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Transport processes in rock and soil

Lecture 5

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Plan

- Boundary conditions for solute transport equation (advection-diffusion)

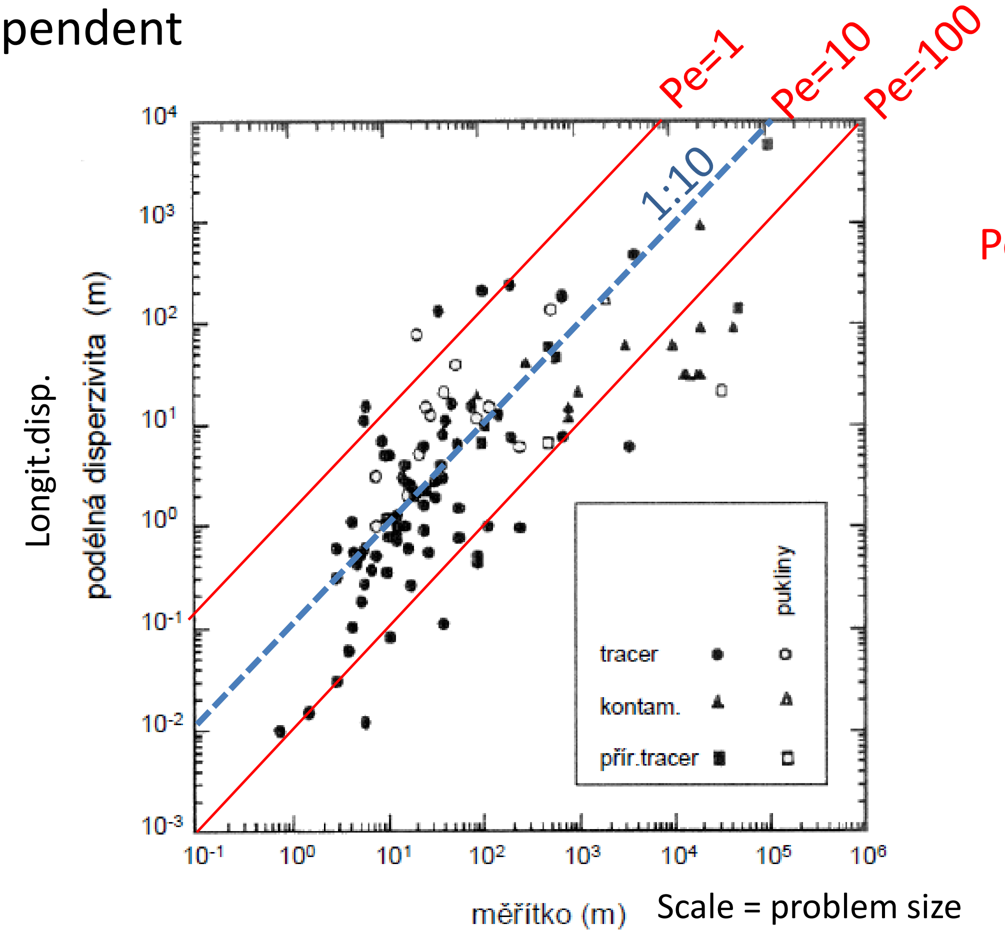
- Sorption
  - Another transport process
  - Liquid phase / solid phase interaction
  - Little change of the governing equation but possibly substantially changed properties

Discussion

- Which transport phenomena?

Additional comment

- Amount of hydrodynamic dispersion (longitudinal dispersivity)
  - Scale dependent

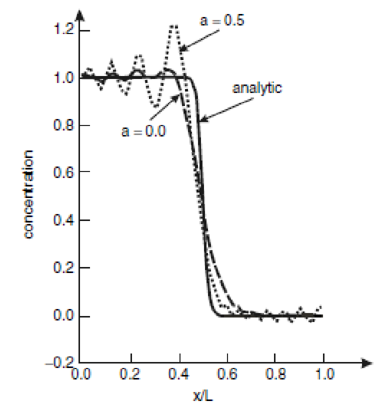


Pe = Lv/D = L/α

- Where is the Peclet number in the diagram?

