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

$$C_s = K_d C$$

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.

Langmiur isotherm

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

α 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 Freudlich isotherm

$$C_s = K_f C^N$$

If solid-phase sorption follows a Langmuir isotherm

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

Non-equilibrium (kinetic) sorption

Irreversible first-order kinetic sorption model

Reversible linear kinetic sorption model

Non-equilibrium (kinetic) sorption

<u>Two-site</u> nonequilibrium sorption model
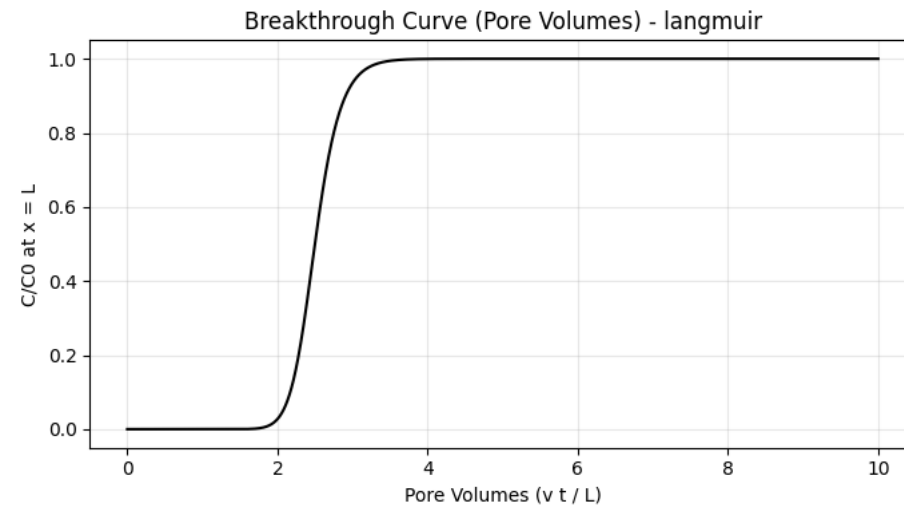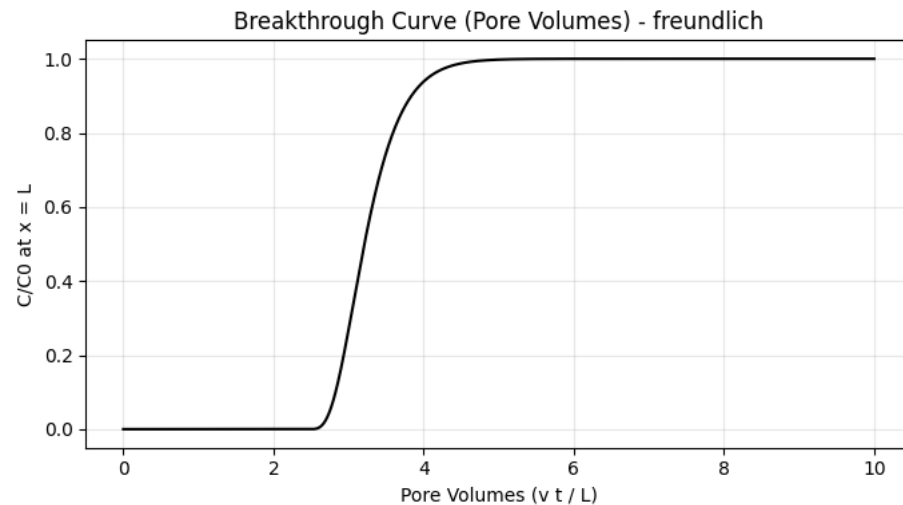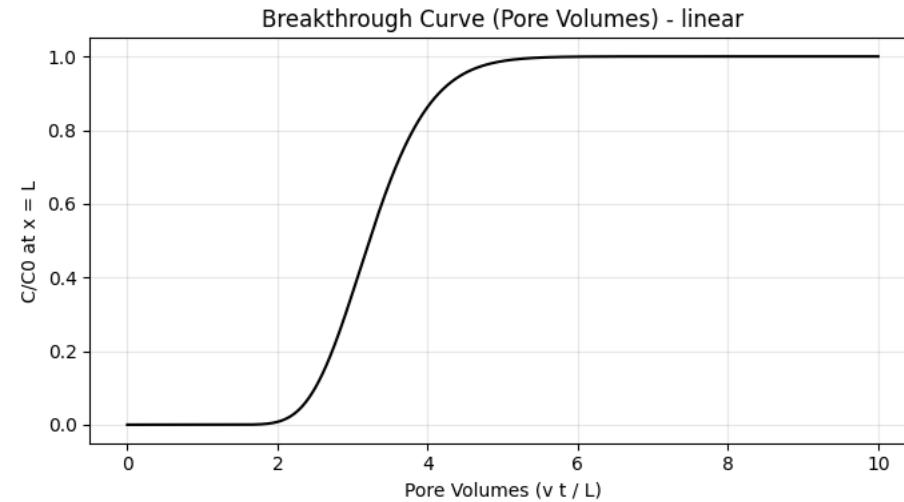
Non-equilibrium (kinetic) sorption
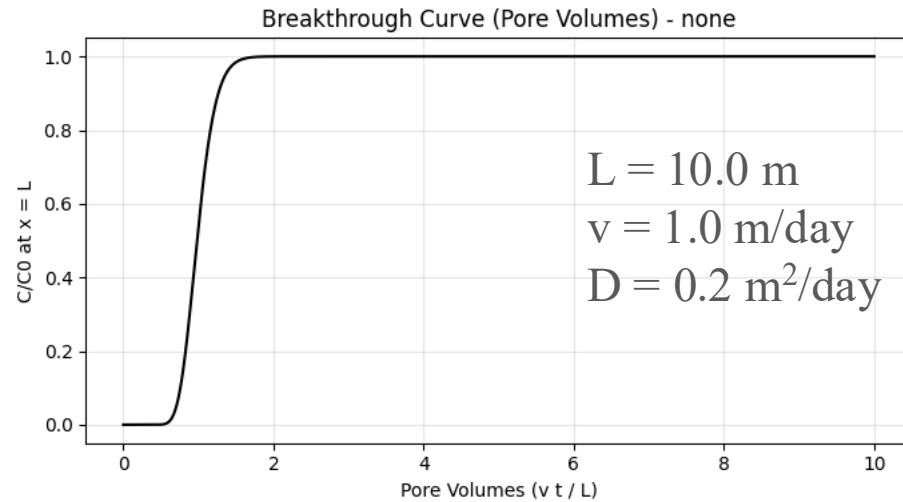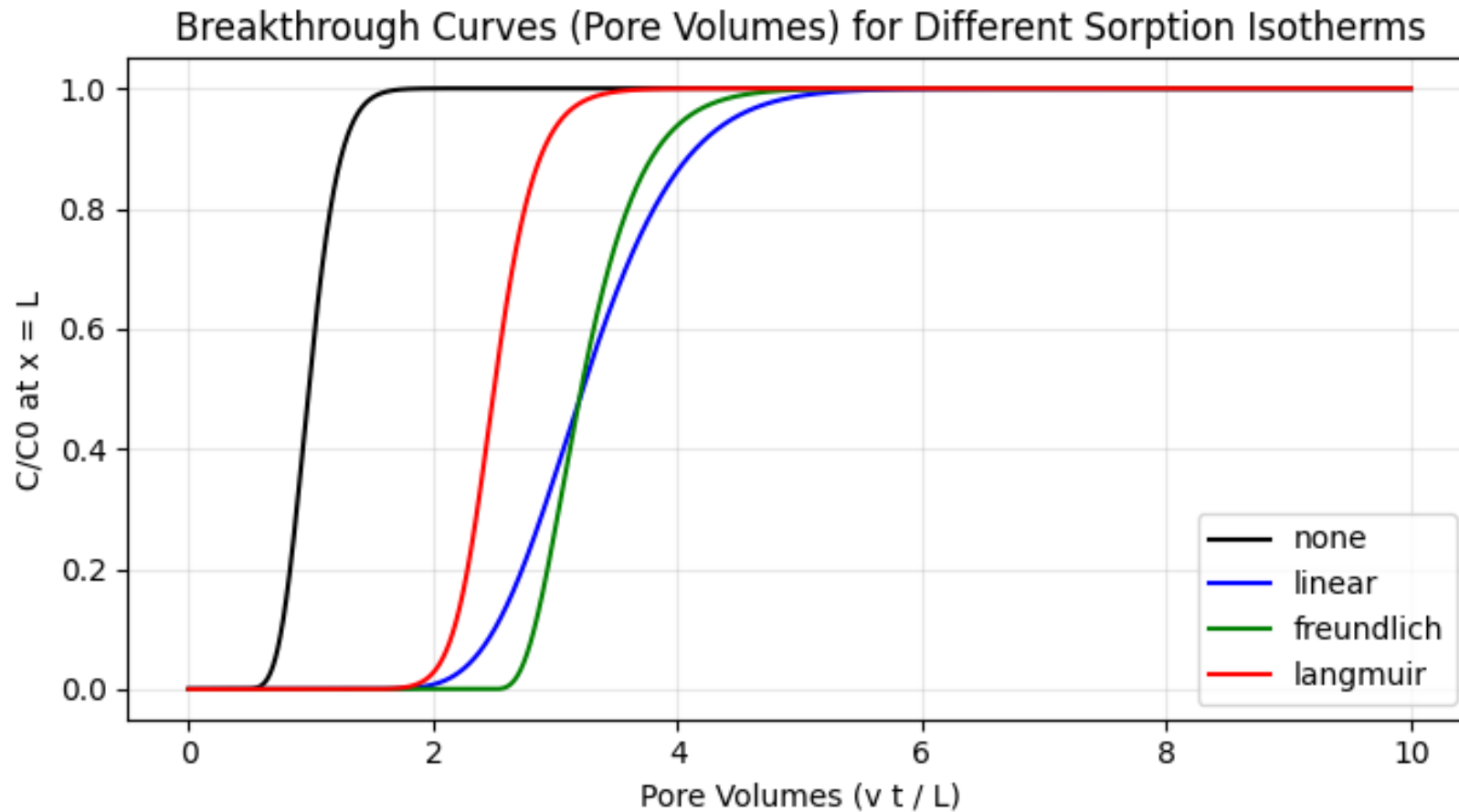
Two-domain nonequilibrium sorption model

