

Non-Equilibrium Sorption

Exercise 2: Retardation Factor

Can the retardation become factor $R < 1$?

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

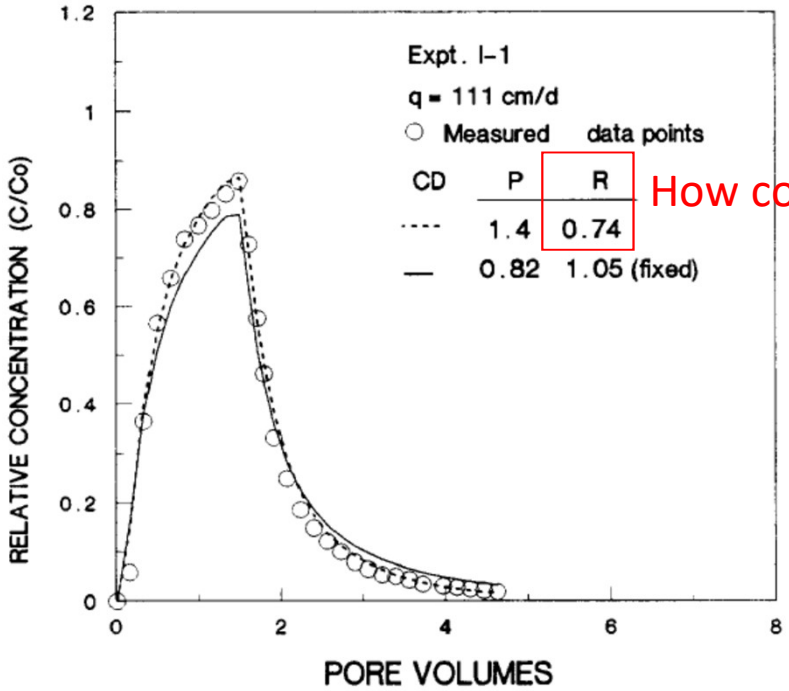
Note that for Langmuir sorption isotherm: S_{\max} [$M_{\text{solute}}/M_{\text{solid}}$] is the sorption site density generally reported in mol/kg, and K [M/L^3] is the half-saturation concentration at which the sorbed concentration s equals exactly 50% of its maximum value.

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

Exercise 2: Retardation Factor (continued)

However, Anamosa et al. [1990] fitted a breakthrough curve to a tritium $^3\text{H}_2\text{O}$ transport column experiment with retardation factor $R=0.74$?!

Note: The most important thing to learn about breakthrough curves is that we usually do not plot observed concentration C [M/L^3] versus time $[T]$. Rather we plot C/C_{IN} [-] in which C_{IN} [M/L^3] is the injection concentration. Note: Here they used the notation C_0 but I prefer the notation C_{IN} .

