

Primary Controls on the Natural Denitrification Potential of Aquifers

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Abstract

Elevated nitrate concentrations in groundwater are observed in regions of intensive agriculture worldwide, threatening the safety of drinking-water production. Aquifers may contain geogenic reduced constituents, such as natural organic matter (NOM), pyrite, or biotite, facilitating aerobic respiration and denitrification. Because these electron donors are not replenished, the breakthrough of nitrate (and eventually dissolved oxygen) in production wells is only delayed. Frameworks of modeling nitrate fate and transport that assume constant rate coefficients of nitrate elimination cannot address the reduction of the aquifer's denitrification potential by the reaction itself. We have tested several approaches of modeling the fate of dissolved oxygen and nitrate in aquifers, including multi-dimensional bioreactive transport models with dynamic abundances of aerobic and denitrifying bacteria, approaches neglecting the dynamics of biomass and dispersive mixing, and simple models based on an electron balance. We found that the primary control on the timing of nitrate breakthrough is the ratio of the bioavailable electron-donor content in the aquifer material to the electron-acceptor load in the infiltrating water. Combined spatial variability of groundwater velocities and electron-donor content can explain most of the spread in nitrate breakthrough, whereas kinetics of the reaction plays a minor role under most conditions. Our modeling study highlights the need for field surveys on joined physical and chemical heterogeneity of aquifers under the stress of pollutants that can react with the aquifer material.



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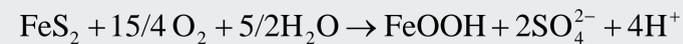
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Electron Donors in the Matrix Prevent Nitrate Breakthrough

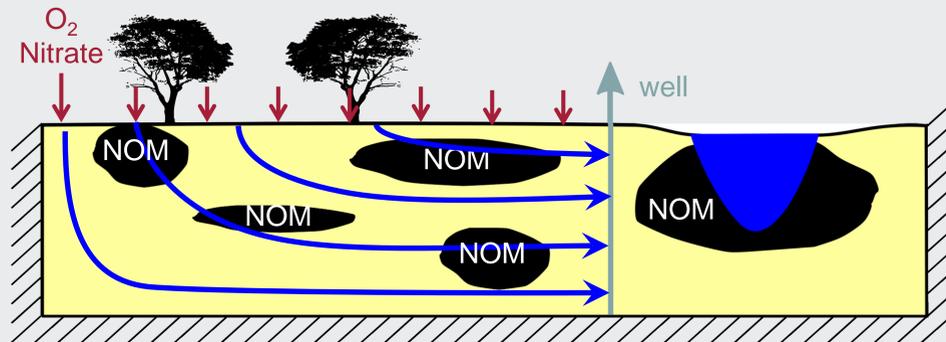
- Intensive agriculture ⇒ high NO₃⁻ load
- Natural organic matter (NOM) and pyrite are natural electron donors



- Dissolved oxygen inhibits denitrification



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



How long will the natural denitrification potential last?

☞ Uncertainty requires a stochastic approach!

Transport Calculations

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

CPU intensive

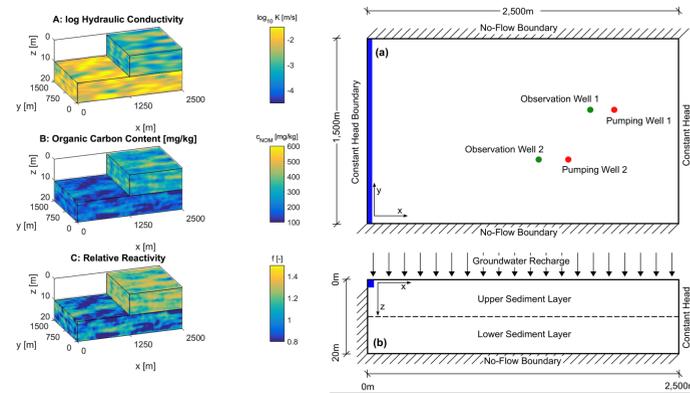
- Diffuse input of reactants that react with the matrix
- ⇒ Neglect dispersion and replace spatial coordinates by advective travel time (from particle tracking)

