

HWRS 561b: Physical Hydrogeology II

Solute transport (Part 4)

Agenda:

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

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

$$C_s = K_d C$$

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)

Nonlinear isotherm

Freundlich isotherm

$$C_s = K_f C^N$$

K_f and N are fitting parameters to measured isotherms.

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)

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

$$C_s = K_d C$$

We obtain

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

ADE with sorption

If solid-phase sorption follows a Freundlich isotherm

$$C_s = K_f C^N$$

If solid-phase sorption follows a Langmuir isotherm

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

Non-equilibrium (kinetic) sorption

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Irreversible first-order kinetic sorption model

Reversible linear kinetic sorption model

Non-equilibrium (kinetic) sorption

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Two-site nonequilibrium sorption model

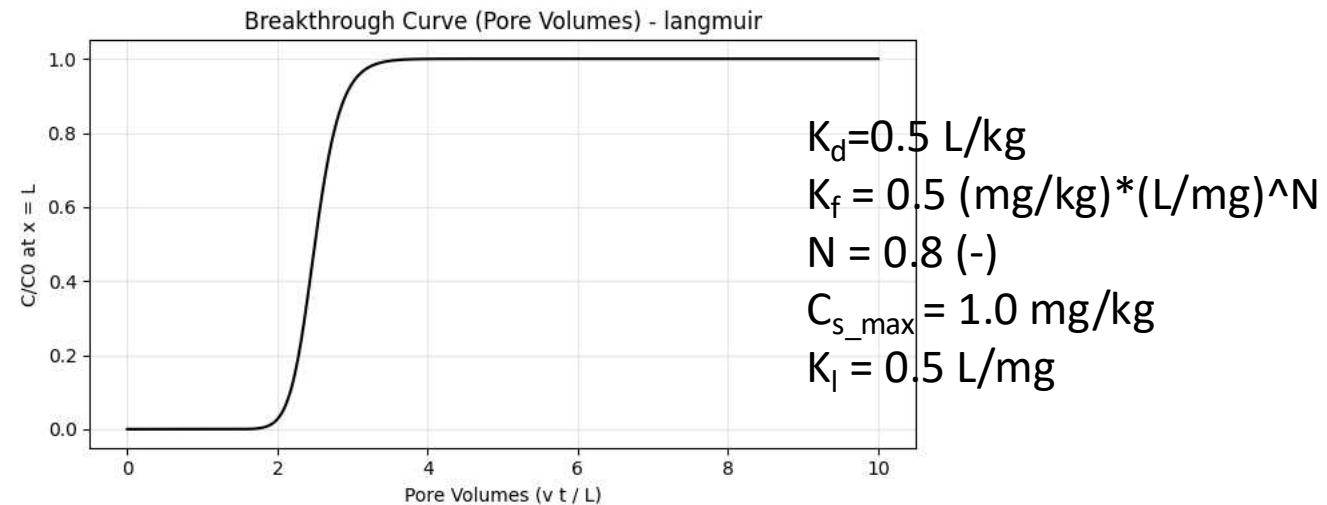
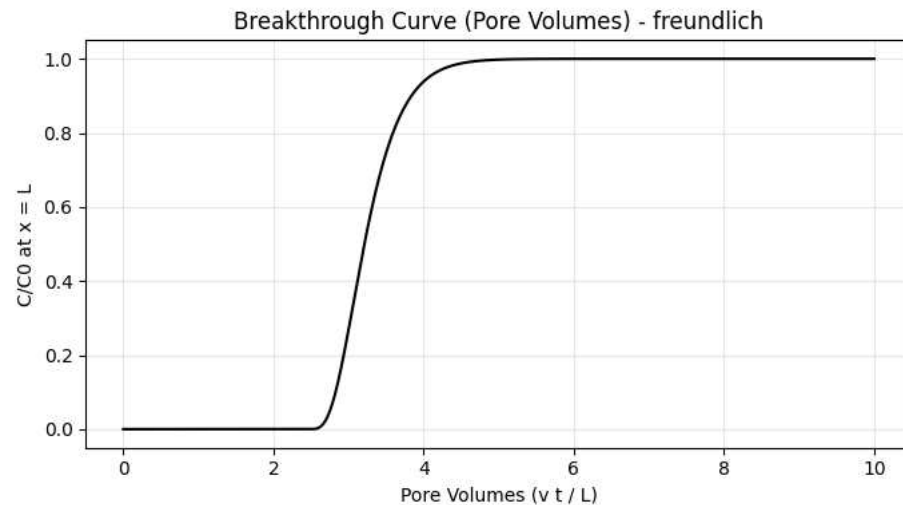
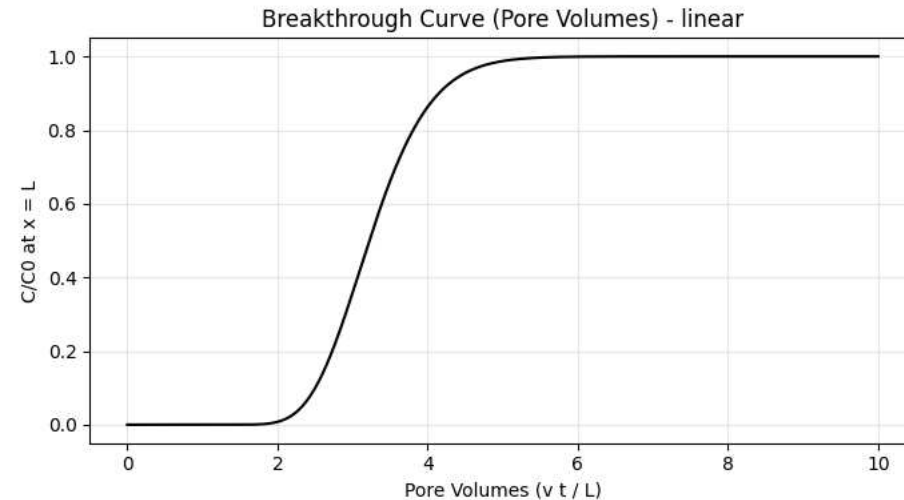
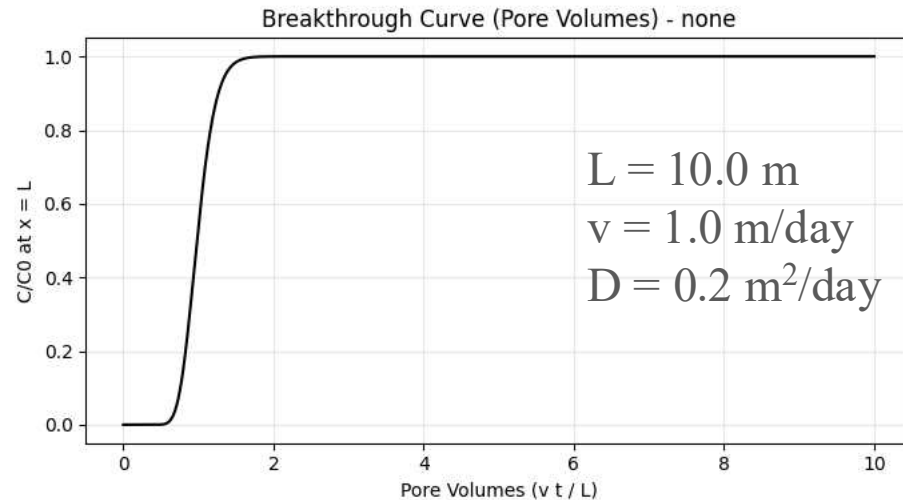
Non-equilibrium (kinetic) sorption

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Two-domain nonequilibrium sorption model

