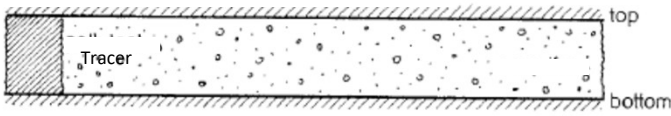# Sorption

Exercise 1: Breakthrough Curve
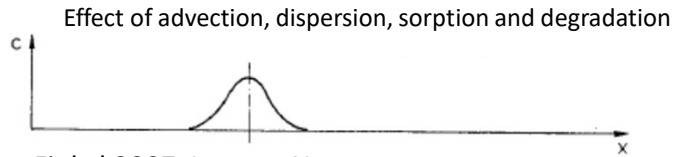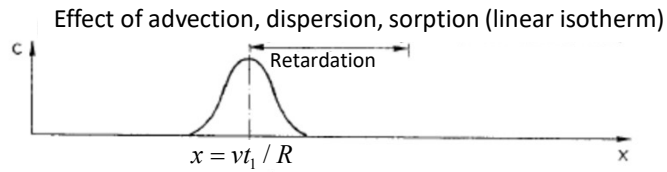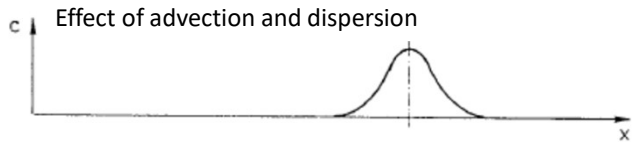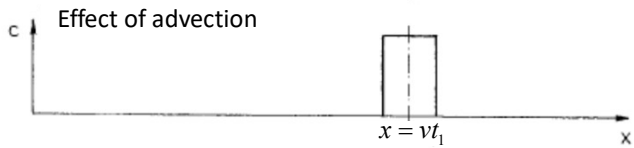
Concentration Distribution at time t=0

A pulse injection

Concentration Distribution at time $t_1 > 0$

Effect of advection

$$\frac{\partial c}{\partial t} = -v\frac{\partial c}{\partial x}$$

$x = vt_1$

Effect of advection and dispersion

$$\frac{\partial c}{\partial t} = -v\frac{\partial c}{\partial x} + D\frac{\partial^2 c}{\partial x^2}$$

Effect of advection, dispersion, sorption (linear isotherm)

Retardation

$$R\frac{\partial c}{\partial t} = -v\frac{\partial c}{\partial x} + D\frac{\partial^2 c}{\partial x^2}$$

$x = vt_1 / R$

Effect of advection, dispersion, sorption and degradation

$$R\frac{\partial c}{\partial t} = -v\frac{\partial c}{\partial x} + D\frac{\partial^2 c}{\partial x^2} + r_w + \frac{(1-n_e)}{n_e}r_s$$

Finkel 2007, Lecture Notes

A Sorbing Phase

The mass fluxes are not affected by sorption, but the solute can also be stored in the solid phase. The volumetric water content is the effective porosity n_e and the volumetric content of solids is $(1-n_e)$. The new mass balance with a solid sorbing phase:

$$m = [n_e c_w + (1-n_e)c_s]A\Delta x$$

$$\frac{\partial c}{\partial t} = -v\frac{\partial c}{\partial x} \qquad \frac{\partial}{\partial t}(n_e c_w + (1-n_e)c_s) = -q\frac{\partial c_w}{\partial x} \qquad \frac{\partial}{\partial t}\left(c_w + \frac{(1-n_e)}{n_e}c_s\right) = -v\frac{\partial c_w}{\partial x}$$

One thing to note is that Sorbing compounds are often quantified as mass fraction s [M_{solute}/M_{solid}] in the solid. ρ_s [M_{soild}/L^3] is the density of the solids.

$$c_s = \rho_s s$$

$$\frac{\partial}{\partial t}\left(c_w + \frac{(1-n_e)}{n_e}\rho_s s\right) = -v\frac{\partial c_w}{\partial x}$$