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

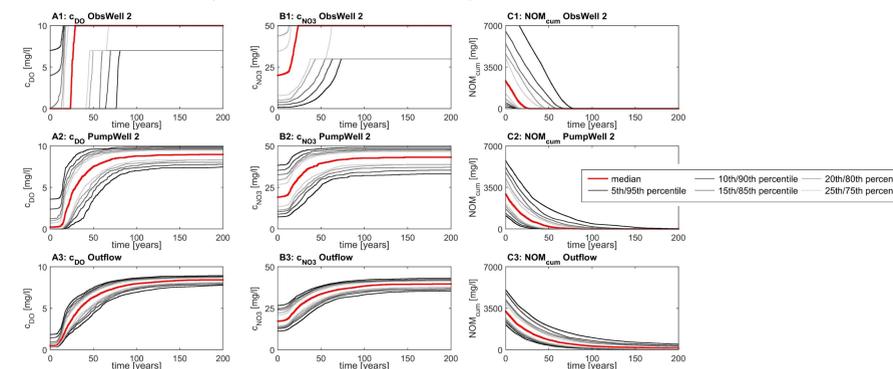
- Electron-donor release parameterized as relative reactivity $f(\mathbf{x}, t)$ in comparison to a reference state
- Depends on the e-donor content of the matrix
- Electron-donor consumed by the reaction
- ⇒ Update relative reactivity along each streamline

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

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



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



The Minimalist's Version: Electron Balance

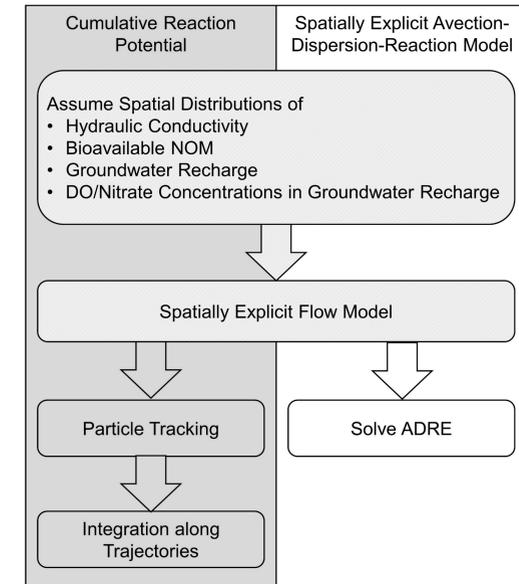
- At which time would an advective-reactive front arrive if the reaction between the electron donors in the matrix and the dissolved electron acceptors was instantaneous? ⇒ cumulative reaction potential τ_{pot}

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

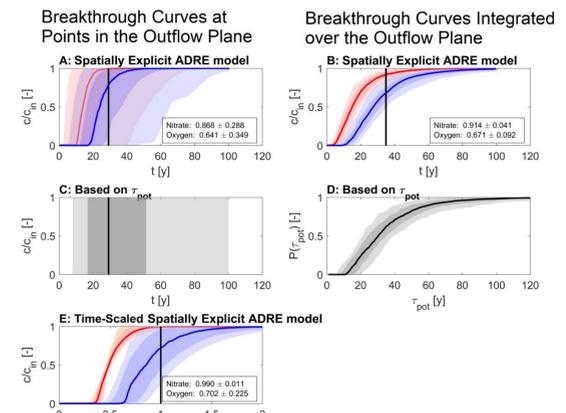
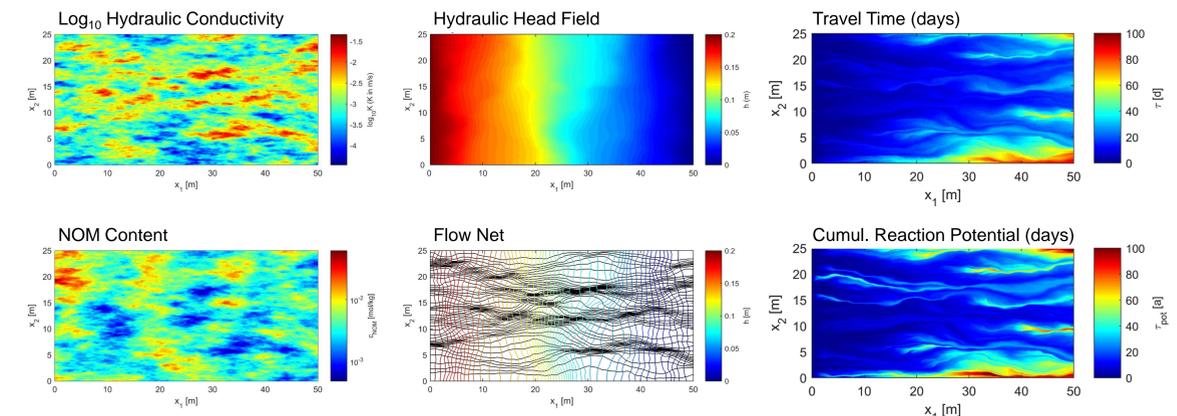
denominator: C_{org} -demand of injected solution
 s_{NOM} : C_{org} content of aquifer material
 ρ_b : dry bulk density



⇒ 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