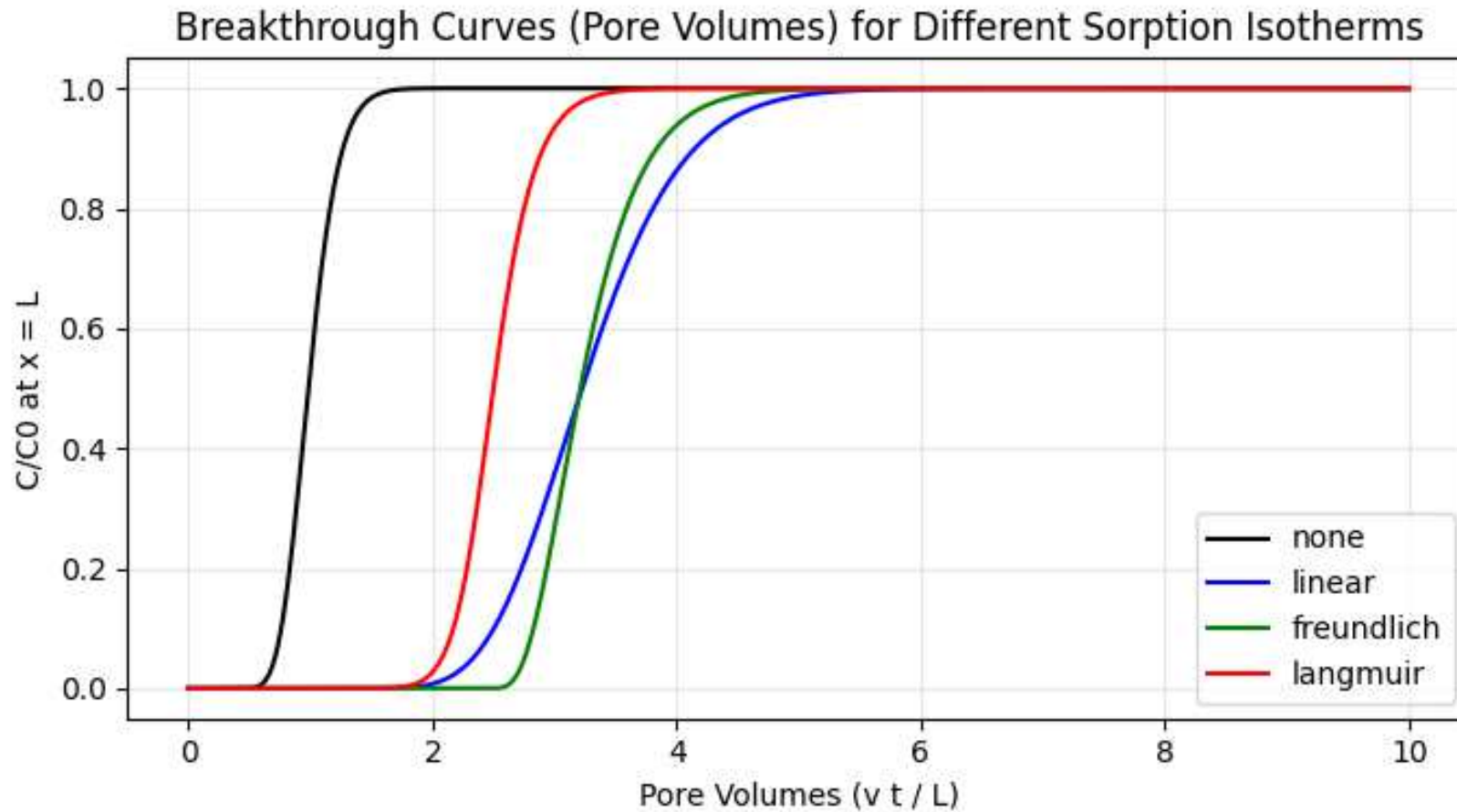
Solute transport under different isotherms

Continuous injection at a constant concentration (numerical solutions)