A Sorbing Phase: Equilibrium

Only when we assume that sorption is at equilibrium at any point within the domain, the relationship between the two concentrations is unique with functional relationship $f(c_w(x))$ known as sorption isotherm

$$s(x) = f(c_w(x))$$

Advective transport equation

$$\frac{\partial}{\partial t}\left(c_w + \frac{(1-n_e)}{n_e}\underbrace{\rho_s s}_{c_s}\right) = -v\frac{\partial c_w}{\partial x}$$

Advective transport with a sorbing phase

$$R\frac{\partial c_w}{\partial t} = -v\frac{\partial c_w}{\partial x}$$

Using chain-rule

$$\frac{\partial c_s}{\partial t} = \frac{\partial c_w}{\partial t}\frac{\partial c_s}{\partial c_w}$$

$$\frac{\partial}{\partial t}\left(c_w + \frac{(1-n_e)}{n_e}c_s\right) = \underbrace{\left(1 + \frac{(1-n_e)}{n_e}\frac{\partial c_s}{\partial c_w}\right)}_{R(c)}\frac{\partial c_w}{\partial t}$$

How to define the sorption isotherm for the retardation factor R ?

It depends whether you have
o   Linear sorption
o   Non-linear sorption

Retardation Factor: Linear Equilibrium Sorption

$$\frac{\partial}{\partial t}\left(c_w + \frac{(1-n_e)}{n_e}c_s\right) = \underbrace{\left(1 + \frac{(1-n_e)}{n_e}\frac{\partial c_s}{\partial c_w}\right)}_{R(c)}\frac{\partial c_w}{\partial t} \qquad c_s = \rho_s s$$

$$s(x) = f(c_w(x))$$

$$s = K_d c_w$$

K_d [L^3/M_{solid}] is partitioning coefficient between the solid and the aqueous phase.

What is the retardation factor for linear equilibrium sorption?
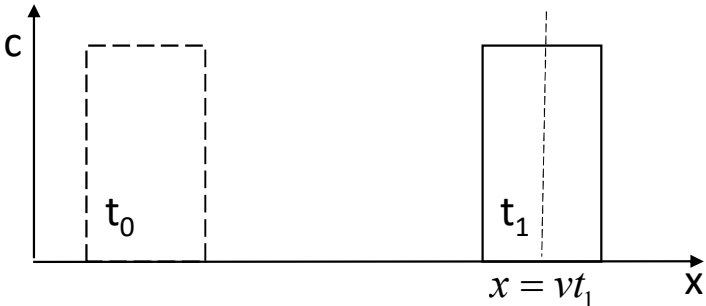
$$R = 1 + \frac{(1-n_e)}{n_e}\rho_s K_d$$

$$K_d = K_{oc} f_{oc}$$

K_{OC} [L^3/M_{Corg}] partitioning coefficient between organic carbon and water
f_{OC} [-] fraction of organic carbon.

Retardation Factor: Linear Equilibrium Sorption
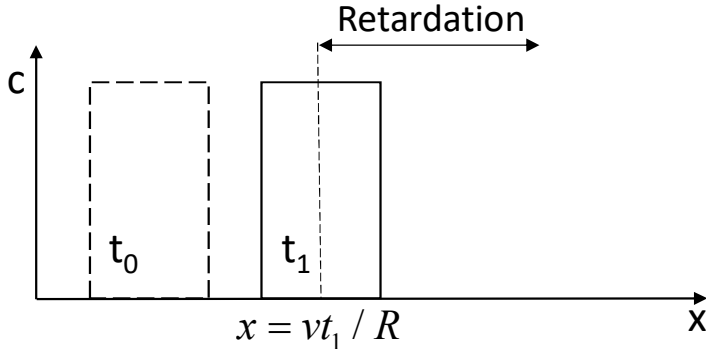
Advection

