Primary Controls on the Natural Denitrification Potential of Aquifers

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Electron Donors in the Matrix Prevent Nitrate Breakthrough

- Intensive agriculture ⇨ high NO_3^- load
- Natural organic matter (NOM) and pyrite are natural electron donors

$$5\,CH_2O + 4\,NO_3^- \rightarrow 4HCO_3^- + CO_2 + 2N_2 + 3H_2O$$

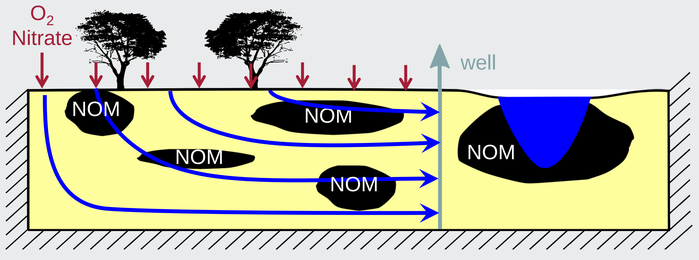
$$FeS_2 + 3\,NO_3^- + H_2O \rightarrow FeOOH + 3/2N_2 + 2SO_4^{2-} + H^+$$

- Dissolved oxygen inhibits denitrification

$$CH_2O + O_2 \rightarrow CO_2 + H_2O$$

$$FeS_2 + 15/4\,O_2 + 5/2H_2O \rightarrow FeOOH + 2SO_4^{2-} + 4H^+$$

- The reactions make the aquifer loose its natural denitrification potential over decades



How long will the natural denitrification potential last?
☞ Uncertainty requires a stochastic approach!

Transport Calculations

$$\frac{\partial c_i}{\partial t} + \mathbf{v}\cdot\nabla c_i - \nabla\cdot\left(\mathbf{D}_i\nabla c_i\right) = r_i(\mathbf{c}(\mathbf{x},t),\mathbf{x},t)$$ CPU intensive

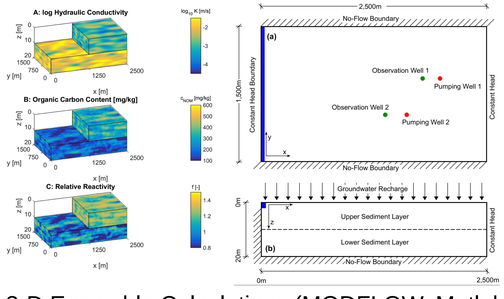
- Diffuse input of reactants that react with the matrix
⇨ Neglect dispersion and replace spatial coordinates by advective travel time (from particle tracking)

- Bacteria are active where conditions are right
⇨ No dynamic calculation of microbial biomass

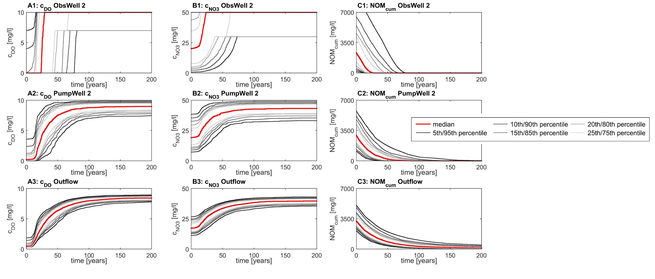
- Electron-donor release parameterized as relative reactivity $f(\mathbf{x},t)$ in comparison to a reference state
- Depends on the e-donor content of the matrix
- Electron-donor consumbed by the reaction
⇨ Update relative reactivity along each streamline

$$\frac{\partial c_{DO}}{\partial t} + \frac{\partial c_{DO}}{\partial \tau} = f\left(s_{NOM}(\mathbf{x},t)\right) r_{\max,0}^{DO} \frac{c_{DO}}{c_{DO} + K_{DO}}$$

$$\frac{\partial c_{nit}}{\partial t} + \frac{\partial c_{nit}}{\partial \tau} = f\left(s_{NOM}(\mathbf{x},t)\right) r_{\max,0}^{nit} \frac{c_{nit}}{c_{nit} + K_{nit}} \frac{K_{DO}^{inh}}{c_{DO} + K_{DO}^{inh}}$$



