Using Travel Times in Reactive Transport

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Advection-Dispersion-Reaction Equation of Compound *i*

$$\theta_w \frac{\partial c_i}{\partial t} + \rho_b \frac{\partial s_i}{\partial t} + \mathbf{q} \cdot \nabla c_i - \nabla \cdot \left(\theta_w \mathbf{D}_i \nabla c_i \right) = \theta_w r_i^{(w)} + \rho_b r_i^{(s)}$$

c_i	aqueous-phase concentration [mol/L]
s_i	solid-phase concentration [mol/kg]
$\mathbf{q}$	specific-discharge vector [m/s]
$\mathbf{D}_i$	dispersion tensor [m^2/s]
θ_w	volumetric water content [-]
ρ_b	dry bulk mass density of the solids [kg/L]
$r_i^{(*)}$	reaction rate within phase * [conc./s]

Advection-Dispersion-Reaction Equation of Compound *i*

$$\theta_w \frac{\partial c_i}{\partial t} + \rho_b \frac{\partial s_i}{\partial t} + \mathbf{q} \cdot \nabla c_i - \nabla \cdot \left(\theta_w \mathbf{D}_i \nabla c_i \right) = \theta_w r_i^{(w)} + \rho_b r_i^{(s)}$$

Additionally needed:

- Law for mass-exchange between the aqueous and solid phases
- Rate laws for the reactions
- Initial and boundary conditions
- Parameters, parameters, parameters...

Divide by the Volumetric Water Content

$$\frac{\partial c_i}{\partial t} + \frac{\rho_b}{\theta_w}\frac{\partial s_i}{\partial t} + \mathbf{v}\cdot\nabla c_i - \nabla\cdot\left(\mathbf{D}_i\nabla c_i\right) = r_i^{(w)} + \frac{\rho_b}{\theta_w} r_i^{(s)}$$

with the seepage-velocity vector $\mathbf{v} = \mathbf{q}/\theta_w$

- Requires the 3-D vector field of velocities...

…which is spatially variable in heterogeneous domains

- Large CPU times for spatially explicit schemes
- Various issues with Eulerian numerical discretization (numerical oscillations; numerical dispersion)
- Particle-based methods have issues too (express rate laws as particle-particle interactions; hardly any particles in low-velocity zones;...)

Dilemma of Reactive Transport Simulations in Heterogeneous Domains

- Nonlinear rate laws
+ Spatial variability of hydraulic and chemical parameters (with unknown details)
+ Need fine resolution to overcome numerical problems of spatially explicit schemes
⇨ Very high computational effort
✋ Uncertainty of parameters (and concepts) call out for ensemble-based stochastic analysis
💣 But ensemble runs are hardly affordable

Major Objective

- Find a conceptually simplified description of reactive transport that
  1. covers the major controls
  2. is computationally efficient

  … and can thus be used in ensemble calculations

☝ Try to get rid of a spatially variable 3-D description in the calculation of nonlinear reactive transport!

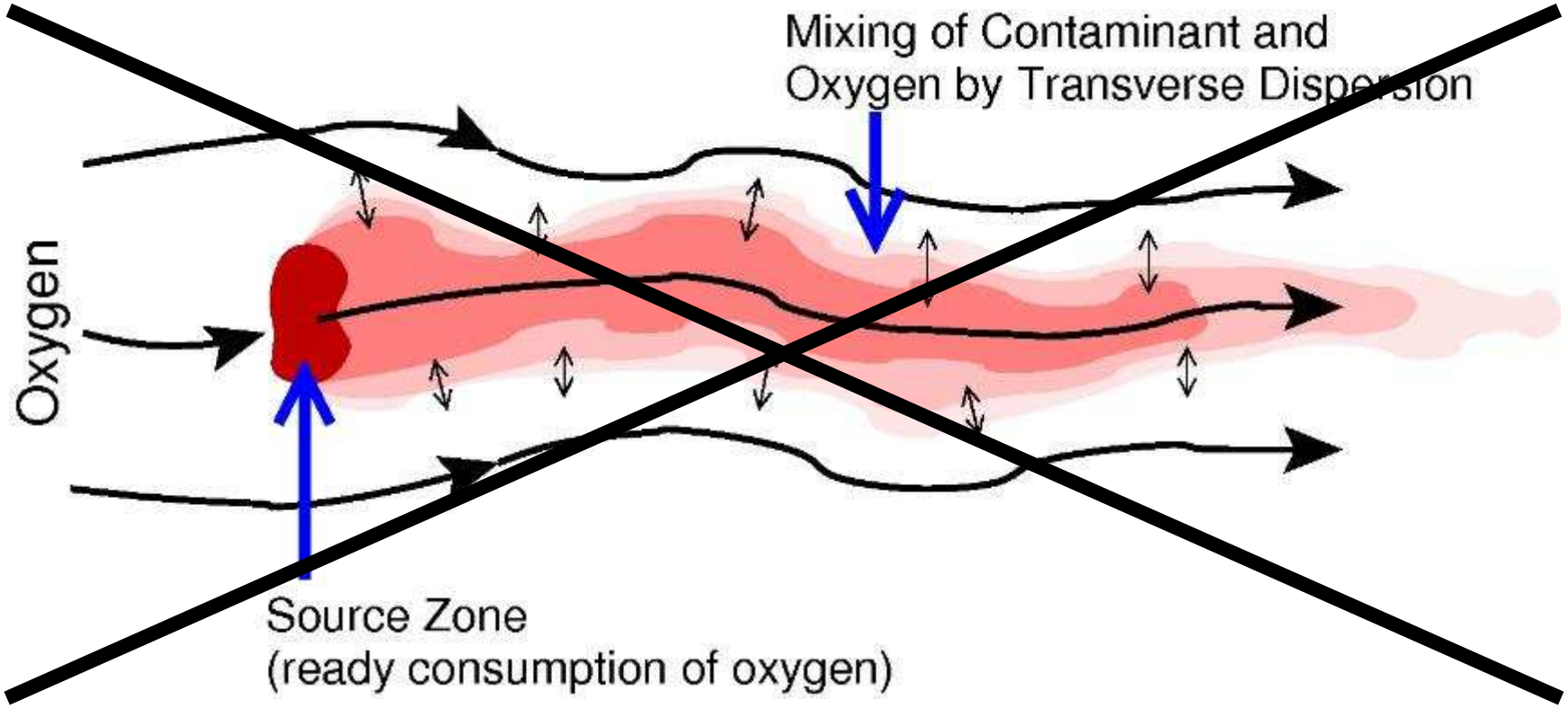
- Can only be achieved under specific conditions.