Solute transport under different isotherms

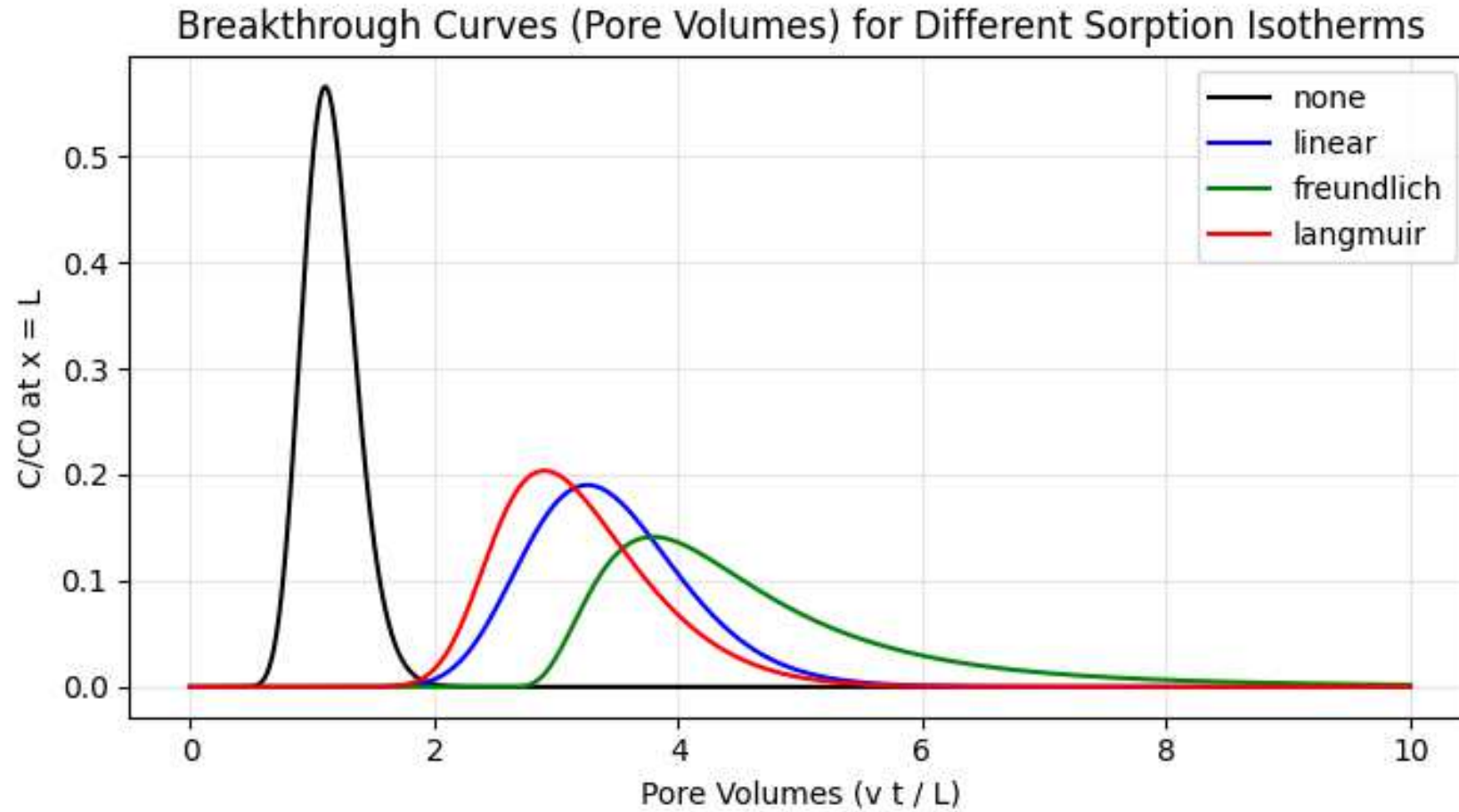
Continuous injection at a constant concentration (numerical solutions)



$L = 10.0$ m
 $v = 1.0$ m/day
 $D = 0.2$ m²/day

Solute transport under different isotherms

Pulse injection at a constant concentration (numerical solutions)



$L = 10.0$ m

$v = 1.0$ m/day

$D = 0.2$ m²/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.

