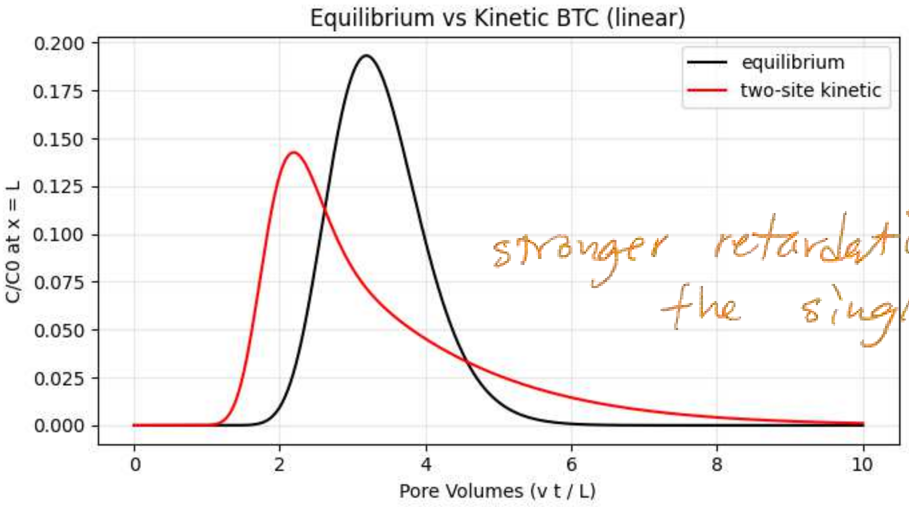


Fs = 0, effective single-site.

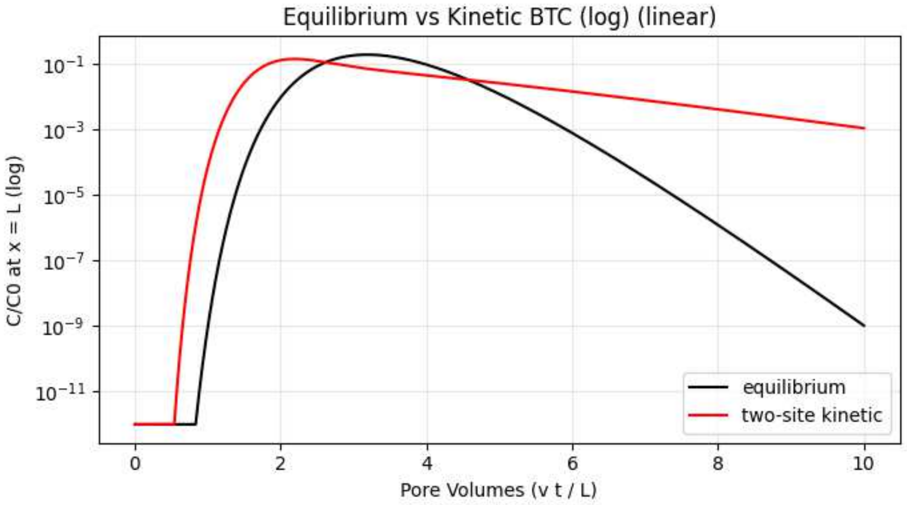


L = 10.0 m
v = 1.0 m/day
D = 0.2 m^2/day
Pulse duration = 3 days
Fs = 0 single-site
alpha_s = 0.1/day

Solute transport under kinetic sorption



stronger retardation than the single-site.



L = 10.0 m
v = 1.0 m/day
D = 0.2 m^2/day
Pulse duration = 3 days
Fs = 0.5
alpha_s = 0.1/day