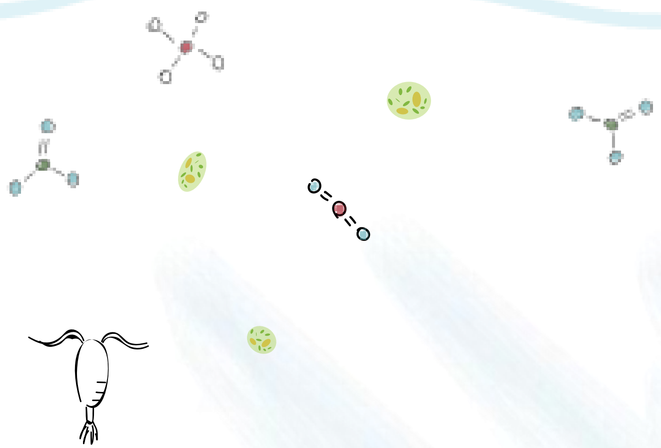

Reactive Transport in the Hydrosphere

Department of Earth Sciences, Faculty of Geosciences, Utrecht University

Lecturers: Lubos Polerecky and Karline Soetaert

Illustrations, narration and video editing: Renee Hageman
Additional contributions: Dries Bonte, University Ghent
Audio effects: mixkit.co

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Reaction-transport modeling

Mass balance equation:

$$\frac{\partial C}{\partial t} = -\frac{1}{A} \cdot \frac{\partial (A \cdot J)}{\partial x} + R$$

Expression for **transport flux**:

$$J = -D\frac{\partial C}{\partial x} + v \cdot C$$

Reaction-transport equation:

$$\frac{\partial C}{\partial t} = \frac{1}{A}\frac{\partial}{\partial x}\left(A \cdot D \cdot \frac{\partial C}{\partial x}\right) - \frac{1}{A}\frac{\partial}{\partial x}(A \cdot v \cdot C) + R$$

Modelling **early diagenesis in aquatic sediments**

- How to incorporate porosity?
- Modelling of multiple components

Reaction-transport equation

General form:

$$\frac{\partial C}{\partial t} = \frac{1}{A}\frac{\partial}{\partial x}\left(A \cdot D \cdot \frac{\partial C}{\partial x}\right) - \frac{1}{A}\frac{\partial}{\partial x}(A \cdot v \cdot C) + R$$

assuming $A \neq A(x)$

Simplified form:

$$\boxed{\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D \cdot \frac{\partial C}{\partial x}\right) - \frac{\partial}{\partial x}(v \cdot C) + R}$$

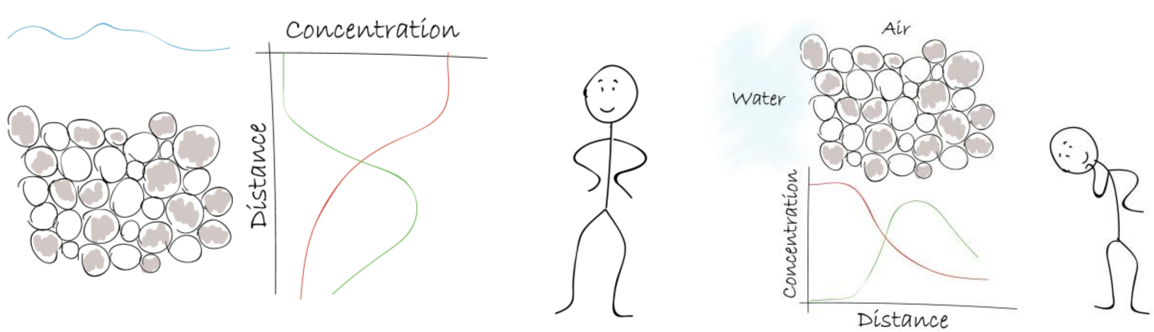
Rate of change

Diffusion term

Advection term

Net reaction term

Solution: A **function** of time and space: C(t,x)