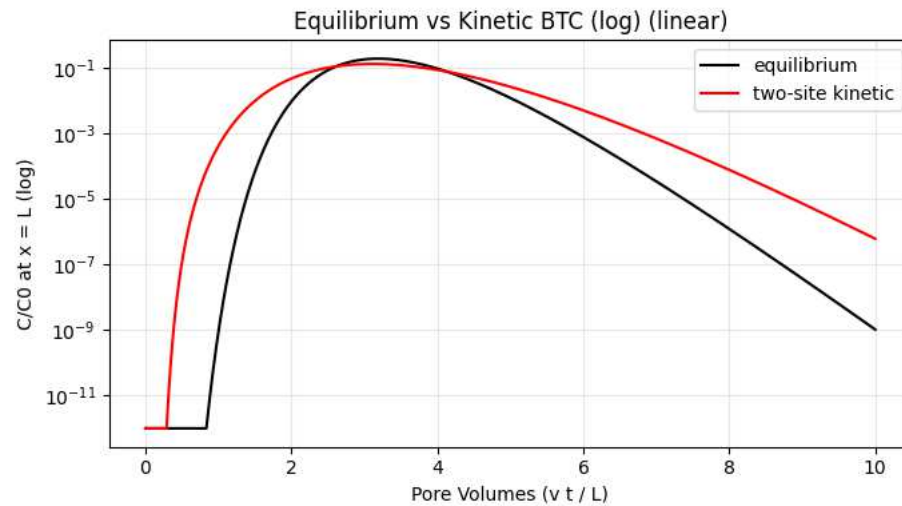
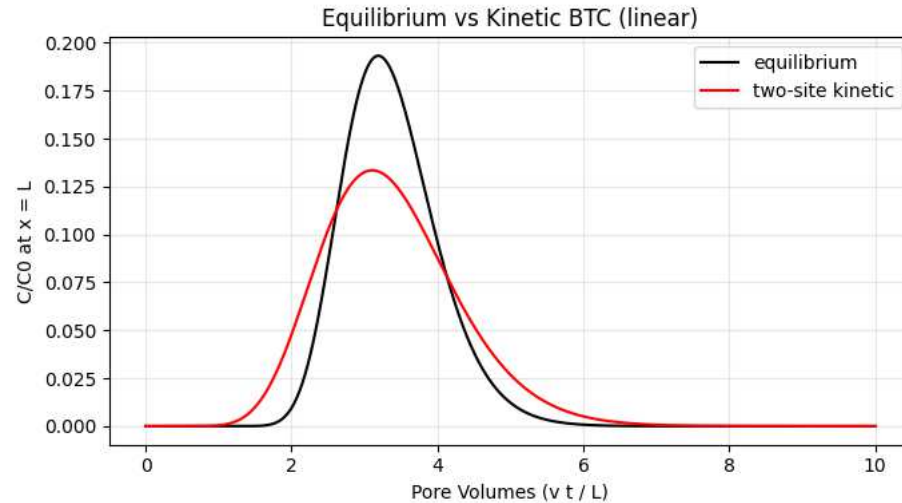
Freundlich isotherm

Langmuir isotherm

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.