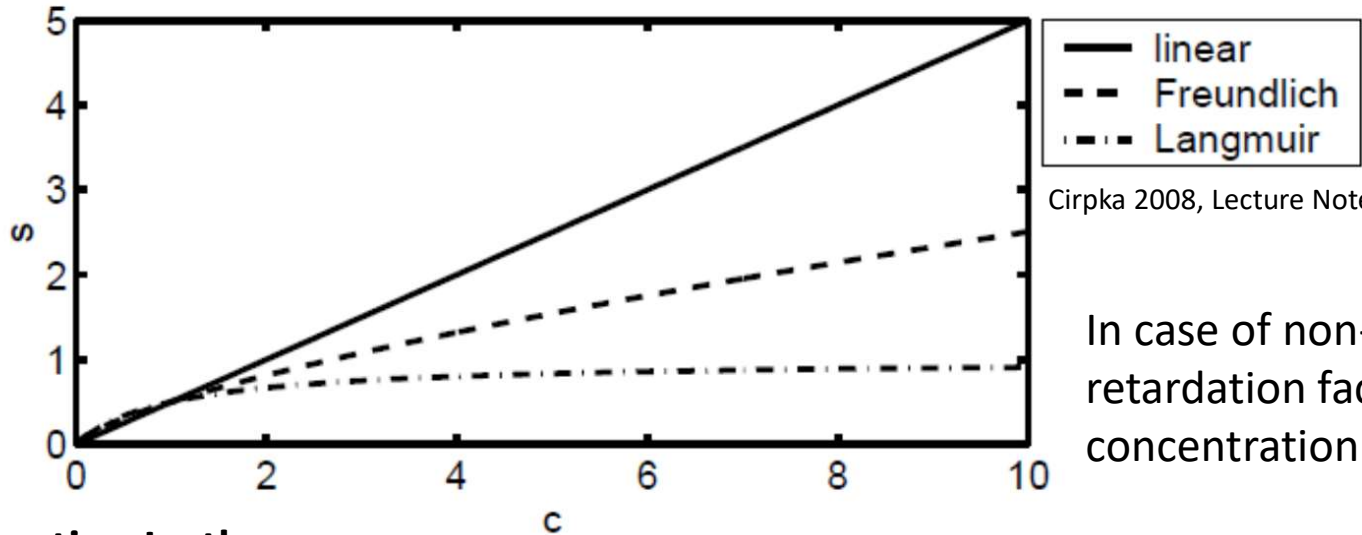$$\frac{\partial c}{\partial t} = -v\frac{\partial c}{\partial x}$$

Advection+ Linear Sorption

$$R\frac{\partial c_w}{\partial t} = -v\frac{\partial c_w}{\partial x}$$

For linear sorption at equilibrium: the non-retarded and retarded concentration profiles are identical. The only difference is that everything happens at later time.

Retardation Factor: Non-Linear Equilibrium Sorption

Cirpka 2008, Lecture Notes

In case of non-linear sorption, the retardation factor depends on the concentration