Gross Simplifications

- Steady-state flow
- Neglect dispersion (⇦ reactants are either already mixed in the inflow or mix due to exchange with the solid phase)
- Uniform initial conditions
- Uniform reaction parameters
- Spatially uniform concentrations in the inflow (⇦ diffuse input)

A Favorite Case of Mine that Does Not Work

- Steady-state plume where the reaction partner mixes in from the side



Advection-Reaction Equation of Compound *i*

$$\frac{\partial c_i}{\partial t} + \frac{\rho_b}{\theta_w}\frac{\partial s_i}{\partial t} + \mathbf{v}\cdot\nabla c_i = r_i^{(w)}(\mathbf{c},\mathbf{s}) + \frac{\rho_b}{\theta_w} r_i^{(s)}(\mathbf{c},\mathbf{s})$$

- Introduce the advective travel time τ_a:

$$\mathbf{v}\cdot\nabla\tau_a = 1$$

…and apply the chain-rule of differentiation:

$$\mathbf{v}\cdot\nabla c_i = \mathbf{v}\cdot\nabla\tau_a \frac{\partial c_i}{\partial \tau_a} = \frac{\partial c_i}{\partial \tau_a}$$

$$\frac{\partial c_i}{\partial t} + \frac{\rho_b}{\theta_w}\frac{\partial s_i}{\partial t} + \frac{\partial c_i}{\partial \tau_a} = r_i^{(w)}(\mathbf{c},\mathbf{s}) + \frac{\rho_b}{\theta_w} r_i^{(s)}(\mathbf{c},\mathbf{s})$$

Advection-Reaction Equation of Compound *i* in Travel-Time Domain

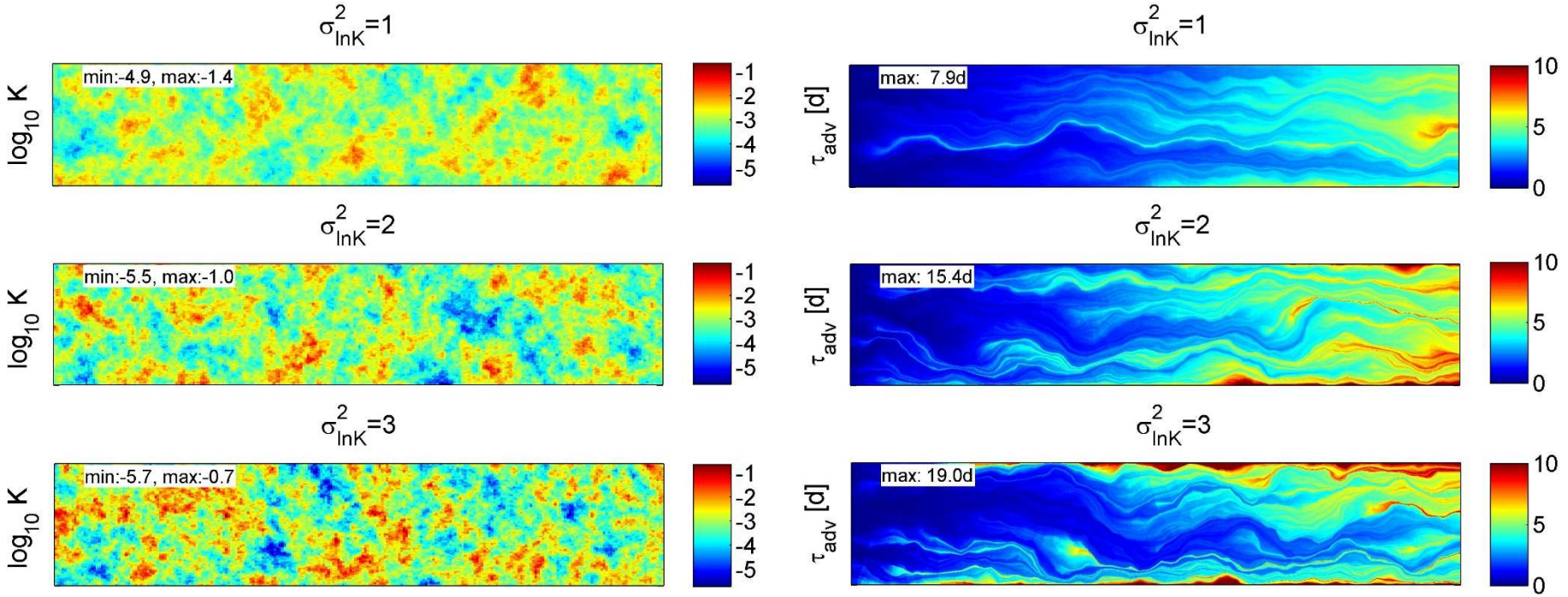
$$\frac{\partial c_i}{\partial t} + \frac{\rho_b}{\theta_w}\frac{\partial s_i}{\partial t} + \frac{\partial c_i}{\partial \tau_a} = r_i^{(w)}(\mathbf{c},\mathbf{s}) + \frac{\rho_b}{\theta_w} r_i^{(s)}(\mathbf{c},\mathbf{s})$$

- 3 spatial coordinates replaced by 1 travel-time coordinate
- Variable velocity replaced by constant factor of 1
- Uniform chemical parameters and initial conditions imply that the reaction rates depend on concentrations only (which depend on reactive transport)

⇨ Self-organization of concentration fronts

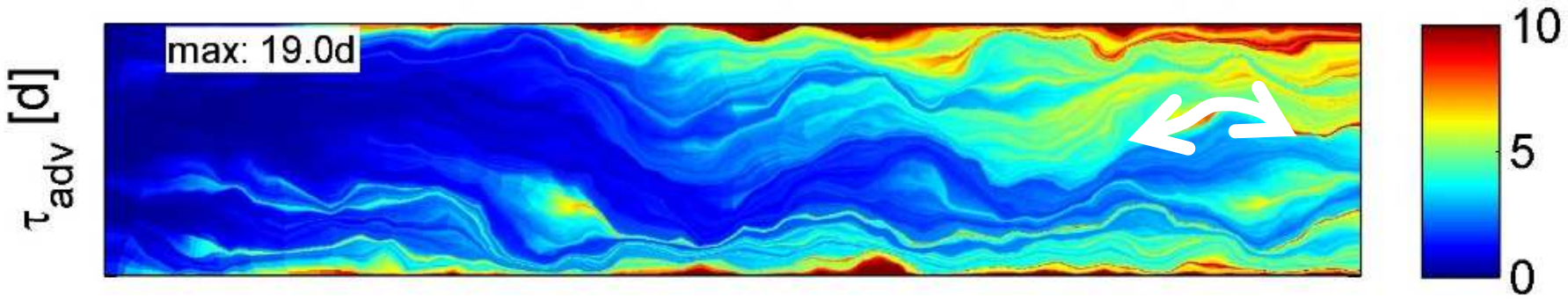
- Compute everything in the 1-D travel-time domain and map results to the spatial domain $c_i(\mathbf{x},t) = c_i(\tau_a(\mathbf{x}),t)$

Example Calculations of Kinematic Age



Effects of Local Dispersion

- Still steady-state flow, uniform initial & inflow concentrations, uniform chemical parameters

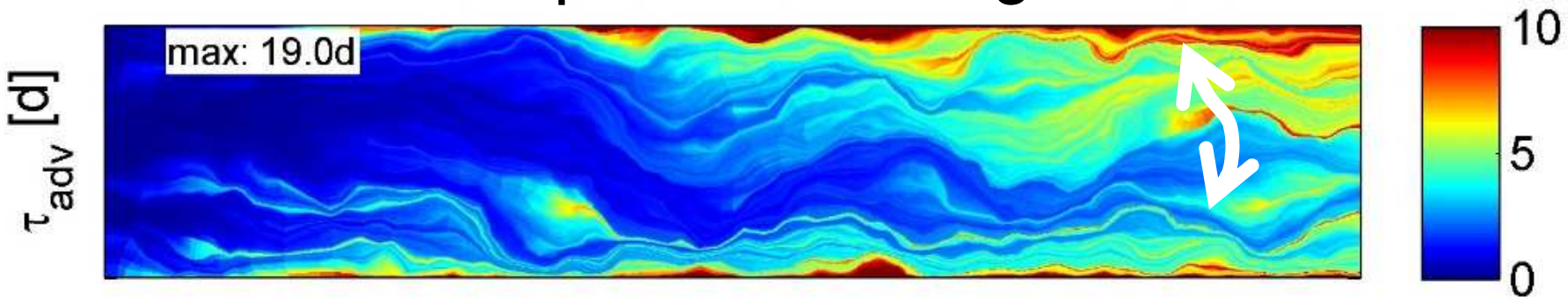


- Longitudinal dispersive mixing:

$$\frac{\partial}{\partial x_\ell}\left(D_\ell \frac{\partial c_i}{\partial x_\ell}\right) = \frac{1}{\|\mathbf{v}\|}\frac{\partial}{\partial \tau_a}\left(\frac{D_\ell}{\|\mathbf{v}\|}\frac{\partial c_i}{\partial \tau_a}\right) \approx \frac{\partial}{\partial \tau_a}\left(D_\tau \frac{\partial c_i}{\partial \tau_a}\right)$$