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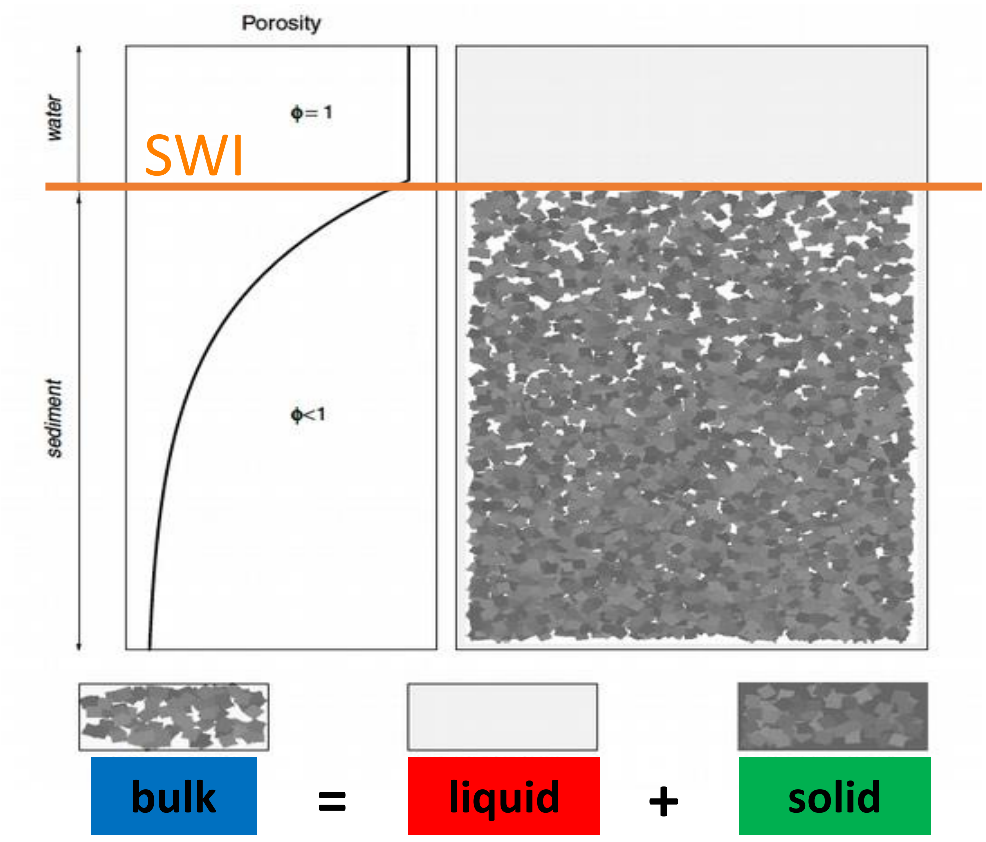
Reaction-transport modeling in sediments

Role of porosity



Porosity:

$$\phi = \frac{liquid\ volume}{bulk\ volume}$$

$$unit = \frac{m_L^3}{m_b^3}$$

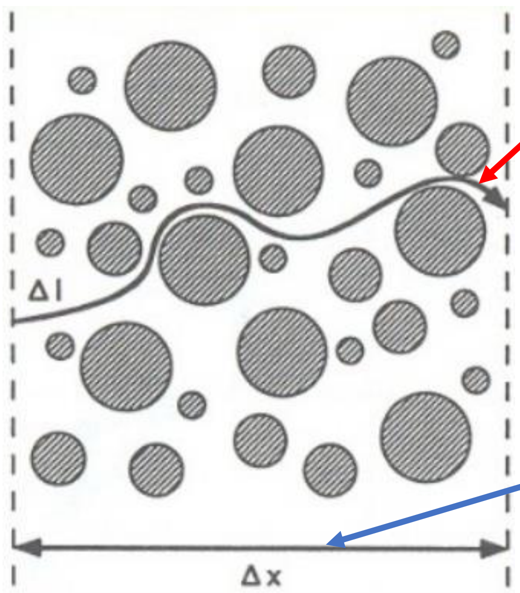
Solid volume fraction :

$$svf = \frac{solid\ volume}{bulk\ volume} = 1 - \phi$$

$$unit = \frac{m_s^3}{m_b^3}$$

Reaction-transport modeling in sediments

Role of porosity on molecular diffusion



True distance travelled

Effective distance travelled

Tortuosity: $\theta = \frac{\Delta l}{\Delta x}$

(Path prolongation)