Solute transport under different isotherms

Continuous injection at a constant concentration (numerical solutions)

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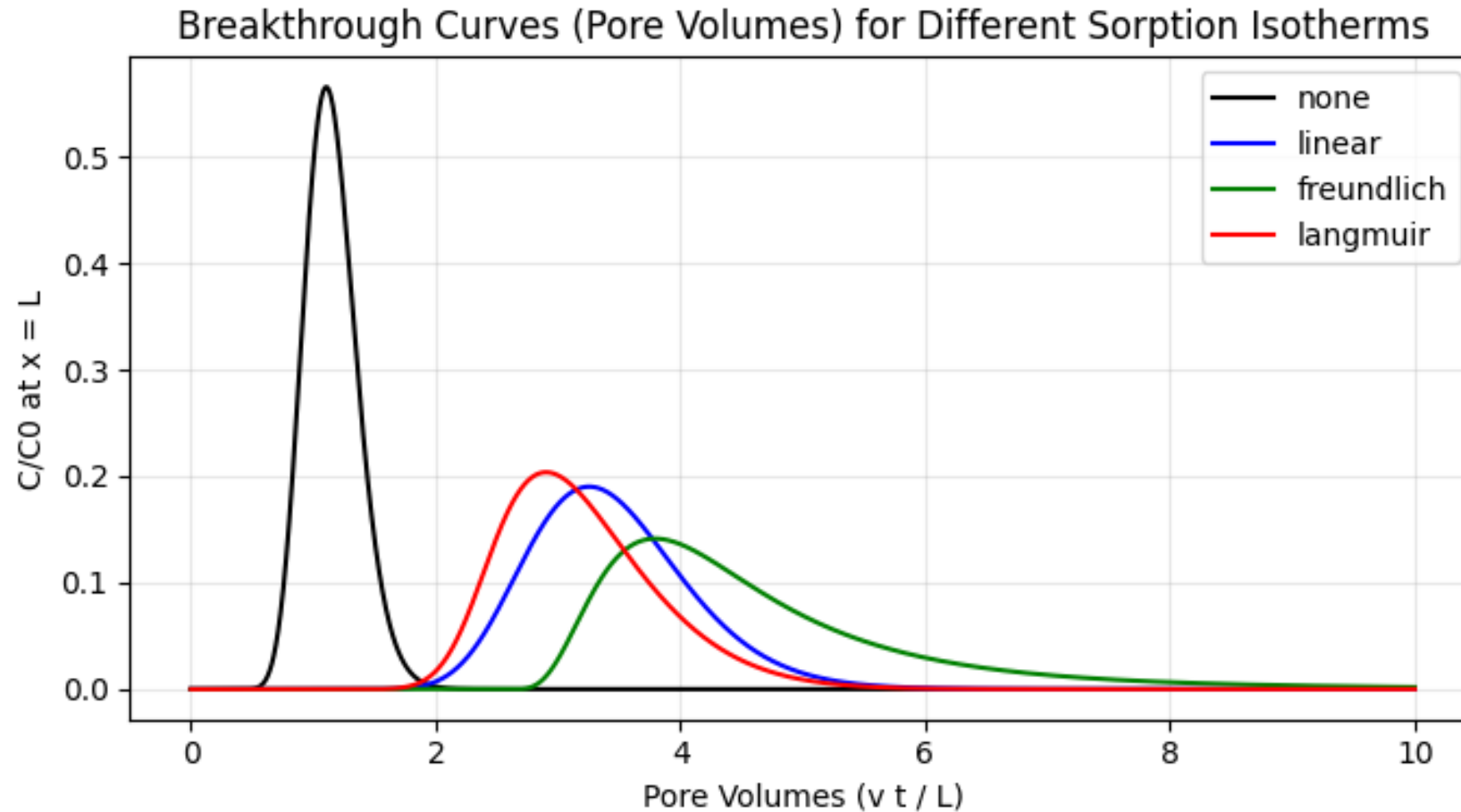v = 1.0 m/day
D = 0.2 m^2/day