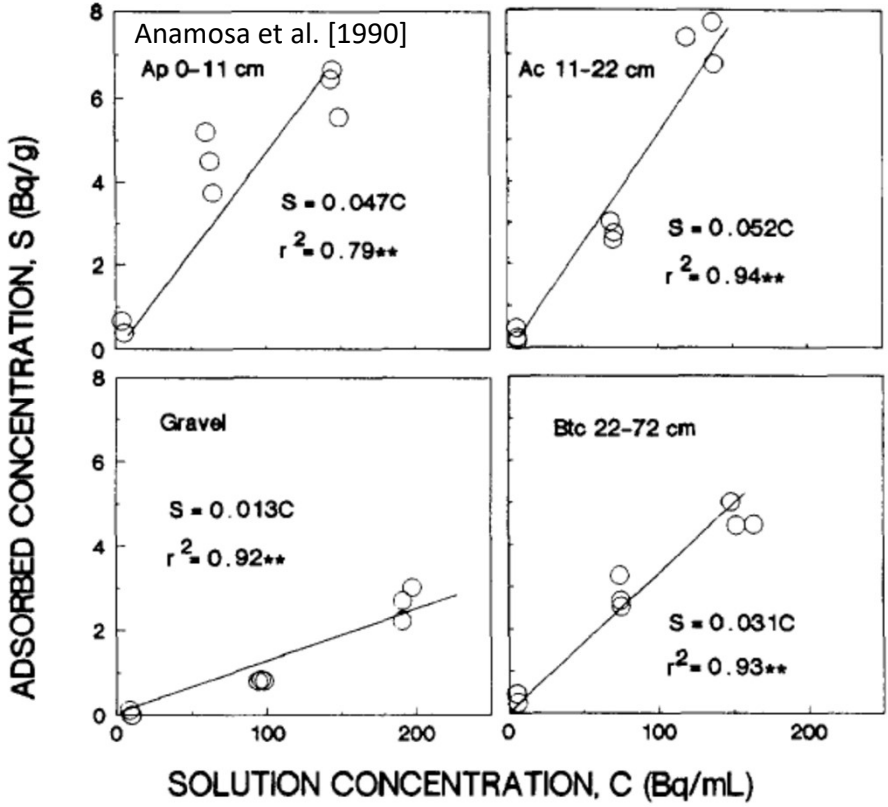


$$PV = \frac{V_{\text{effluent}}}{V_{\text{porewater}}} = \frac{vt}{L}$$

Similarly, instead of time $[T]$ we use pore volume $[-]$ as a dimensionless time. A pore volume in a column is the volume of water that will completely fill all of the voids in the column.

Exercise 2: Retardation Factor (continued)

Retardation factor R estimation using a batch experiment



Using Linear sorption isotherm, they found that tritium will slightly sorbe with retardation factor R=1.05.

			1/n	1/n _e	(1-n _e)/n _e
	ρ	K _d	R (n=0.525)	R (n _e =0.278)	R (n _e =0.278)
Fine_Ap	0.88	0.047	1.079	1.149	1.107
Fine_Ac	1	0.052	1.099	1.187	1.135
Fine_Btc	1.46	0.031	1.086	1.163	1.117
Gravel_Ap	0.335	0.013	1.008	1.016	1.011
Gravel_Ac	0.588	0.013	1.015	1.027	1.020
Gravel_Btc	0.72	0.013	1.018	1.034	1.024
Mean Retardation Factor [-]			1.051	1.096	1.069

$R = 1 + \frac{1}{n} \rho K_d$ Using Porosity n=0.525 (i.e. the volumetric soil water content) gives R=1.05. not rigorous and effective porosity n_e is generally used instead.

Using effective porosity n_e = (1-0.47)*0.525=0.278, gives R=1.1 instead of 1.05. Also, using (1-n_e)/n_e is more rigorous (as we can analytically drive it).

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

Using our expression for R with n_e=0.278 gives R=1.07. This is a better estimate (see calibrated R for exp. 1-3).

Exercise 2: Retardation Factor (continued)

Uncertainty of retardation factor R estimation using a batch experiment

			1/n	1/n _e	(1-n _e)/n _e
	ρ	K _d	R (n=0.525)	R (n _e =0.278)	R (n _e =0.278)
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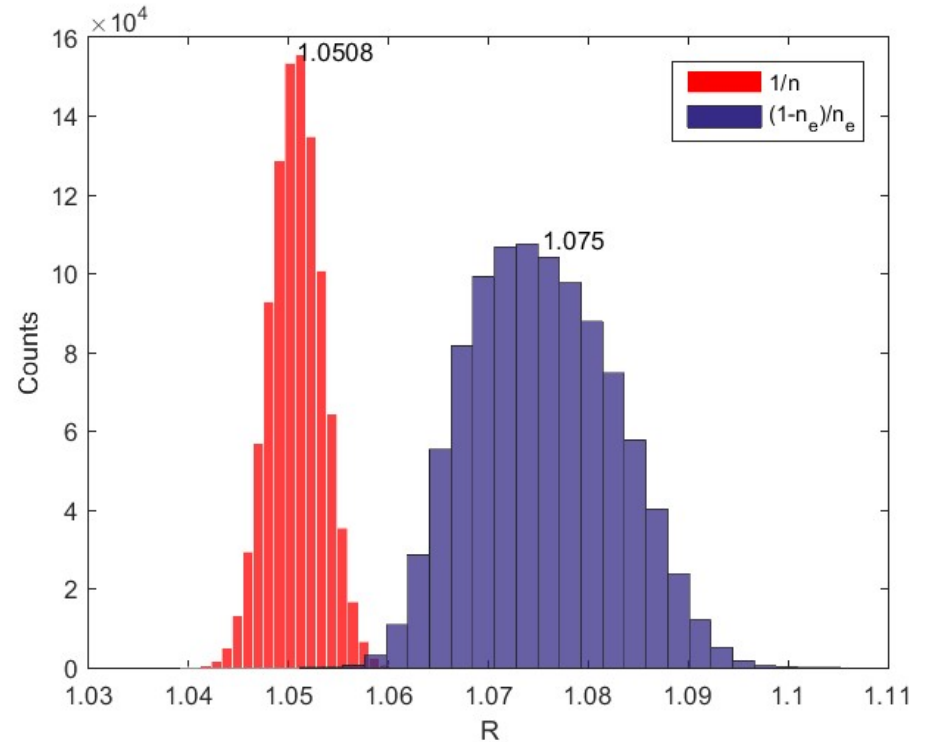
$$R = 1 + \frac{1}{n} \rho K_d \quad R = 1 + \frac{(1-n_e)}{n_e} \rho K_d$$