3-D Ensemble Calculations (MODFLOW, Matlab & GPU)
750‘000 Cells, 200 Realizations, CPU-time: 4000min



The Minimalist‘s Version: Electron Balance

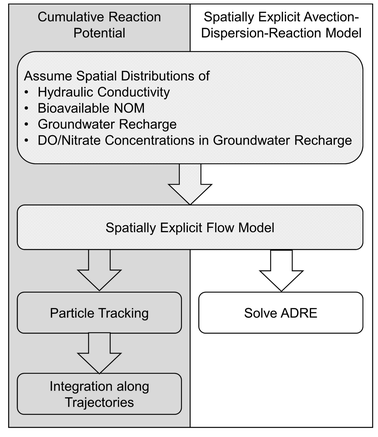
- At which time would an advective-reactive front arrive if the reaction between the electron donors in the matrix and the dissolved electron acceptors was instantaneous? ⇨ cumulative reaction potential τ_{pot}

$$\tau_{pot} = \frac{1}{\sum_{i=1}^{n_{EA_i}} c_{EA_i}^{in}\,\gamma_{C_{org}/EA_i}} \int_{x_{in}}^{x_{obs}} \frac{1}{|\mathbf{q}|}\,\rho_b\,s_{NOM}\,dx$$

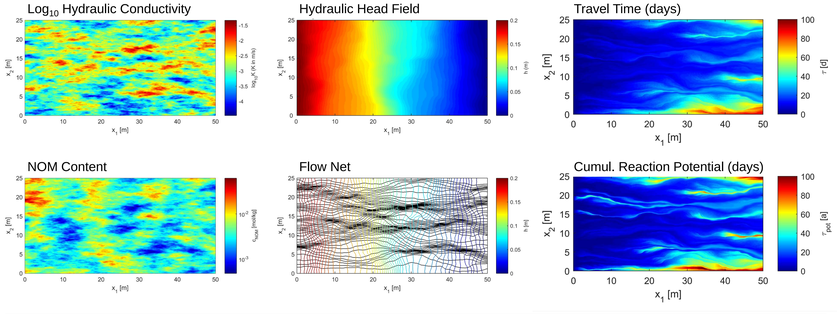
denominator: C_{org}-demand of injected solution
s_{NOM}: C_{org} content of aquifer material
ρ_b: dry bulk density

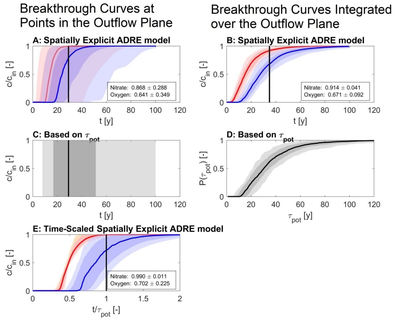
Cumulative Reaction Potential

⇨ Can easily be evaluated by particle tracking



2-D Ensemble Calculation (100 realizations, 4.5h vs. 10s per realization)





- M. Loschko, T. Wöhling, D.L. Rudolph, O.A. Cirpka: Cumulative relative reactivity: a concept for modeling aquifer-scale reactive transport. *Water Resour. Res.* 52(10): 8117-8137, 2016, doi: 10.1002/2016WR019080.
- M. Loschko, T. Wöhling, D.L. Rudolph, O.A. Cirpka: Accounting for the decreasing reaction potential of heterogeneous aquifers in a stochastic framework of aquifer-scale reactive transport. *Water Resour. Res.* 54(1): 442-463, 2018, doi: 10.1002/2017WR021645.
- M. Loschko, T. Wöhling, D.L. Rudolph, O.A. Cirpka: An electron-balance based approach to predict the decreasing denitrification potential of an aquifer. *Groundwater* (submitted), 2018.

⇨ The spread of the flux-averaged nitrate breakthrough curve is dominated by the spread of cumulative reaction potential

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