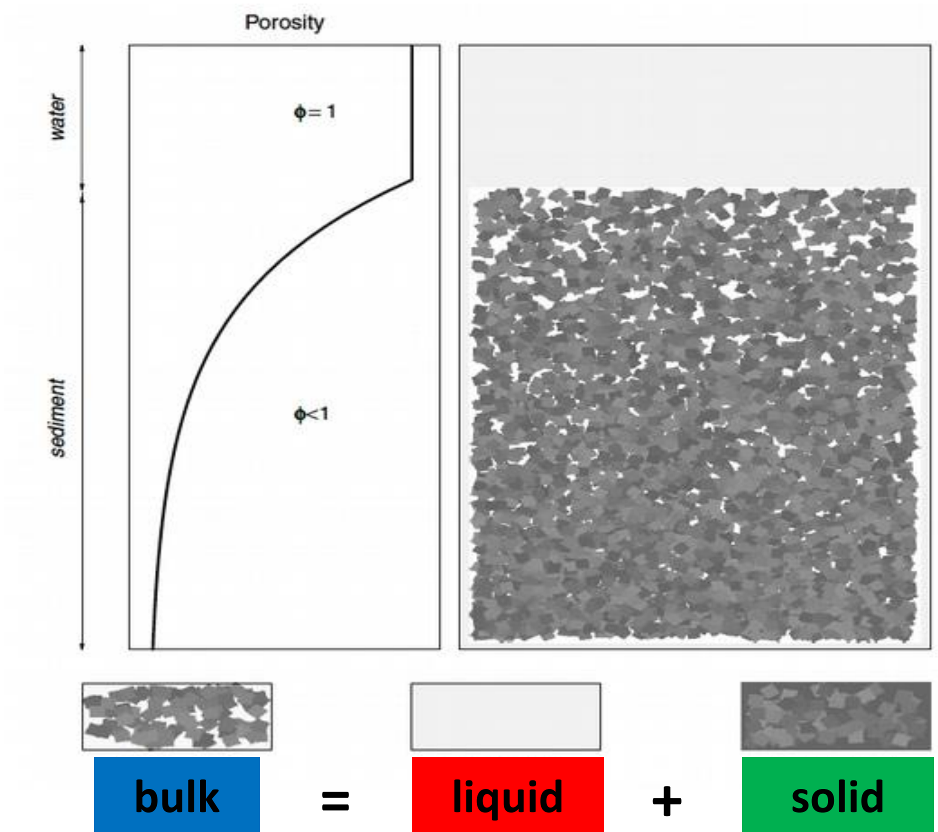
In bulk water

Effective diffusion coefficient of solutes in porous media: $D_{eff} = \frac{D_{mol}}{\theta^2}$

In sediments: $\theta^2 \approx 1 - \ln(\phi^2)$ $\Rightarrow$ $D_{sed} = \frac{D_{mol}}{1 - \ln(\phi^2)}$

Reaction-transport modeling in sediments

Role of porosity on how we measure and report concentrations



Dissolved substances (C_L)

Solid substances (C_s)

Typically:

Dissolved substances (C_L)

mol m^{-3} of liquid

Solid substances (C_s)

mol m^{-3} of solid

= mol kg^{-1} of dry solid

× **density** of bulk solid (kg m^{-3} of solid)

Reaction-transport modeling in sediments

Role of porosity on the reaction-transport equation

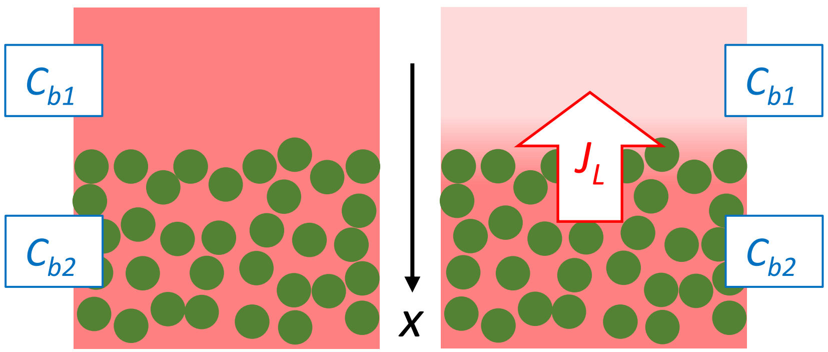
Mass balance equation is formulated for: $\frac{\partial C_b}{\partial t} = \cdots$ ← mol m^{-3} of bulk

Transport fluxes of solutes are **determined** by concentrations in the liquid phase!