ρ 1 % std from measured value

n 1% std from measured value

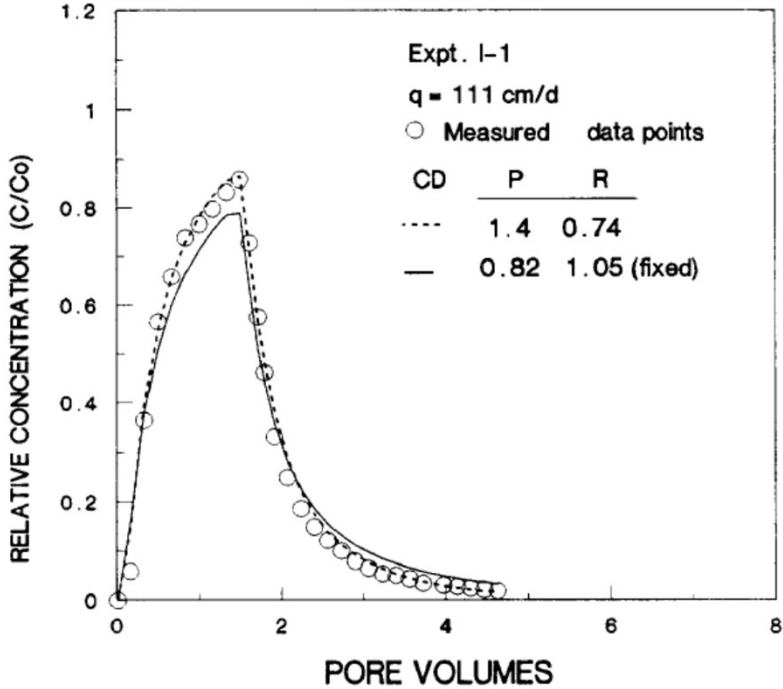
K_d 10% std from estimated value

n_e U(0.45, 0.55)*n based on 0.53 maximum estimated value of mobile water fraction. The n_e ranges from 0.24 to 0.29 which is high for gravelly soil (0.15 to 0.25).



Exercise 2: Retardation Factor (continued)

What does retardation factor $R=0.74$ indicates?



Experimental estimate : $R=1.05$

Calibration estimate: $R=0.74$

When we use correct parameter $R=1.05$ we get a late arriving (solid line).

Why CD model results in biased parameter estimate?

Exercise 2: Retardation Factor (continued)

What does retardation factor $R=0.74$ indicates?

Why CD model results in biased parameter estimate?

CD water mode optimized dimensionless parameters

Experiment No.	Flux q (cm/d)	Peclet number P	Retardation factor R
I-1	111	1.4 (0.2)	0.74 (0.05)
I-4	36.7	1.0 (0.1)	1.02 (0.06)
I-2	16.8	1.9 (0.2)	1.01 (0.05)
I-3	2.71	4.0 (0.3)	1.12 (0.02)

Numbers in parentheses are 95% confidence intervals (\pm)

Anamosa et al. [1990]

At slow flux 2.71 [cm/d] R is always >1 .