Effects of Local Dispersion

- Transverse dispersive mixing

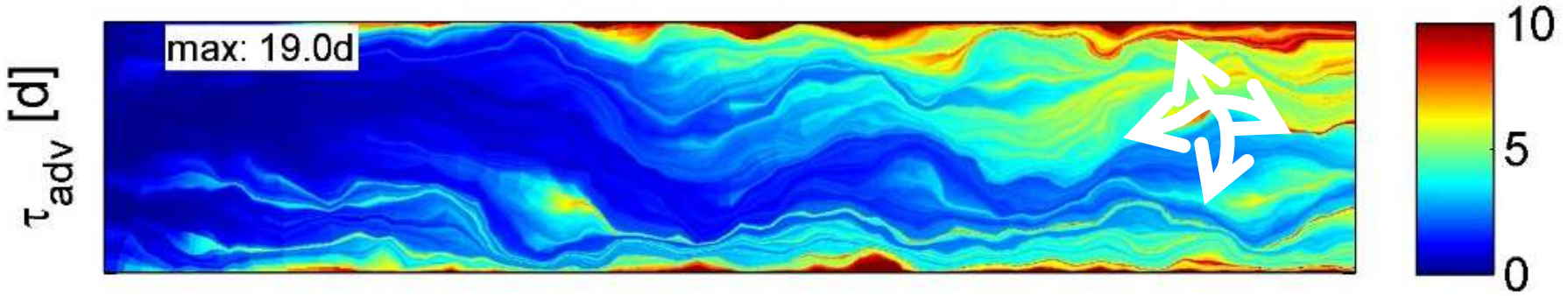


- Also mixes old and young water!
- Parameterization by effective dispersion?

$$\nabla \cdot (\mathbf{D}_i \nabla c_i) \approx \frac{\partial}{\partial \tau}\left(D_{eff,\tau} \frac{\partial c_i}{\partial \tau} \right)$$

- What is the right coefficient $D_{eff,\tau}(\tau)$?

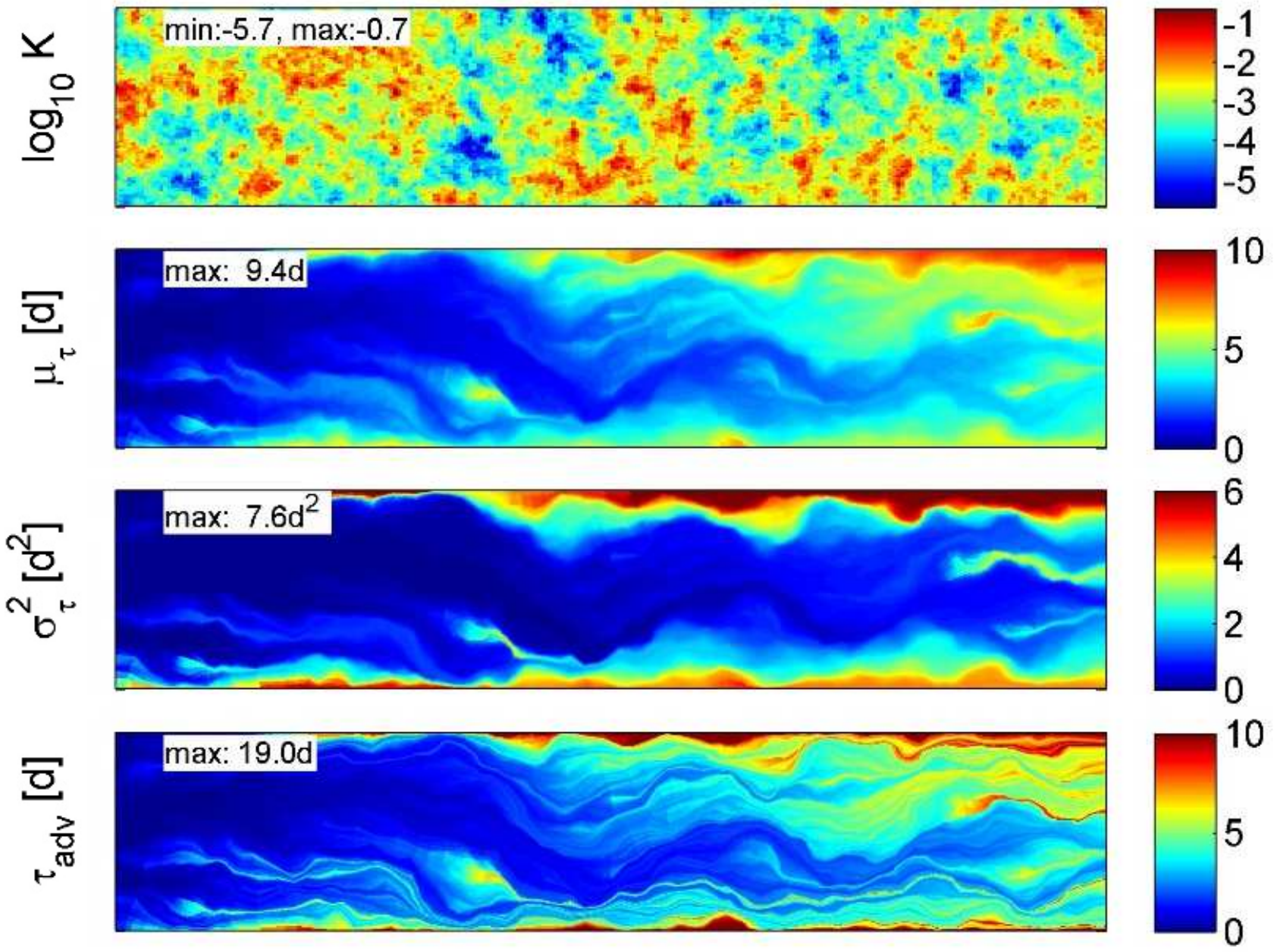
Effects of Local Dispersion



- Upon dispersive mixing, the groundwater age becomes a distribution at each point
- Mean and variance of groundwater age meet:

$$\mathbf{v}\cdot\nabla\mu_\tau-\nabla\cdot\left(\mathbf{D}\nabla\mu_\tau\right)=1$$

$$\mathbf{v}\cdot\nabla\sigma_\tau^2-\nabla\cdot\left(\mathbf{D}\nabla\sigma_\tau^2\right)=2\nabla\mu_\tau\cdot\left(\mathbf{D}\nabla\mu_\tau\right)$$


log10 K
min:-5.7, max:-0.7
-1
-2
-3
-4
-5
μτ [d]
max: 9.4d
10
5
0
στ2 [d2]
max: 7.6d2
6
4
2
0
τadv [d]
max: 19.0d
10
5
0