Okrajové a počáteční podmínky

- Rovnice
  - PDE 2nd order parabolic / 1st order hyperbolic



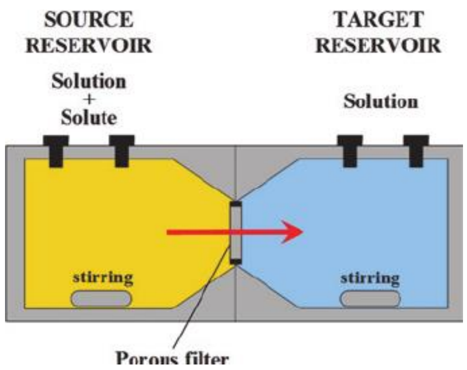
$$n\frac{\partial c}{\partial t} + \nabla \cdot (c\boldsymbol{q}) - n\nabla \cdot (\boldsymbol{D}_h \nabla c) = P^+ c^* + P^- c + r$$

- Boundary conditions classification
  - 1st /2nd /3rd (unknown /derivative)
- Physical meaning
  - concentration / mass flux

?

Boundary condition of the first kind

- Prescribed concentration $c(\boldsymbol{x}, t) = c_D(\boldsymbol{x}, t)$
- Part of the boundary with “inflow” to the domain
  - Assumption of dominant advection (influence only in the flow direction)
- Contact with perfect-mixed reservoir
  - E.g. laboratory diffusion experiment
- Measured temporal evolution of concentration

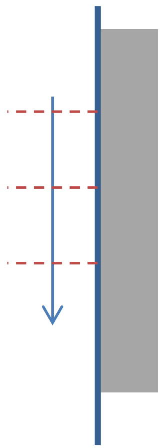


Boundary with prescribed flux

- Total mass flux
- B.c. of the third kind

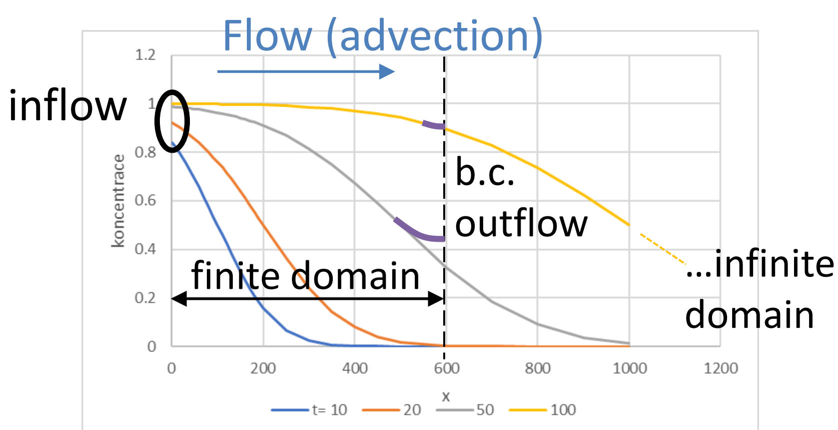
$$\boldsymbol{q}_c = n(c\boldsymbol{v} - \boldsymbol{D}_h \nabla c)$$

- Where is the second kind b.c.?
- “isolated boundary”
  - Zero mass flux, zero water flow (no advection) … $\vec{q} \cdot \vec{v} = 0$ …
  - $D_h \nabla c \cdot \vec{v} = 0$ … homogeneous b.c. 2nd kind



“Outflow” boundary

- No boundary condition for pure advection
  - 1^{st} order equation
    (analog: ordinary diff.e. 1^{st} /2^{nd} order)
  - „one-way interaction“
- Advection-dispersion with dominant advection?
  - Total flux = advective flux … $-(\boldsymbol{D}_h \nabla c)\cdot \boldsymbol{\nu} = q_{\mathrm{disp}}=0$



Analytical solution:

$$\frac{c(x,t)-c_o}{c_C-c_o}=\frac{1}{2}\operatorname{erfc}\left(\frac{Rx-vt}{2\sqrt{DRt}}\right)+\sqrt{\frac{v^2t}{\pi DR}}\exp\left(-\frac{(Rx-vt)^2}{4DRt}\right)-\frac{1}{2}\left(1+\frac{vx}{D}+\frac{v^2t}{DR}\right)\exp\left(\frac{vx}{D}\right)\operatorname{erfc}\left(\frac{Rx+vt}{2\sqrt{DRt}}\right)$$