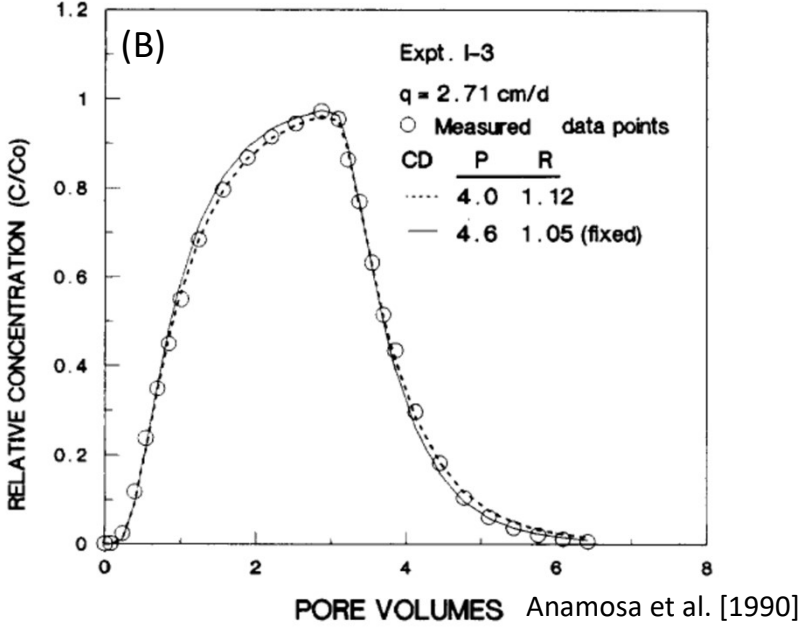
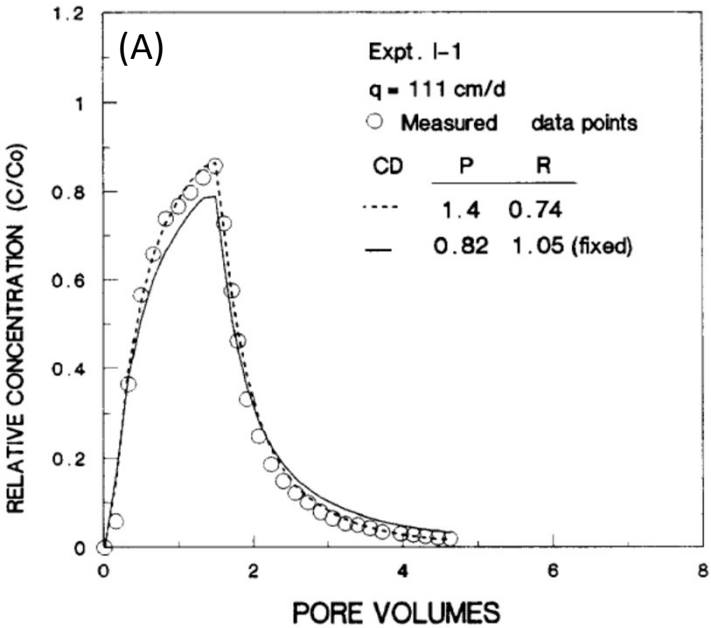
At high flux 111 [cm/d] R is always <1 .

Why simple CD model (i.e. advection dispersion equation) cannot fit the observation at high Darcy velocity q ?

Note: they used the wrong notation convection-dispersion equation (CDE). Convection is commonly use for heat convection through water motion. The correct notation is advective dispersive equation (ADE) which refers to dissolved substances (tracer, salt, soluble contaminants, particulate, etc.) advection through moving water. Also, a separate fluid phase transported along a gravity gradient is referred to as migration.

Exercise 2: Retardation Factor (continued)

What does retardation factor $R=0.74$ indicates?



Why simple CD model (i.e. advection dispersion equation) cannot fit the observation at high Darcy velocity q ?