Parameterization of Dispersive Mixing in Travel-Time Framework of Reactive Transport

$$\frac{\partial c_i}{\partial t} + \frac{\rho_b}{\theta_w}\frac{\partial s_i}{\partial t} + \frac{\partial c_i}{\partial \mu_\tau} - \frac{\partial}{\partial \mu_\tau}\left(D_{eff,\tau}\frac{\partial c_i}{\partial \mu_\tau} \right) = r_i^{(w)} + \frac{\rho_b}{\theta_w} r_i^{(s)}$$

- Still 1-D model
- All mixing is between young and old water
- Definitely requires spatially uniform inflow concentrations
- $D_{eff,\tau}$ can vary with (and only with) μ_τ
- Obtain $D_{eff,\tau}$ from dependence of σ_τ^2 on μ_τ

Aerobic Degradation and Denitrification in Bank Filtration (River-Water Infiltration)

- Oxygen and nitrate are the electron acceptors
- Dissolved organic carbon is the electron donor
- Elevated oxygen concentrations inhibit denitrification
- The reactants are mixed in the river and jointly transported into the riverbed
- Immobile aerobic and denitrifying microbes grow upon their reactions
- There is a maximum biomass concentration („carrying capacity“)

Stoichiometry of Reactions

- Net reaction using organic carbon as electron donor:

  $CH_2O + (1\text{-}Y_{den})\ 4/5\ NO_3^{\ominus} \rightarrow (1\text{-}Y_{den})\ 2/5\ N_2 + Y_{den} bio_{den} + \ldots$

- Aerobic metabolism:

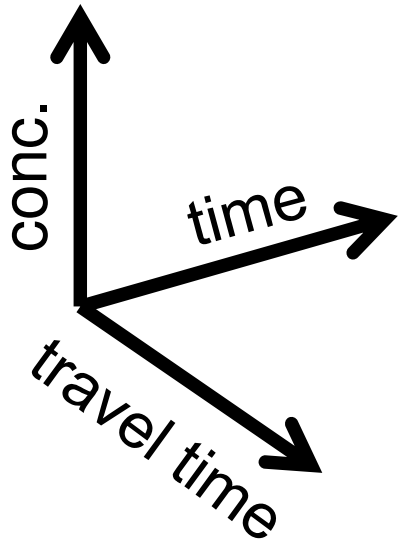
  $CH_2O + (1\text{-}Y_{aer})\ O_2 \rightarrow Y_{aer} bio_{aer} + \ldots$

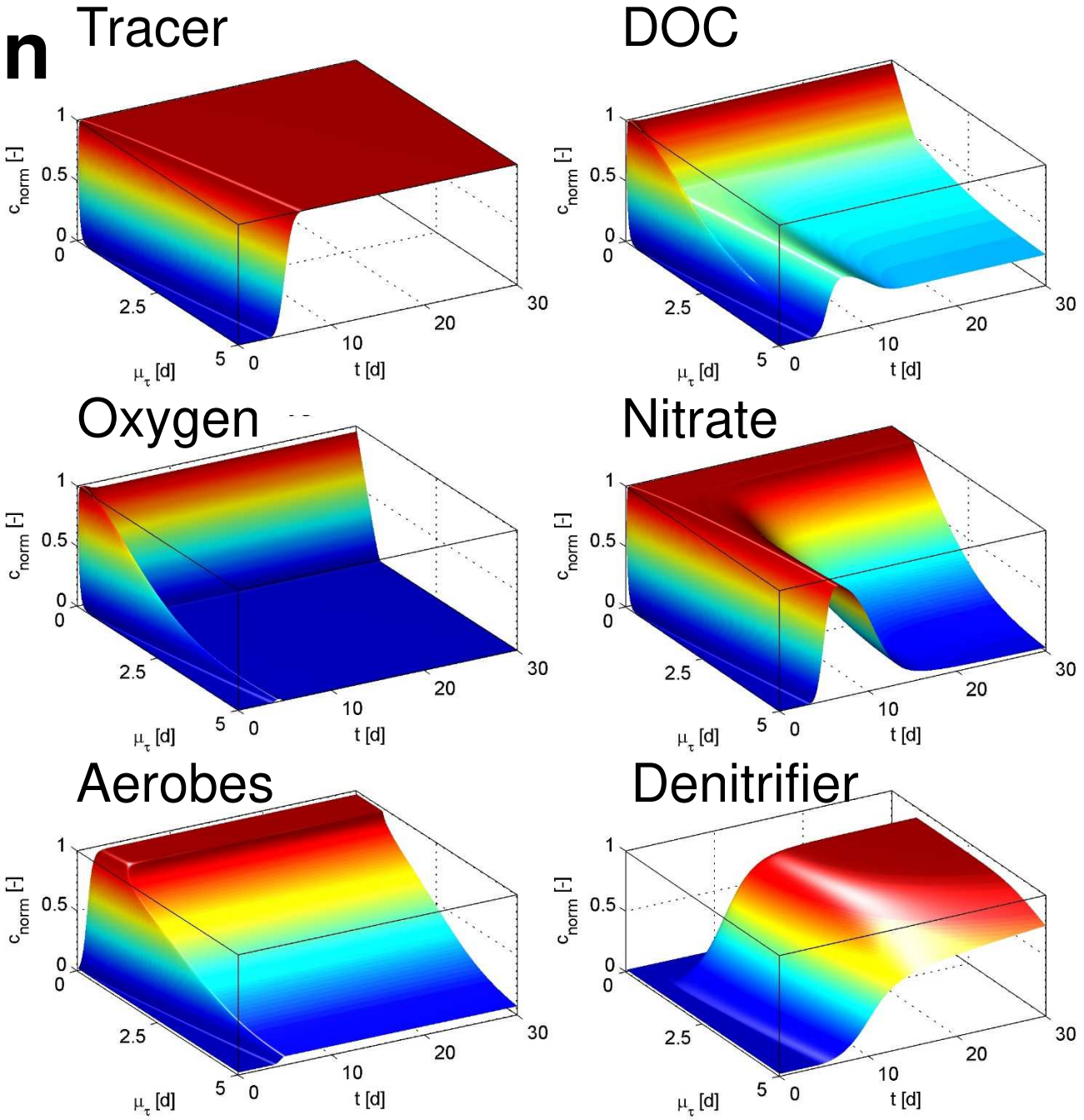
  with specific yield coefficients Y_i and biomass concentrations bio_i (measured in carbon) related to biomass type i

- Double-Monod kinetics as typical rate law:

$$r_{aer} = \frac{c_{DOC}}{c_{DOC} + K_{DOC}} \cdot \frac{c_{Ox}}{c_{Ox} + K_{Ox}} \cdot \frac{\mu_{aer,\max}}{Y_{aer}} \cdot c_{bio}^{aer}$$

1-D Invasion

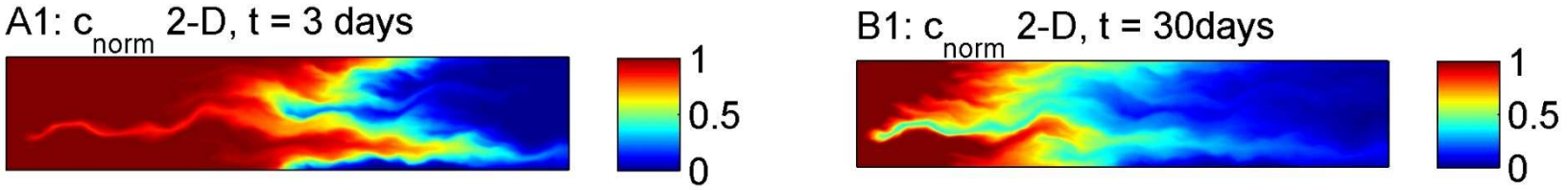

conc.
time
travel time


Tracer
DOC
Oxygen
Nitrate
Aerobes
Denitrifier
c_{norm} [-]
μ_τ [d]
t [d]
0
0.5
1
2.5
5
10
20
30