(Císlerová, Vogel – equation 139)

Solute transport – additional processes

- Mass balance:

accumulation — flux — production/consumption

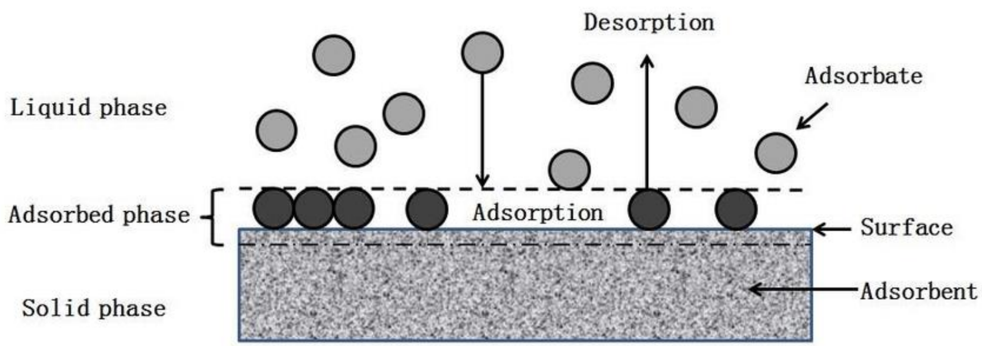
$$\frac{\partial}{\partial t}\int_V nc\,\mathrm{d}V = -\int_{\partial V} \boldsymbol{q}_c \cdot \mathrm{d}\boldsymbol{S} + \int_V (P^+c^* + P^-c)\,\mathrm{d}V + \int_V r\,\mathrm{d}V$$

$$n\frac{\partial c}{\partial t} + \nabla\cdot(c\boldsymbol{q}) - n\nabla\cdot(\boldsymbol{D}_h\nabla c) = P^+c^* + P^-c + r$$

advection — dispersion

  - In the solution only

- Other form (phase) of the transported substance = adsorbed



Sorption

Immobilization of mass from pore solution at the surface of solid particles (matrix)
Either as chemical bond or by physical interaction
Direction: adsorption / desorption
Distinguish adsorption (surface) / absorption (volume)

For transport in porous medium – more generalized mass balance expression … mass in two forms (two positions)

	Solute (liquid)	Solid phase
Per volume of the same phase	Dissolve mass / water volume … c	Adsorbed mass per solid matrix volume … s
Per mass of the same phase		$\bar{s}$
Per volume of whole p.m.	$\tilde{c} = nc$	$\tilde{s}$ $\tilde{s} = (1-n)s$

Conversions:

Solid phase density ϱ_s
Bulk density … "dry density" of p.m. $\varrho_b = (1-n)\varrho_s$
(suchá objemová hmotnost)

$$\bar{s} = \frac{s}{\varrho_s} = \frac{\tilde{s}}{\varrho_b}$$

Mass balance equation

accumulation:
both solute and adsorbed

$$\frac{\partial}{\partial t}\int_V (\tilde{c}+\tilde{s})\,\mathrm{d}V = -\int_{\partial V} \boldsymbol{q}_c \cdot \mathrm{d}\boldsymbol{S} + \int_V (P^+ c^* + P^- c)\,\mathrm{d}V$$

$$-\nabla \cdot (c\boldsymbol{v}) + \nabla \cdot (\boldsymbol{D}_h \nabla c)$$

The same transport mechanisms in solute phase (pore water)

- Two unknown functions: c(x,t), s(x,t)
- New constitutive relation needed between *c* a *s*

Classification

- Equilibrium
  - Immediate mass transfer (infinite rate)
  - Relation s=f(c)
- Non-equilibrium
  - Limited rate
  - Controlled by “distance” from equilibrium
  - Relation: rate(c,s) or g(f(c)-s)
- s=f(c) linear/non-linear

Sorption isotherms (shown 3 simplified semi-empirical relations)