Not C_b!!!

$$J_L = v_L \cdot C_L - D_{sed} \frac{\partial C_L}{\partial x}$$

moles / area of liquid phase / time



$C_{b1} > C_{b2}$ but $J_L = 0$ $C_{b1} = C_{b2}$ but $J_L \neq 0$

If a reaction occurs between solutes: R_L ← moles / volume of liquid phase / time

Conversions between liquid and bulk

Porosity: $$\phi = \frac{liquid\ volume}{bulk\ volume} \qquad unit = \frac{m_L^3}{m_b^3}$$

Conversion from liquid to bulk:

$$C_b = \phi \cdot C_L \qquad \frac{mol}{m_b^3} = \frac{m_L^3}{m_b^3} \cdot \frac{mol}{m_L^3}$$

$$J_b = \phi \cdot J_L \qquad \frac{mol}{area_b \cdot time} = \frac{m_L^3}{m_b^3} \cdot \frac{mol}{area_L \cdot time}$$

$$R_b = \phi \cdot R_L \qquad \frac{mol}{m_b^3 \cdot time} = \frac{m_L^3}{m_b^3} \cdot \frac{mol}{m_L^3 \cdot time}$$

Reaction-transport modeling in sediments

Reformulated for concentration in the liquid phase:

$$\frac{\partial C_b}{\partial t} = \frac{\partial(\boldsymbol{\phi} \cdot C_L)}{\partial t} = \frac{\partial}{\partial x}\left(\boldsymbol{\phi} \cdot D_{sed} \cdot \frac{\partial C_L}{\partial x}\right) - \frac{\partial}{\partial x}(\boldsymbol{\phi} \cdot v_L \cdot C_L) + \boldsymbol{\phi} \cdot R_L$$

assuming $\boldsymbol{\phi} \neq \boldsymbol{\phi}(t)$

$$\frac{\partial C_L}{\partial t} = \frac{1}{\boldsymbol{\phi}} \cdot \frac{\partial}{\partial x}\left(\boldsymbol{\phi} \cdot D_{sed} \cdot \frac{\partial C_L}{\partial x}\right) - \frac{1}{\boldsymbol{\phi}} \cdot \frac{\partial}{\partial x}(\boldsymbol{\phi} \cdot v_L \cdot C_L) + R_L$$

All terms in mol m^{-3} **liquid** s^{-1}

Note: ***ϕ* changes in space** (sediment compaction), so ***ϕ* cannot** be taken out of the spatial derivative and cancelled out!

Conversions between solid and bulk

Solid volume fraction: $1-\phi = \frac{solid\ volume}{bulk\ volume}$ $\quad unit = \frac{m_s^3}{m_b^3}$

Conversion from liquid to bulk:

$$C_b = (1-\phi)\cdot C_s \qquad \frac{mol}{m_b^3} = \frac{m_s^3}{m_b^3}\cdot\frac{mol}{m_s^3}$$

$$J_b = (1-\phi)\cdot J_s \qquad \frac{mol}{area_b\cdot time} = \frac{m_s^3}{m_b^3}\cdot\frac{mol}{area_s\cdot time}$$

$$R_b = (1-\phi)\cdot R_s \qquad \frac{mol}{m_b^3\cdot time} = \frac{m_s^3}{m_b^3}\cdot\frac{mol}{m_s^3\cdot time}$$

Reaction-transport modeling in sediments

Reformulated for porous media (sediments), assuming $\boldsymbol{\phi} \neq \boldsymbol{\phi}(\mathrm{t})$:

$$\frac{\partial C_f}{\partial t} = \frac{1}{\boldsymbol{f}} \cdot \frac{\partial}{\partial x}\left(\boldsymbol{f} \cdot D_f \cdot \frac{\partial C_f}{\partial x}\right) - \frac{1}{\boldsymbol{f}} \cdot \frac{\partial}{\partial x}\left(\boldsymbol{f} \cdot v_f \cdot C_f\right) + R_f$$

For dissolved substances:

$$\boldsymbol{f} = \boldsymbol{\phi} \qquad C_f = C_L \qquad D_f = D_{sed} \qquad v_f = v_L$$

For concentrations of solids:

$$\boldsymbol{f} = \mathbf{1} - \boldsymbol{\phi} \qquad C_f = C_s \qquad D_f = D_s \qquad v_f = v_s$$

Note: $\boldsymbol{\phi}$ changes in space (sediment compaction), so $\boldsymbol{f}$ **cannot** be taken out of the spatial derivative and cancelled out!