2-D Heterogeneous Domain

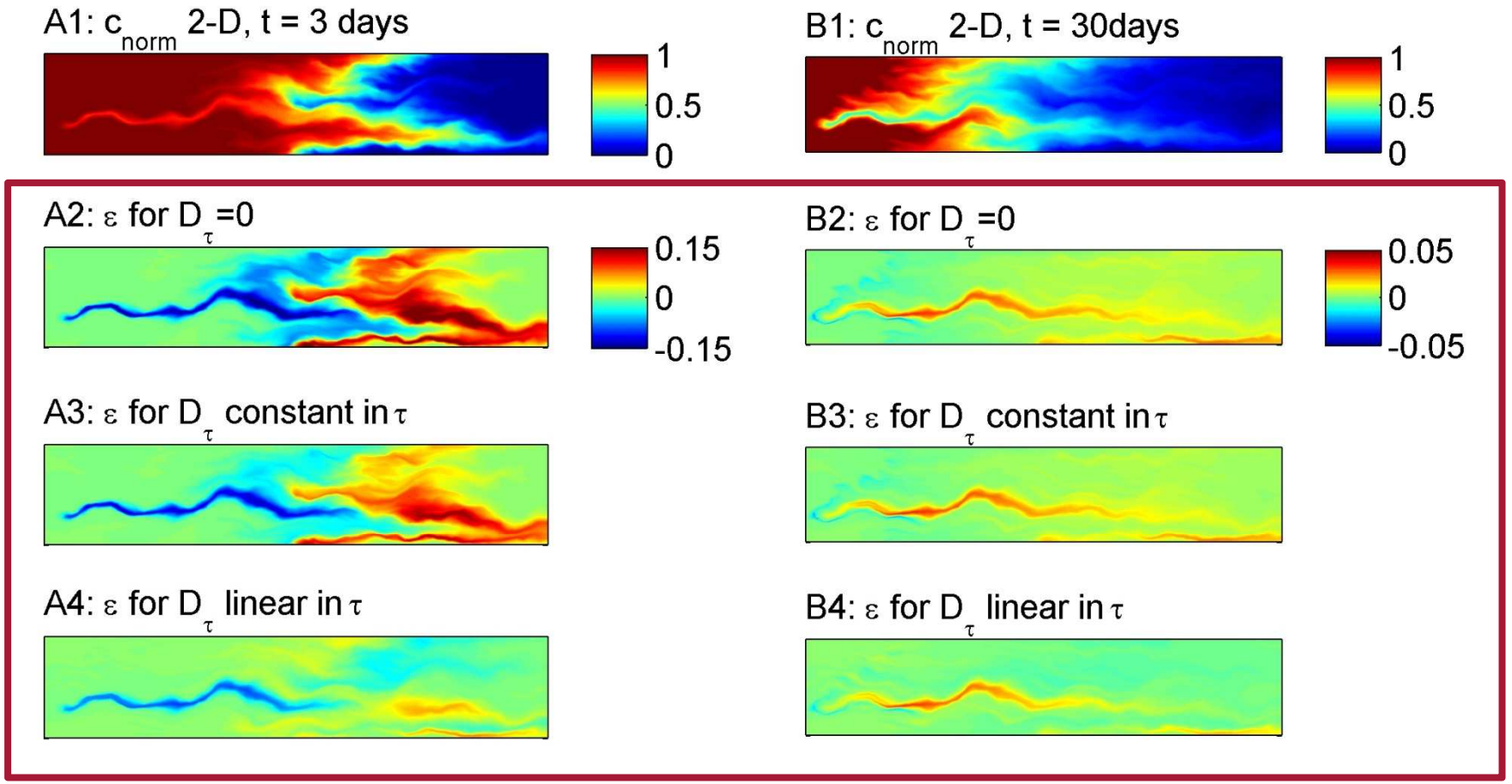
- Reference case: 2-D spatially explicit, reactive transport model
- Several mapping approaches from travel-time domain to spatial domain:
  - Neglecting dispersion altogether
  - Considering the local longitudinal dispersion coefficient at the average velocity
  - Considering an effective longitudinal dispersion coefficient that increases linearly with mean travel time

Spatial Distribution of Nitrate (worst)



normalized concentrations of spatially explicit calculation

Spatial Distribution of Nitrate (worst)