= at fixed temperature … $s=f_{(T)}(c)$

Sorption isotherms

- Linear $\bar{s} = K_D c$ K_D $[\mathrm{m}^3/\mathrm{kg}]$

  [kg/kg] [kg/m³] k_D $[1]$

  – One parameter: distribution coefficient K_D
  – Other form $s = k_D c = \varrho_s K_D c$
  – Typically valid for very low concentrations

- Freundlich $\bar{s} = K_F c^a$
  – Nonlinear, two parameters
  – Typically a<1
  – Empirical: linear regression of measured data in log-log graph

Sorption isotherms

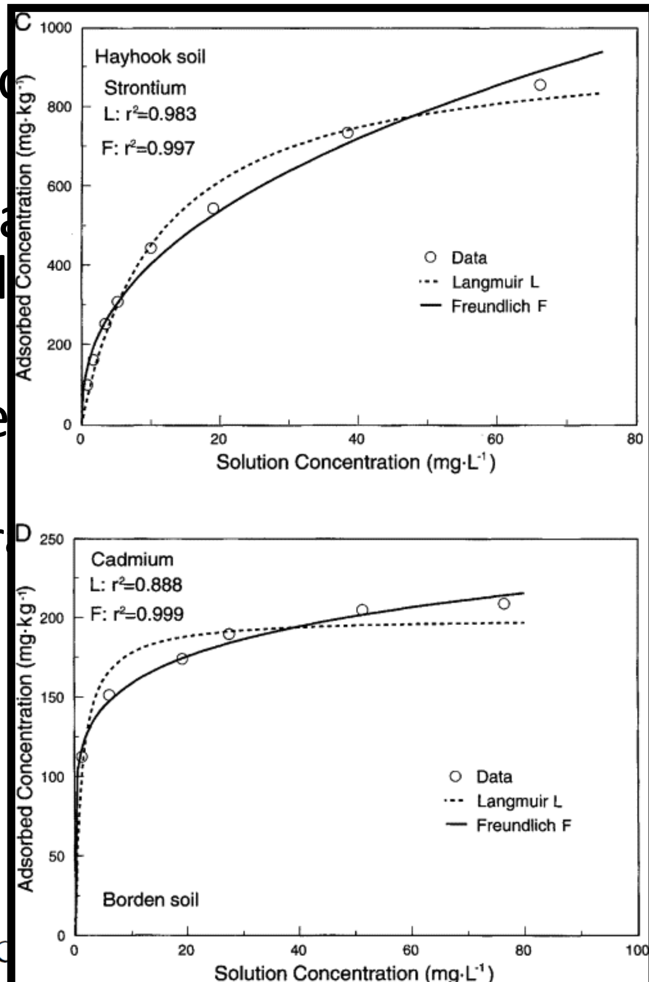
- Langmuir
  - Closest to c
    principles
  - Respects sa
    sorption pl
    surface
  - Asymptote
    - Maximal
      concentr

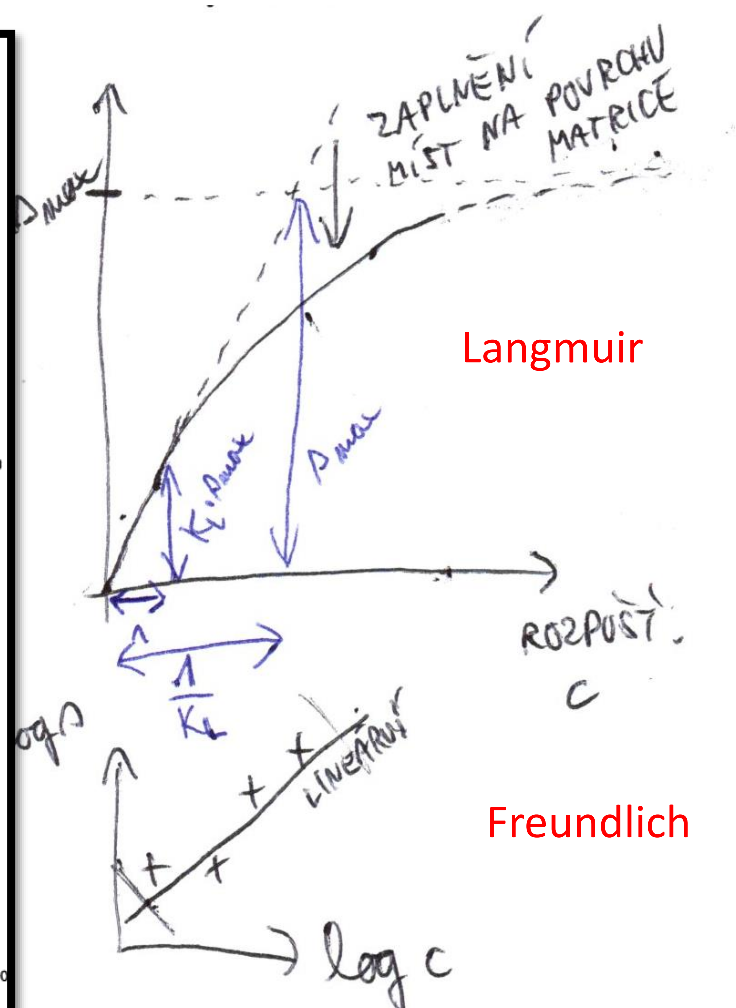
$$\bar{s} = \frac{K_L \bar{s}_{\max} c}{1 + K_L c}$$