- Figure(A): The solute is traveling faster due to the inability of CD model to account for diffusive mass transfer of water into immobile water region due to short residence time (immobile water fraction is estimated to be at least 0.47).
- Figure(B): At a slower flux, the pulse resided in the column long enough to allow diffusion to bring the mobile and immobile regions closer to physical equilibrium, and thus CD model assumption is satisfied.

What is physical non-equilibrium transport?

Exercise 2: Retardation Factor (continued)

What does retardation factor $R < 1$ indicates?

1. Anion exclusion (e.g. exclusion of tritium from some regions in the soil)
2. An overestimation of the water content (i.e. an estimated effective greater than the actual water content). On the other hand, if you underestimated your water content then the solutes will arrive later than they are expected).
3. You are using the wrong model structure (e.g. not accounting for non-equilibrium such as mobile-immobile water)

What is Physical non-equilibrium transport?

Evolution of sorption models

Linear equilibrium sorption (1960s)

- Cannot model early arrival and asymmetrical curves

Non-linear equilibrium sorption (early 1970s):

- leads to better prediction but no accurate

Kinetic (chemical) non- equilibrium sorption (early 1970s):

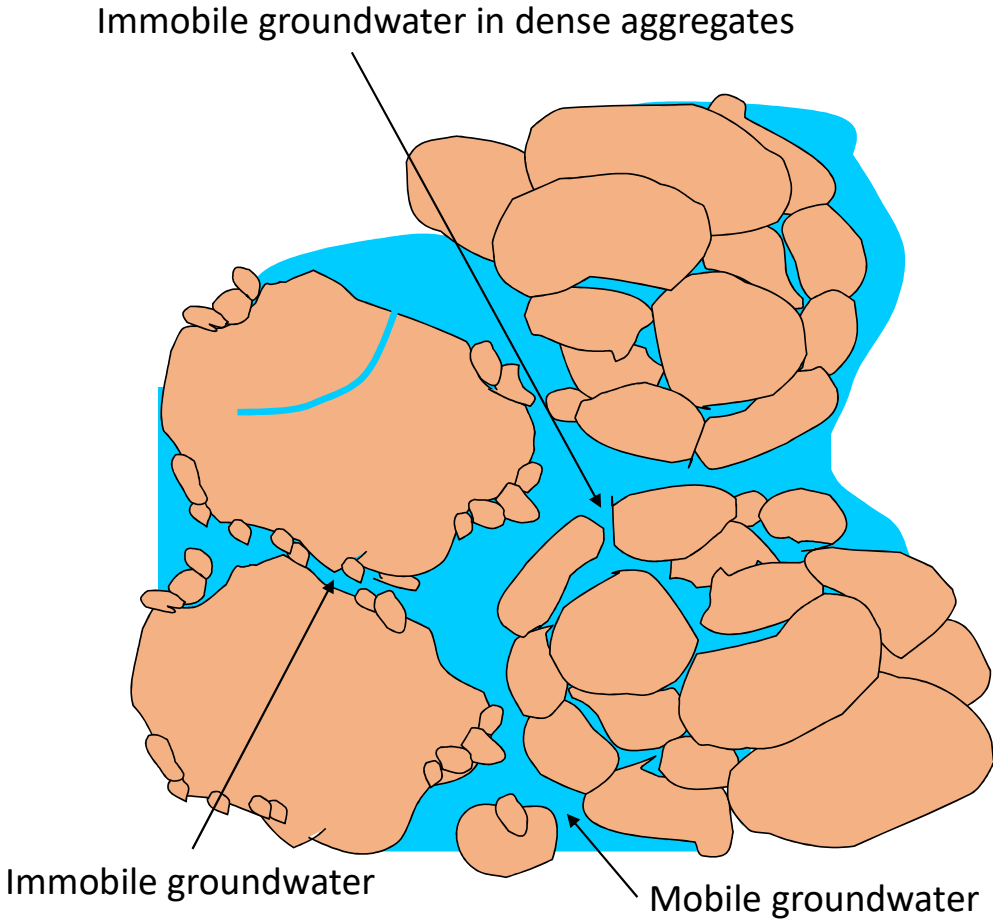
- lead to some success but limited to experiments conducted at low seepage velocity

Two-sorption sites (late 1970s)

- to describe tailing (asymmetric, skewed and non-sigmoid curves): one at equilibrium and the other at kinetics