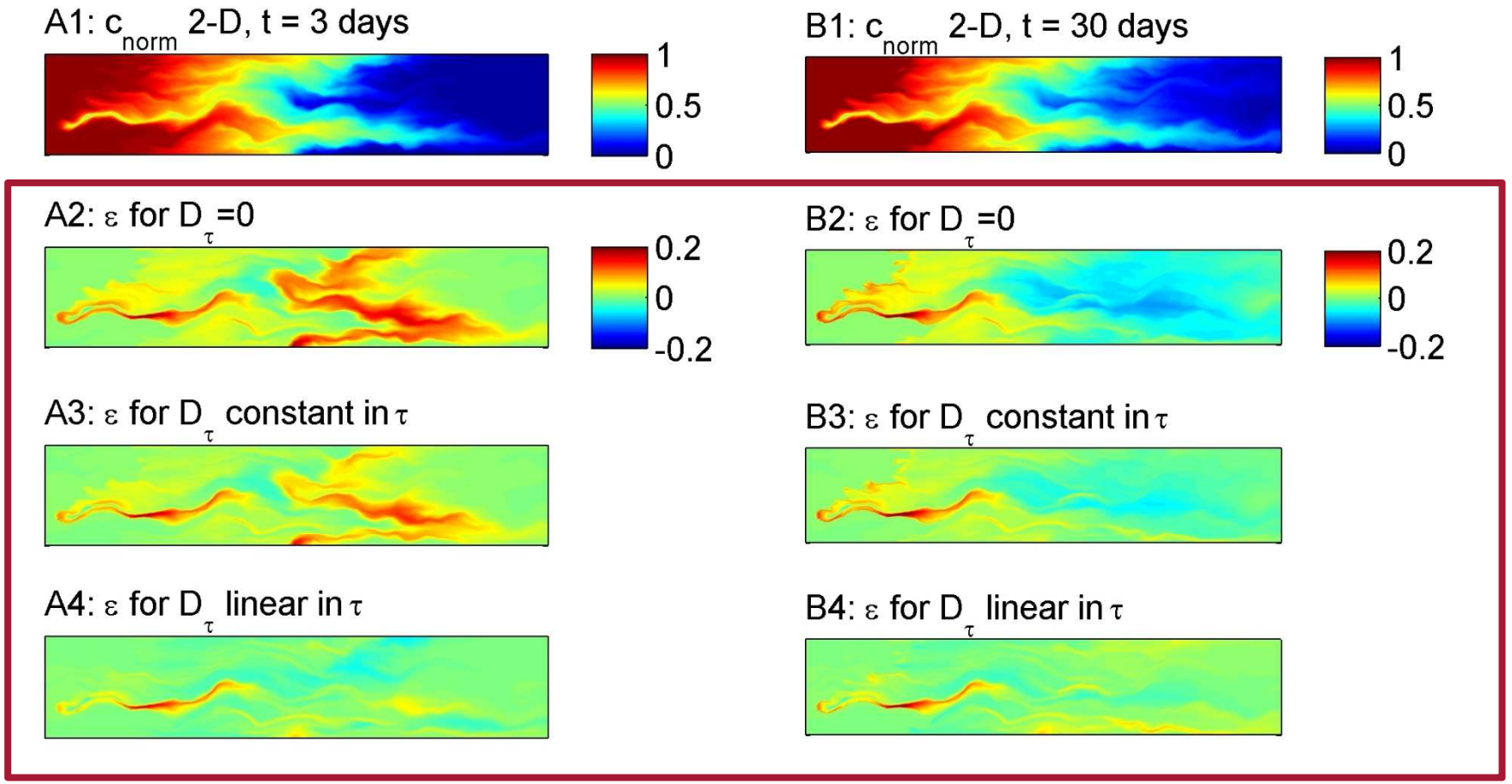


normalized errors

Spatial Distribution of Aerobic Bacteria

normalized concentrations of spatially explicit calculation

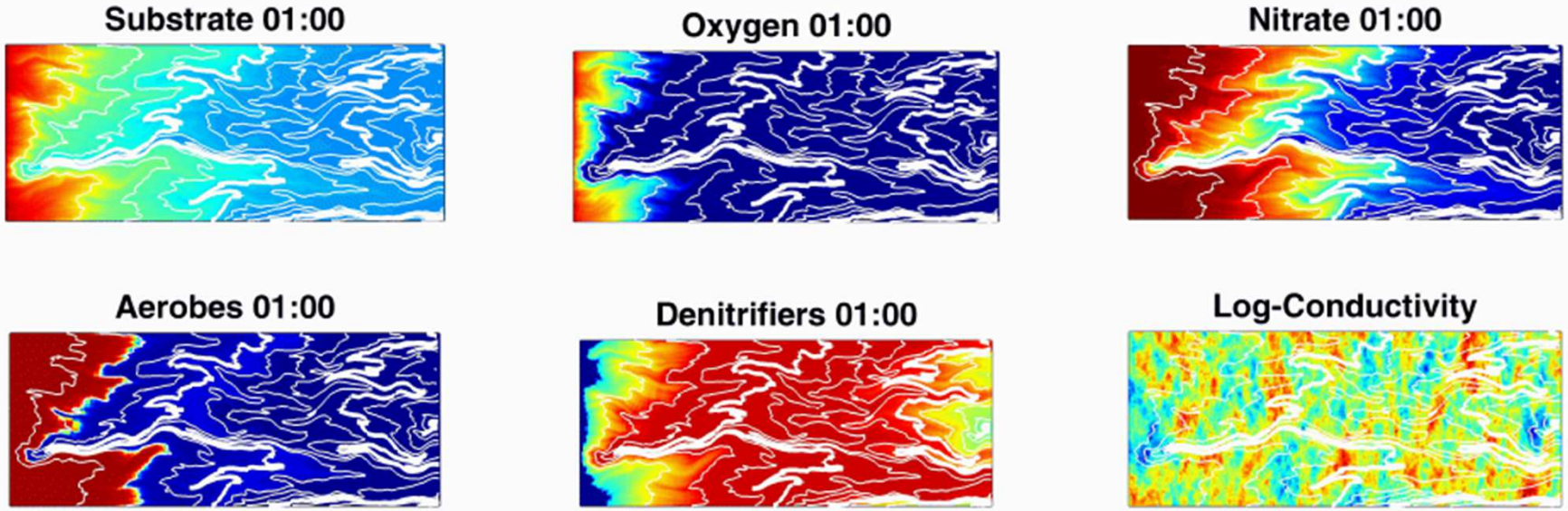
Spatial Distribution of Aerobic Bacteria



normalized errors

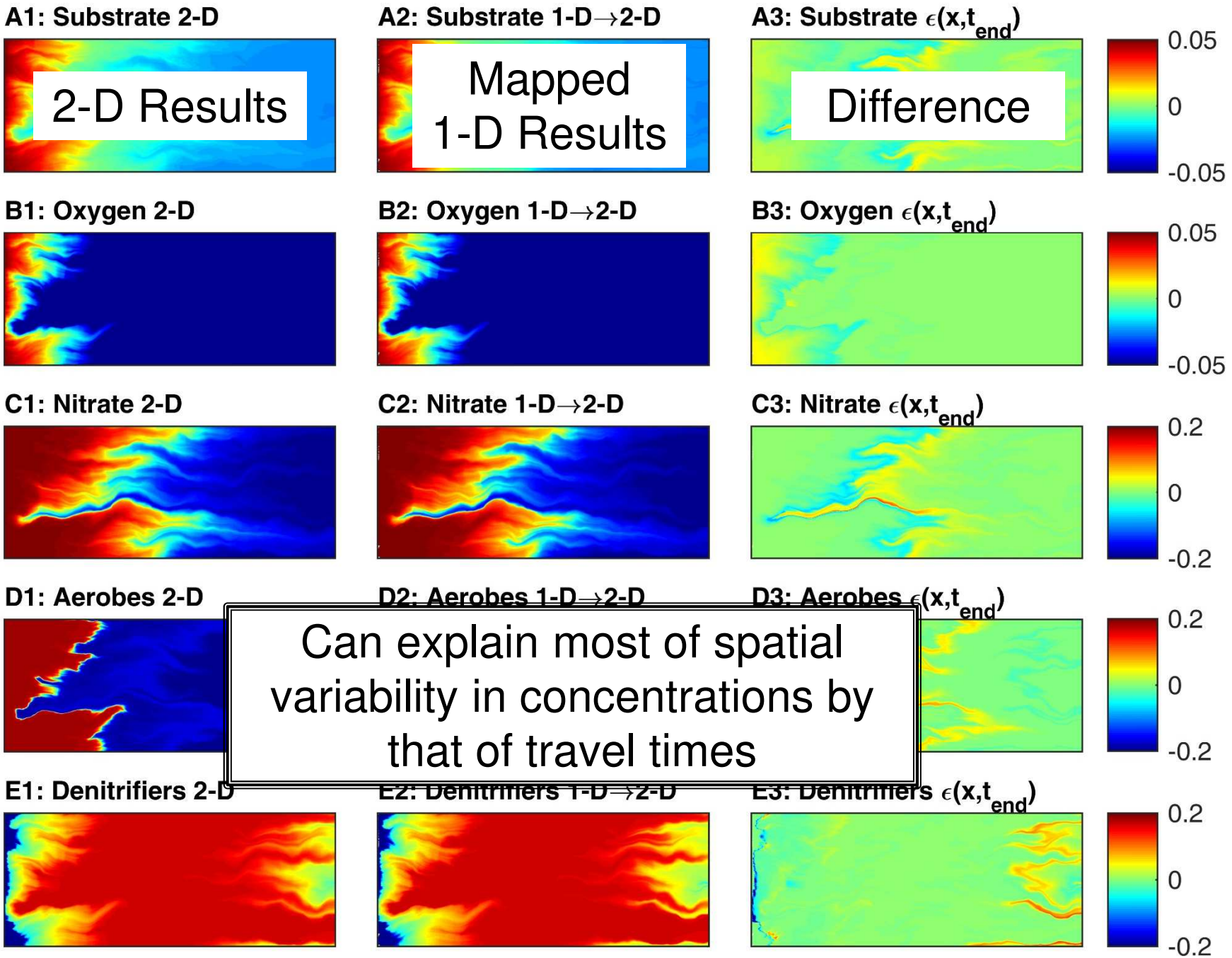
More on Relationship between Concentrations and Travel Times in Bioreactive Transport

- Joint injection of substrate, oxygen, and nitrate
- Diurnal fluctuations of velocity magnitude, but not direction
- 2-D spatially explicit advective-dispersive-bioreactive transport



Sanz-Prat et al. (2016)

- Lines: Isochrones for time-averaged velocity.