Check behaviour: $c \to 0$

$c \to \infty$

Fitting data example





Langmuir

Freundlich

Mass balance equation

accumulation:
both solute and adsorbed

$$\frac{\partial}{\partial t}\int\limits_V (\tilde{c}+\tilde{s})\,\mathrm{d}V = -\int\limits_{\partial V} \boldsymbol{q}_c\cdot\mathrm{d}\boldsymbol{S} + \int\limits_V (P^+c^* + P^-c)\,\mathrm{d}V$$

$$-\nabla\cdot(c\boldsymbol{v}) + \nabla\cdot(\boldsymbol{D}_h\nabla c)$$

The same transport mechanisms in solute phase (pore water)

- Two unknown functions: c(x,t), s(x,t)
- New constitutive relation needed between *c* a *s*

Substitution to transport equation (linear case)

$$\tilde{c} = nc$$

$$\tilde{s} = (1-n)s = (1-n)k_D c$$

Linear isotherm

$$\frac{\partial}{\partial t}\Big(nc + (1-n)k_D c\Big) + \nabla\cdot(c\boldsymbol{q}) - n\nabla\cdot(\boldsymbol{D}_h\nabla c) = \ldots$$

$$\Big(n + (1-n)k_D\Big)\frac{\partial c}{\partial t} + \nabla\cdot(c\boldsymbol{q}) - n\nabla\cdot(\boldsymbol{D}_h\nabla c) = \ldots$$

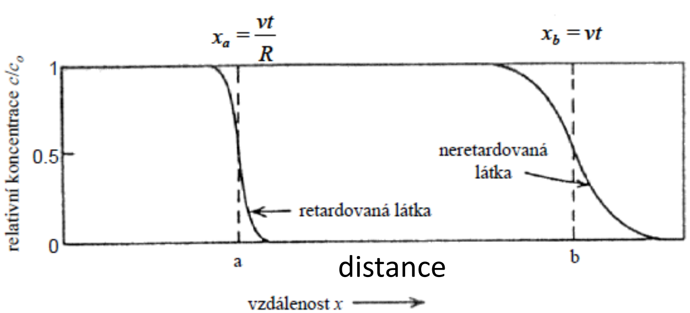
$$\Big(1 + \frac{(1-n)}{n}k_D\Big)\frac{\partial c}{\partial t} + \nabla\cdot(c\boldsymbol{v}) - \nabla\cdot(\boldsymbol{D}_h\nabla c) = \ldots$$

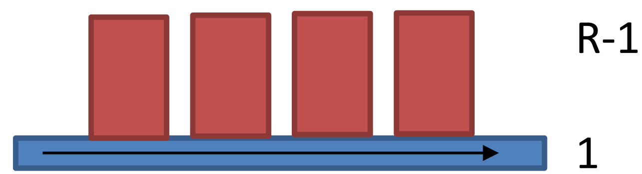
$$R = 1 + k_D\frac{1-n}{n} = 1 + \frac{\varrho_b K_D}{n}$$

Retardation factor

… the same equation/solution

but R times slower evolution in time





Example:

$K_D \ldots 10^{-3}\ m^3/kg$

$c = 1\ g/l$ (kg/m^3) $\quad n = 0{,}05$

1 LITR

ROZP. 0,05 g

$\rho_b = 2000\ kg/m^3$

$(1-0{,}05)\,2000\cdot 10^{-3}\cdot 1$

2g SORB.