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Reaction-transport modeling in sediments

Modeling **multiple components:**

Component A: $$\frac{\partial C_A}{\partial t} = \frac{1}{\boldsymbol{f}_A} \cdot \frac{\partial}{\partial x}\left(\boldsymbol{f}_A \cdot D_A \cdot \frac{\partial C_A}{\partial x}\right) - \frac{1}{\boldsymbol{f}_A} \cdot \frac{\partial}{\partial x}(\boldsymbol{f}_A \cdot v_A \cdot C_A) + R_A$$

Component B: $$\frac{\partial C_B}{\partial t} = \frac{1}{\boldsymbol{f}_B} \cdot \frac{\partial}{\partial x}\left(\boldsymbol{f}_B \cdot D_A \cdot \frac{\partial C_B}{\partial x}\right) - \frac{1}{\boldsymbol{f}_B} \cdot \frac{\partial}{\partial x}(\boldsymbol{f}_B \cdot v_A \cdot C_B) + R_B$$

$\vdots$ $\vdots$ $\vdots$

If A and B react with each other, then R_A and R_B are **not independent!**

Coupled partial differential equations**!!**

How do we deal with the situation if A is a dissolved substance and B is a solid substance?

Rate expressions for processes involving solute and solid substances

Stoichiometry: $(CH_2O)(NH_3)_x(H_3PO_4)_y + O_2 \rightarrow CO_2 + x\,NH_3 + y\,H_3PO_4 + H_2O$

POC (solid!)

Rate expression: $R = r_C \dfrac{[O_2]}{[O_2] + K_{O2}} [\mathrm{OM}]$

Units: $[OM]: \dfrac{mol\ C}{m_s^3}$ $R: \dfrac{mol\ C}{m_s^3 \cdot s}$

Mass balance equation for OM: $\dfrac{d[\mathrm{OM}]}{dt} = -R + \ ...$ ✓

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Mass balance equation for OM: $\dfrac{d[\mathrm{OM}]}{dt} = -R + \ldots$

Mass balance equation for O_2: $\dfrac{d[\mathrm{O_2}]}{dt} = -R + \ldots$

Based on stoichiometry

Units: $[O_2]: \dfrac{mol\ O_2}{m_L^3}$ $R: \dfrac{mol\ C}{m_S^3 \cdot s}$

Rate expressions for processes involving solute and solid substances

Stoichiometry: $(CH_2O)(NH_3)_x(H_3PO_4)_y + O_2 \rightarrow CO_2 + x\,NH_3 + y\,H_3PO_4 + H_2O$

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Mass balance equation for OM: $$\frac{d[\mathrm{OM}]}{dt} = -R + \ldots$$ ✓

Mass balance equation for O_2: $$\frac{d[\mathrm{O_2}]}{dt} \cancel{=} -R + \ldots$$

Units: $[O_2]: \frac{mol\ O_2}{m_L^3}$ $R: \frac{mol\ C}{m_S^3 \cdot s}$

Based on stoichiometry

Based on stoichiometry **& volume fraction correction!**

$$\boxed{\frac{d[\mathrm{O_2}]}{dt} = -R \cdot \frac{1-\boldsymbol{\phi}}{\boldsymbol{\phi}} + \ldots}$$ ✓

Units: $$\frac{mol}{m_L^3 \cdot s} = \frac{mol}{m_S^3 \cdot s} \cdot \frac{m_S^3}{m_b^3} \cdot \frac{m_b^3}{m_L^3}$$

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Reaction-transport modeling in sediments

$$\frac{\partial C_f}{\partial t} = \frac{1}{\boldsymbol{f}} \cdot \frac{\partial}{\partial x}\left(\boldsymbol{f} \cdot D_f \cdot \frac{\partial C_f}{\partial x}\right) - \frac{1}{\boldsymbol{f}} \cdot \frac{\partial}{\partial x}\left(\boldsymbol{f} \cdot v_f \cdot C_f\right) + R_f$$

To formulate . . .

- For **dissolved** substances: $\boldsymbol{f} = \boldsymbol{\phi}$ $\quad \boldsymbol{C_L}$ & $\boldsymbol{R_L}$ per m³ of liquid!
- For **solid** substances: $\boldsymbol{f} = \mathbf{1} - \boldsymbol{\phi}$ $\quad \boldsymbol{C_s}$ & $\boldsymbol{R_s}$ per m³ of solid!

Do not forget to account for porosity in the rate expressions for processes that involve **reactions of dissolved and solid substances**:

$$\frac{1-\boldsymbol{\phi}}{\boldsymbol{\phi}} \quad \left(\frac{m_S^3}{m_L^3}\right) \qquad \text{vs.} \qquad \frac{\boldsymbol{\phi}}{1-\boldsymbol{\phi}} \quad \left(\frac{m_L^3}{m_S^3}\right)$$

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