Sorption Isotherm

$$s(x) = f(c_w(x))$$

$$s(x) = K_d c$$

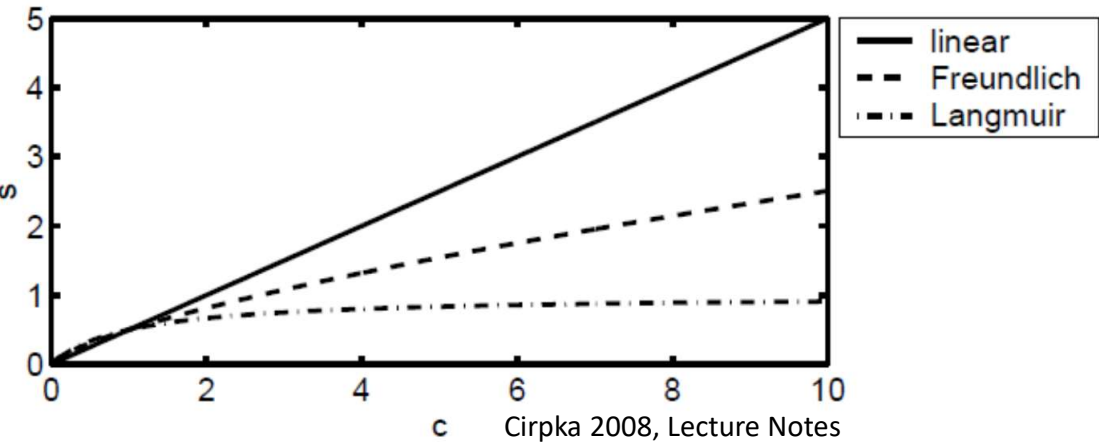$$s(x) = K c^n$$

$$s(x) = \frac{s_{max}K}{c+K}$$

Retardation factor

$$R = 1 + \frac{(1-n_e)}{n_e}\rho_s K_d$$

$$R = 1 + \frac{(1-n_e)}{n_e}\rho_s K n c^{n-1}$$

$$R = 1 + \frac{(1-n_e)}{n_e}\rho_s \frac{s_{max}K}{(c+K)^2}$$

How non-linear sorption affect breakthrough curves?

How Non-Linear Sorption Affect Breakthrough Curve?

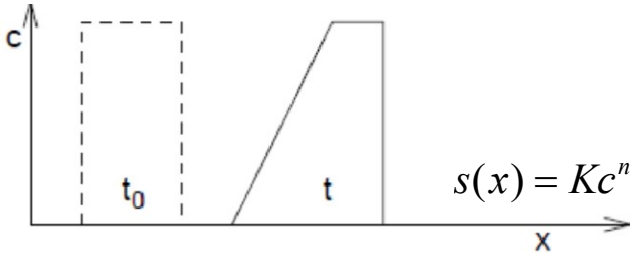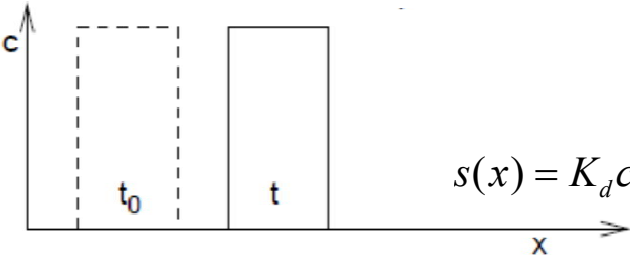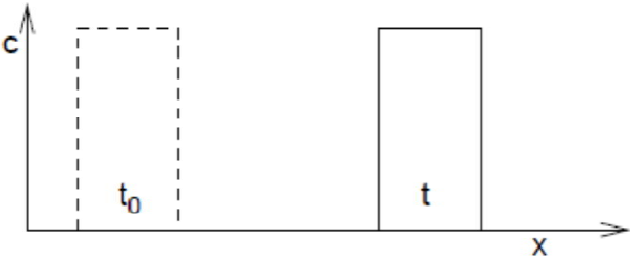Non-linear sorption: the retardation factor depends on the concentration

Cirpka 2008, Lecture Notes

How non-linear sorption affect breakthrough curves?

- Concentration changes are slowed down more dramatically at lower concentrations than at higher concentrations.
- This leads to a deformation of the concentration profiles with sharp front and stronger retardation at smaller concentrations.

$$s(x) = K_d c$$

$$s(x) = K c^n$$

Exercise 2: Retardation Factor

Can the retardation become factor R <1 ?

Name	Sorption Isotherm	Retardation Factor
Linear	$s(c) = K_d c$	$R = 1 + \dfrac{(1 - n_e)}{n_e} \rho_s K_d$
Freundlich	$s(c) = K c^n$	$R = 1 + \dfrac{(1 - n_e)}{n_e} \rho_s K n c^{n-1}$
Langmuir	$s = \dfrac{s_{max} K}{c + K}$	$R = 1 + \dfrac{(1 - n_e)}{n_e} \rho_s \dfrac{s_{max} K}{(c + K)^2}$

Note that for Langmuir sorption isotherm: S_{max} [M_{solute}/M_{solid}] is the sorption site density generally reported in mol/kg, and K [M/L^3] is the half-saturation concentration at which the sorbed concentration s equals exactly 50% of its maximum value.

A retardation factor R < 1, implies K<0,
which is not physically possible.