A1: Substrate 2-D
A2: Substrate 1-D→2-D
A3: Substrate ϵ(x,t_end)
2-D Results
Mapped 1-D Results
Difference
0.05
0
-0.05
B1: Oxygen 2-D
B2: Oxygen 1-D→2-D
B3: Oxygen ϵ(x,t_end)
0.05
0
-0.05
C1: Nitrate 2-D
C2: Nitrate 1-D→2-D
C3: Nitrate ϵ(x,t_end)
0.2
0
-0.2
D1: Aerobes 2-D
D2: Aerobes 1-D→2-D
D3: Aerobes ϵ(x,t_end)
Can explain most of spatial variability in concentrations by that of travel times
0.2
0
-0.2
E1: Denitrifiers 2-D
E2: Denitrifiers 1-D→2-D
E3: Denitrifiers ϵ(x,t_end)
0.2
0
-0.2

Lessons Learned

- Travel-time based simulations of reactive transport are good approximations if
  - macroscopic transverse mixing is not decisive (diffuse input)
  - chemical parameters are spatially uniform
  - direction of flow does not vary in time
- Effective longitudinal mixing needs to be parameterized at an invading front

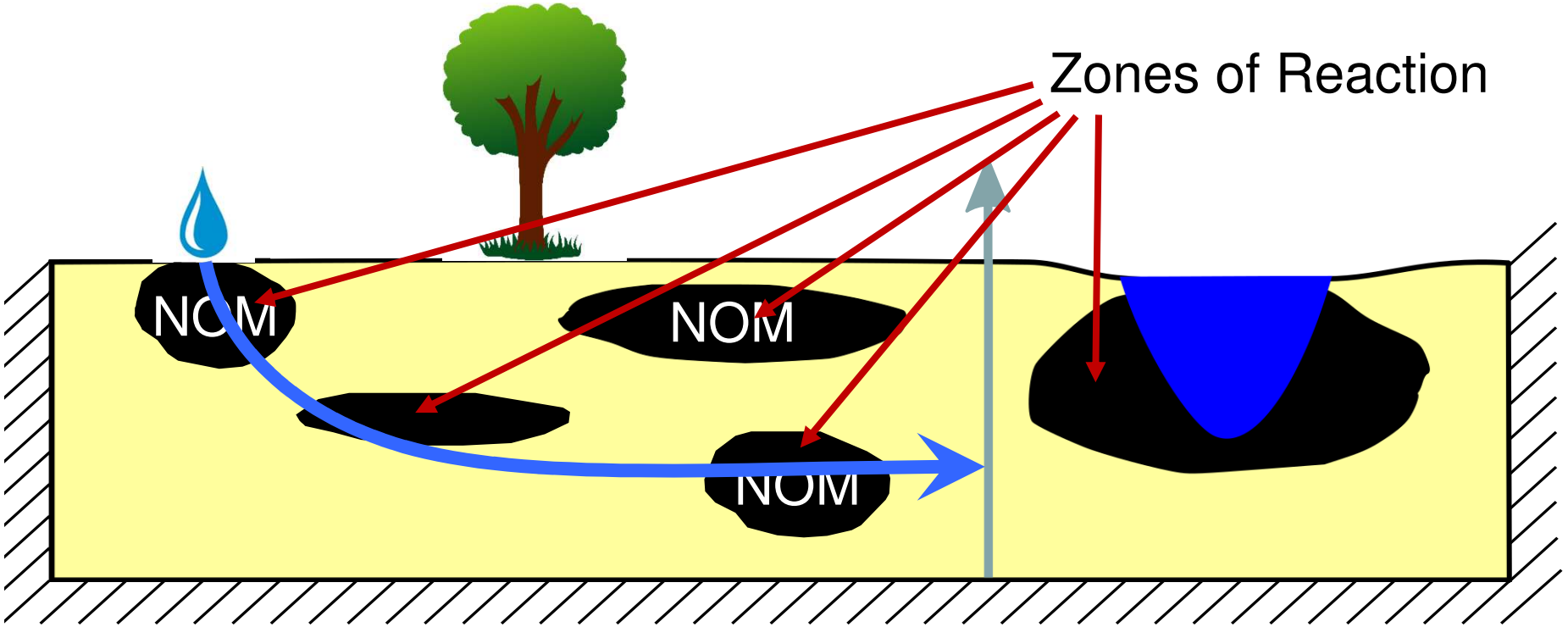
…but is less important at late times

Fate of Nitrate Controlled by e-Donor Release from the Matrix

- Similar calculations as the previous ones, but with first-order release of DOC rather than joint injection.
- Release of DOC is restricted to zones of high Natural Organic Matter (NOM) in the matrix

⇨Binary chemical heterogeneity

Let‘s Follow a Water Parcel Through the Aquifer



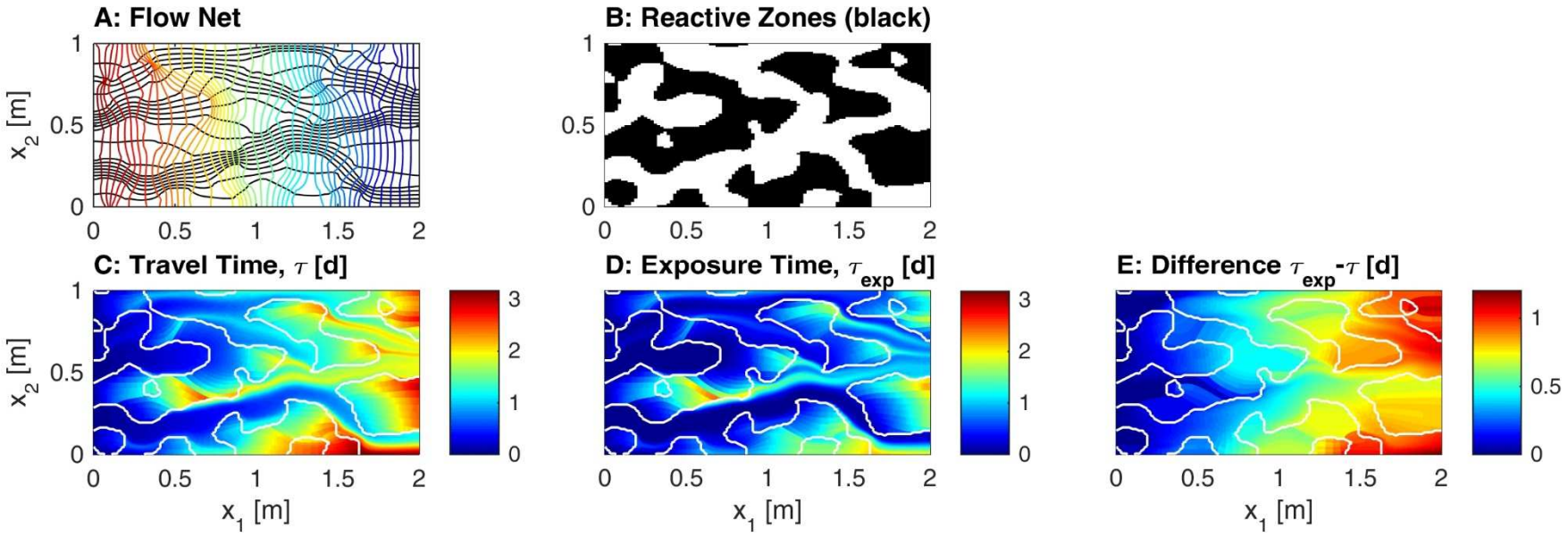
Exposure Time

- Time that a water parcel has spent in the reactive zones:

$$\mathbf{v}\cdot\nabla\tau_{\exp}-\nabla\cdot\left(\mathbf{D}\nabla\tau_{\exp}\right)=\begin{cases}1 & \text{in reactive zones}\\ 0 & \text{elsewhere}\end{cases}$$