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

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 m^2/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

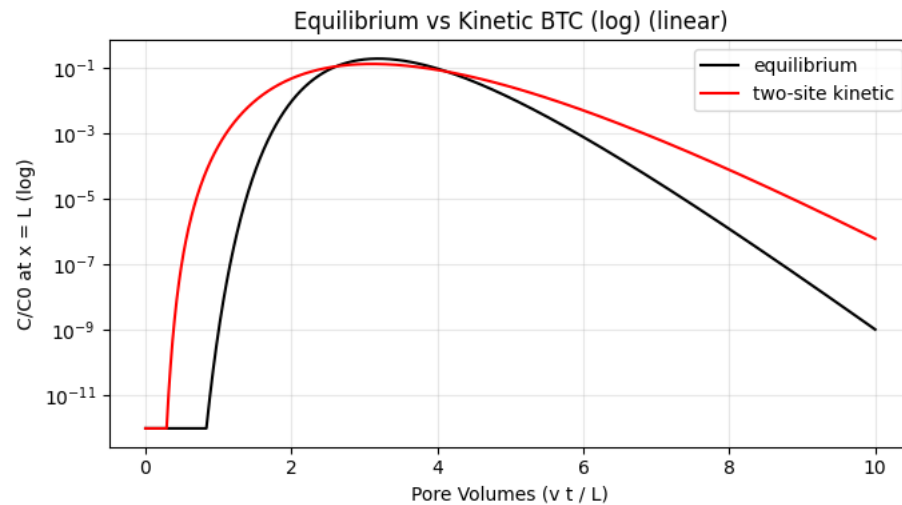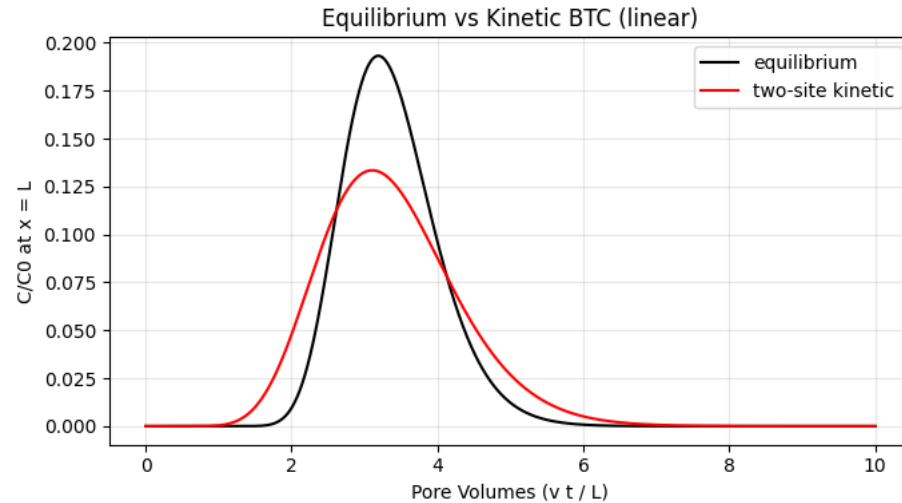$$R = 1 + \frac{\rho_b}{\phi} K_f N C^{N-1}$$