1,95

R=40

Ba na žule granite

$K_D = 0{,}05$ m3/kg $\quad \rho_b = 2700$ kg/m3 $\quad n = 0{,}01$

R=13500

Transport with non-linear isotherm

Equilibrium

Immediate mass transfer (infinite rate)

Relation s=f(c)

→ Gradual change of c(x,t), s(x,t) (infinite rate only possible for initial non-equilibrium)

- Equation
  - Balance for pore water
  - Mass transfer rate between solute and sorbed as the source/sink
    - Transfer rate = rate of change of the sorbed mass
- For linear isotherm – the same form with the retardation factor
- For nonlinear – retardation factor depends on c … nonlinear equation

$$n\frac{\partial c}{\partial t} + \nabla\cdot(c\boldsymbol{q}) - n\nabla\cdot(\boldsymbol{D}_h\nabla c) = P^+c^* + P^-c + r$$

Per total volume

$$\tilde{r}_s = -\frac{\partial(s(1-n))}{\partial t} = -k_D(1-n)\frac{\partial c}{\partial t}$$

Linear isotherm

Per total volume

$$\tilde{r}_s = -\frac{\partial(s(1-n))}{\partial t} = -(1-n)\cdot\frac{\partial s}{\partial c}\cdot\frac{\partial c}{\partial t}$$

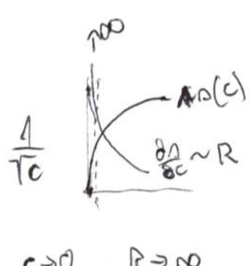
Nonlinear isotherm s(c)

$$R = 1 + \frac{1-n}{n}\cdot\frac{\partial s}{\partial c}$$

Example

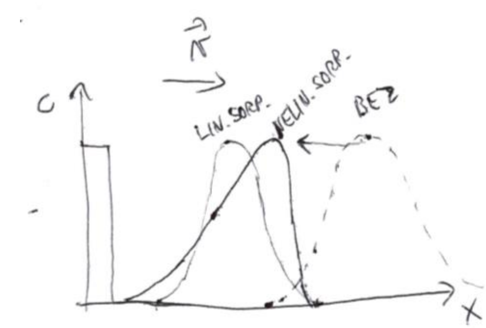
$$\bar{s} = K_F c^{\frac{1}{2}}$$

$$\frac{\partial \bar{s}}{\partial c} = \frac{1}{2}K_F c^{-\frac{1}{2}}$$



MATEMATICKY UMĚLÉ

Artifact of mathematical representation



Non-equilibrium sorption

- Transfer rate as function of c and s
- System of one partial and one ordinary differential equation
  - Unknowns c(x,t), s(x,t)

$$\tilde{r}_s = (1-n)\,\alpha\,(s - k_D c)$$

kg/s/m3 , per total volume

$$\frac{\partial c}{\partial t} = -\nabla \cdot (c\boldsymbol{v}) + \nabla \cdot (\boldsymbol{D}_h \nabla c) + \frac{1-n}{n}\alpha\,(s - k_D c)$$

Per volume of pores

$$\frac{\partial s}{\partial t} = -\alpha\,(s - k_D c)$$

Per volume of solid

- Analogous system for solute transport in dual-porosity media (mobile and immobile pores)

Reaction term (mass source/sink)

- Chemical reactions
- “Multispecies”/”Multicomponent” solute transport … individual ions
- Reactions between ions and with solid minerals
- Later in the semester
- Simple empirical models
  … zero and first order reaction

$$r = \frac{\partial c}{\partial t} = k_0 \,,$$

$$r = \frac{\partial c}{\partial t} = k_1 c$$

- Special case: radioactive decay
  - Possible for single-specie transport if the product is not of interest

$$r = -\lambda c \qquad \lambda = \frac{\ln 2}{T_{1/2}}$$

- End

- Thank you for your attention