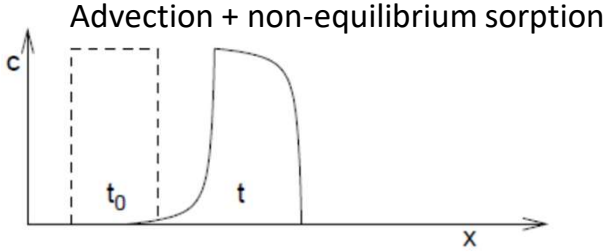
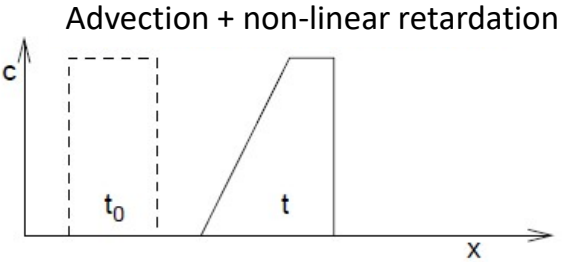
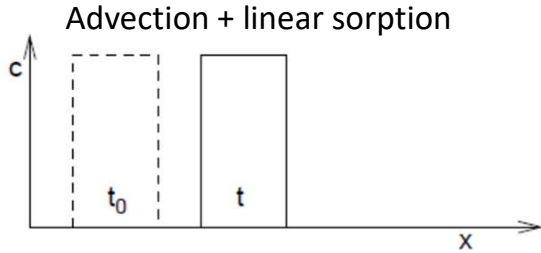
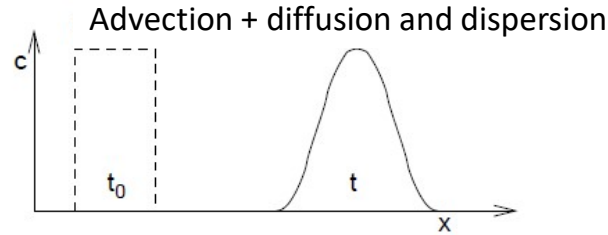
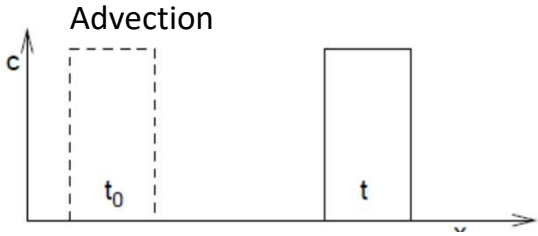
Physical non-equilibrium transport (late 1970s):

- Conservative tracer: will diffuse to immobile dense aggregates for example or macropores
- Sorbing tracer: sorption in the immobile region of the soil is controlled by diffusion through the immobile water fraction.



Modified from Srivastava 2014

Equilibrium versus Non-Equilibrium Sorption



Non-linear sorption in equilibrium leads to concentration-dependent retardation:

- Early arrival and asymmetric breakthrough curves
- Sharp front with increasing concentrations
- Stronger retardation at smaller concentrations (spreading when the concentration decreases)

Non-equilibrium sorption has no point symmetry about the point of average concentration (in contrast to dispersion).

- The breakthrough curves looks \pm exponential (behavior is identical for increasing and decreasing concentrations (fast increase and fast decrease in contraction))
- Characterized by a long tail at decreasing concentration

Non-Equilibrium

Kinetic (chemical) non-equilibrium sorption: the reaction rates did not reach equilibrium and still in the kinetics phase

Physical non-equilibrium transport: Refers to situations in which physical phenomena such as the presence of different water compartments in the medium (e.g. immobile water in aggregated soils, biofilms, fractured rock, etc.) are responsible for the non-equilibrium situation.

Non-Equilibrium Sorption

Equilibrium sorption: there exist a unique (linear or non-linear) relation between the solid and aqueous concentrations that can be described by a sorption isotherm.

Kinetic non-equilibrium sorption: the reaction rates did not reach equilibrium and still in the kinetics phase. Thus, the relation between the concentrations in the aqueous and sorbing phases is not unique and cannot be described by a sorption isotherm.