Langmuir isotherm

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

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.
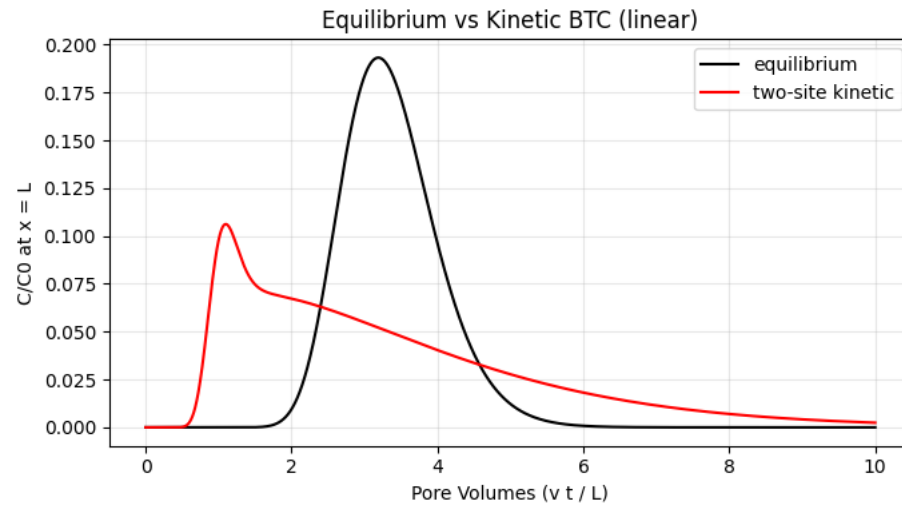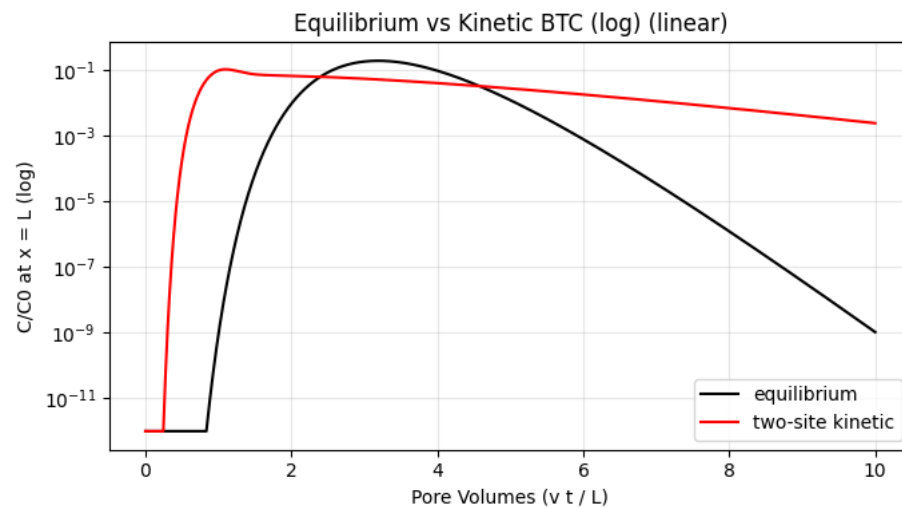
Solute transport under kinetic sorption

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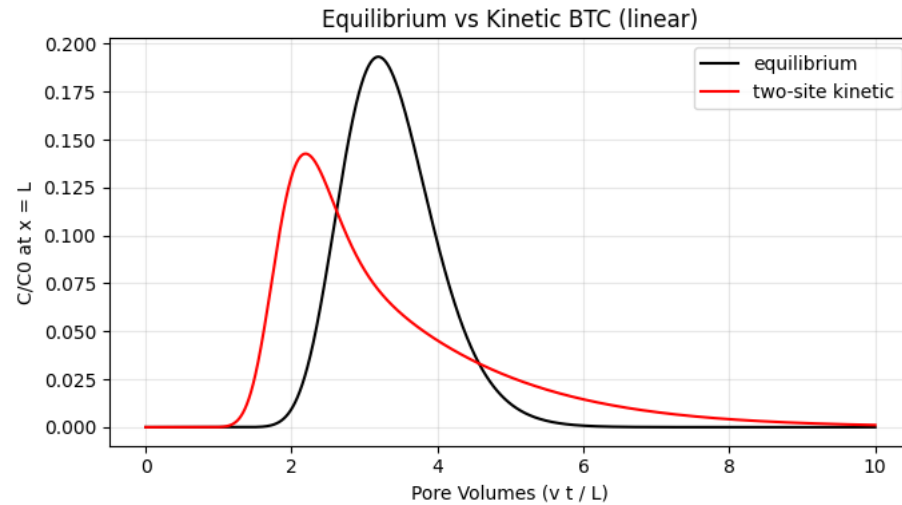
L = 10.0 m
v = 1.0 m/day
D = 0.2 m^2/day
Pulse duration = 3 days
Fs = 0
alpha_s = 0.1/day

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 = 0.5
alpha_s = 0.1/day