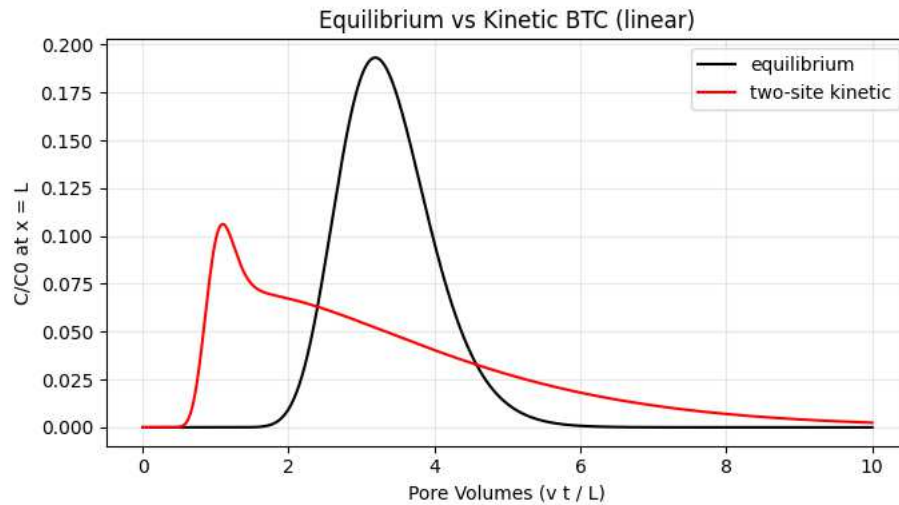
Solute transport under kinetic sorption

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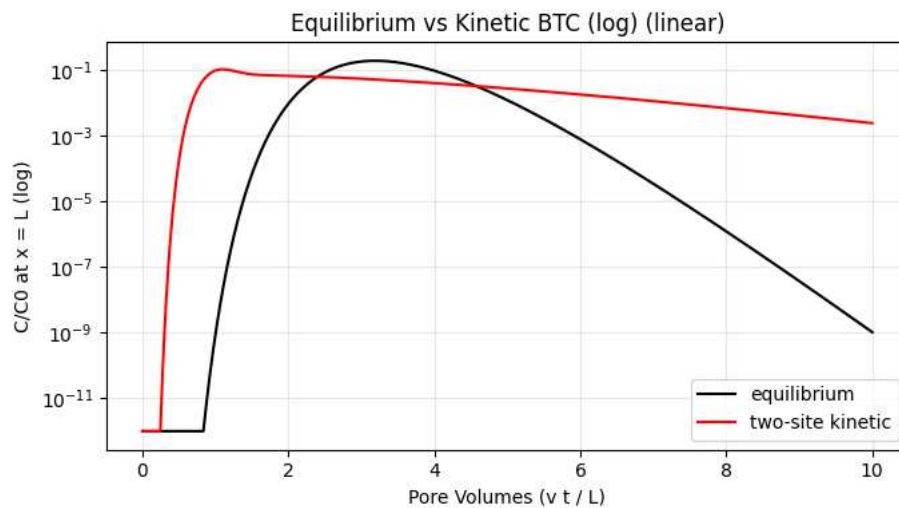


$L = 10.0$ m
 $v = 1.0$ m/day
 $D = 0.2$ m²/day
Pulse duration = 3 days
 $F_s = 0$
 $\alpha_s = 1/\text{day}$

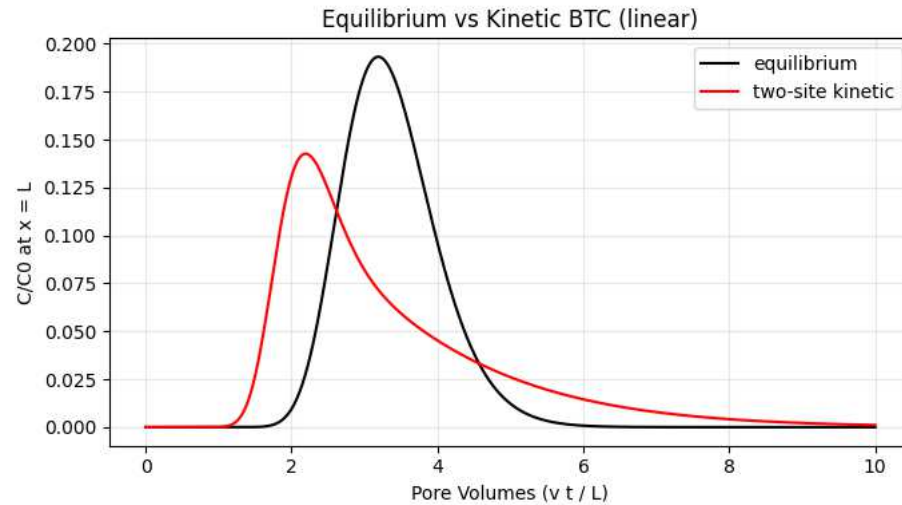
Solute transport under kinetic sorption



$L = 10.0$ m
 $v = 1.0$ m/day
 $D = 0.2$ m²/day
Pulse duration = 3 days
 $F_s = 0$
 $\alpha_s = 0.1$ /day



Solute transport under kinetic sorption



$L = 10.0$ m
 $v = 1.0$ m/day
 $D = 0.2$ m²/day
Pulse duration = 3 days
 $F_s = 0.5$
 $\alpha_s = 0.1$ /day