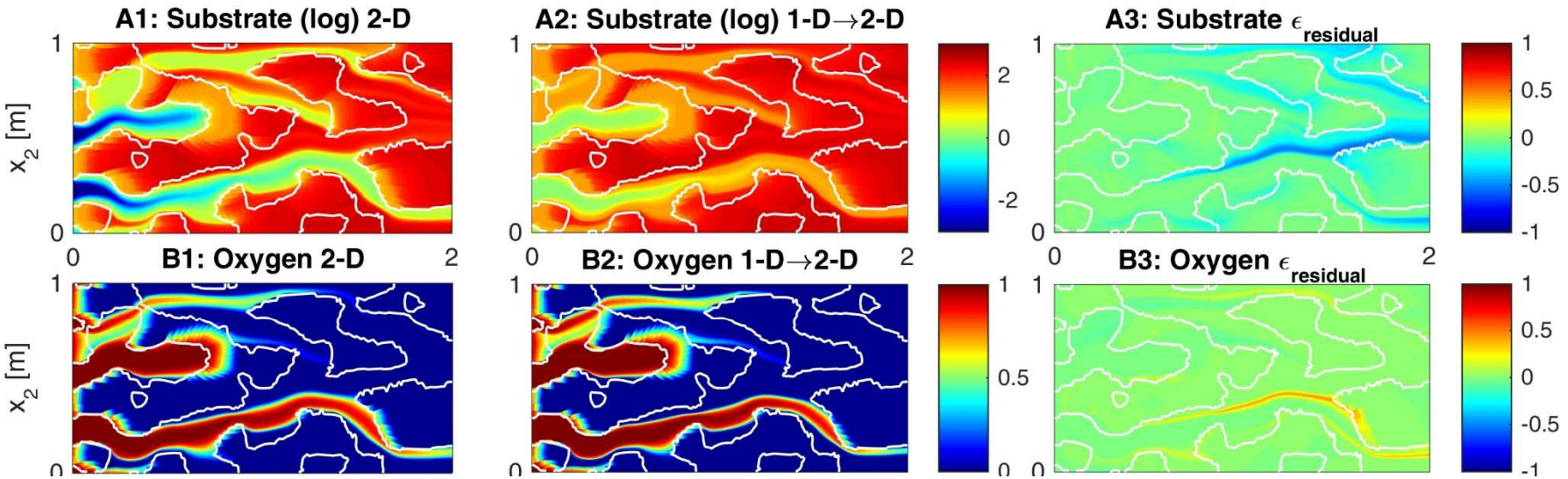
- Use similar mapping approach as before, but with exposure rather than travel time

Travel- and Exposure Times in a Heterogeneous Domain

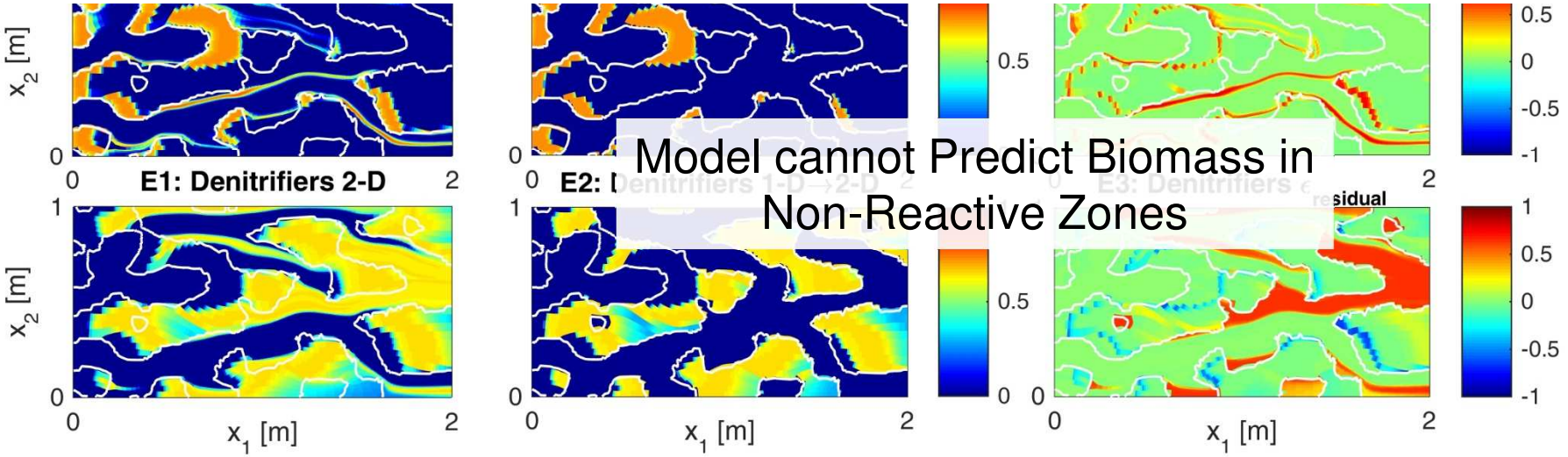


Sanz-Prat et al. (2016)

- Two distinct materials
- Low-conductivity material releases DOC
- High-conductivity material released no DOC



Comparison between full 2-D and Exposure-Time Based Results at Late Times



Model cannot Predict Biomass in Non-Reactive Zones

Simplifications and Extensions

- Build-up of biomass takes days (aerobic) to weeks (denitrifying bacteria)
- Microbes grow until a local steady state of DOC release and consumption is reached, often close to carrying capacity
- Microbes can cope with transient conditions by dormancy and biomass transport

⇨ Explicit consideration of microbes not needed

- With exception of invading fronts, dispersion is not needed
- Reactivity of the aquifer matrix not binary

Relative Reactivity *f*(**x**)

- Release of the electron donor from the matrix addressed as reactivity, relative to a reactivity under reference conditions:

$$\frac{\partial \mathbf{c}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{c} = f\mathbf{r}_0(\mathbf{c})$$

$$\mathbf{c} = \begin{bmatrix} c_{Ox} \\ c_{Nit} \end{bmatrix}; \quad \mathbf{r}_0(\mathbf{c}) = \begin{bmatrix} r_{Ox}^{\max} \cdot \dfrac{c_{Ox}}{c_{Ox} + K_{Ox}} \\ r_{Nit}^{\max} \cdot \dfrac{c_{Nit}}{c_{Nit} + K_{Nit}} \cdot \dfrac{K_{Ox}^{inh}}{c_{Ox} + K_{Ox}^{inh}} \end{bmatrix}$$

Mathematical Tricks in a Nutshell

- Advection-reaction equation with variable relative reactivity:

$$\frac{\partial \mathbf{c}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{c} = f\,\mathbf{r}_0(\mathbf{c})$$

- Total derivative along a trajectory:

$$\frac{D\mathbf{c}}{Dt} = f\,\mathbf{r}_0(\mathbf{c})$$

- Introduce cumulative relative reactivity:

$$F = \int_0^{\tau} f(\mathbf{x}(\tau_*))d\tau_* \text{ along a trajectory}$$

- Then, reactive transport along trajectory becomes:

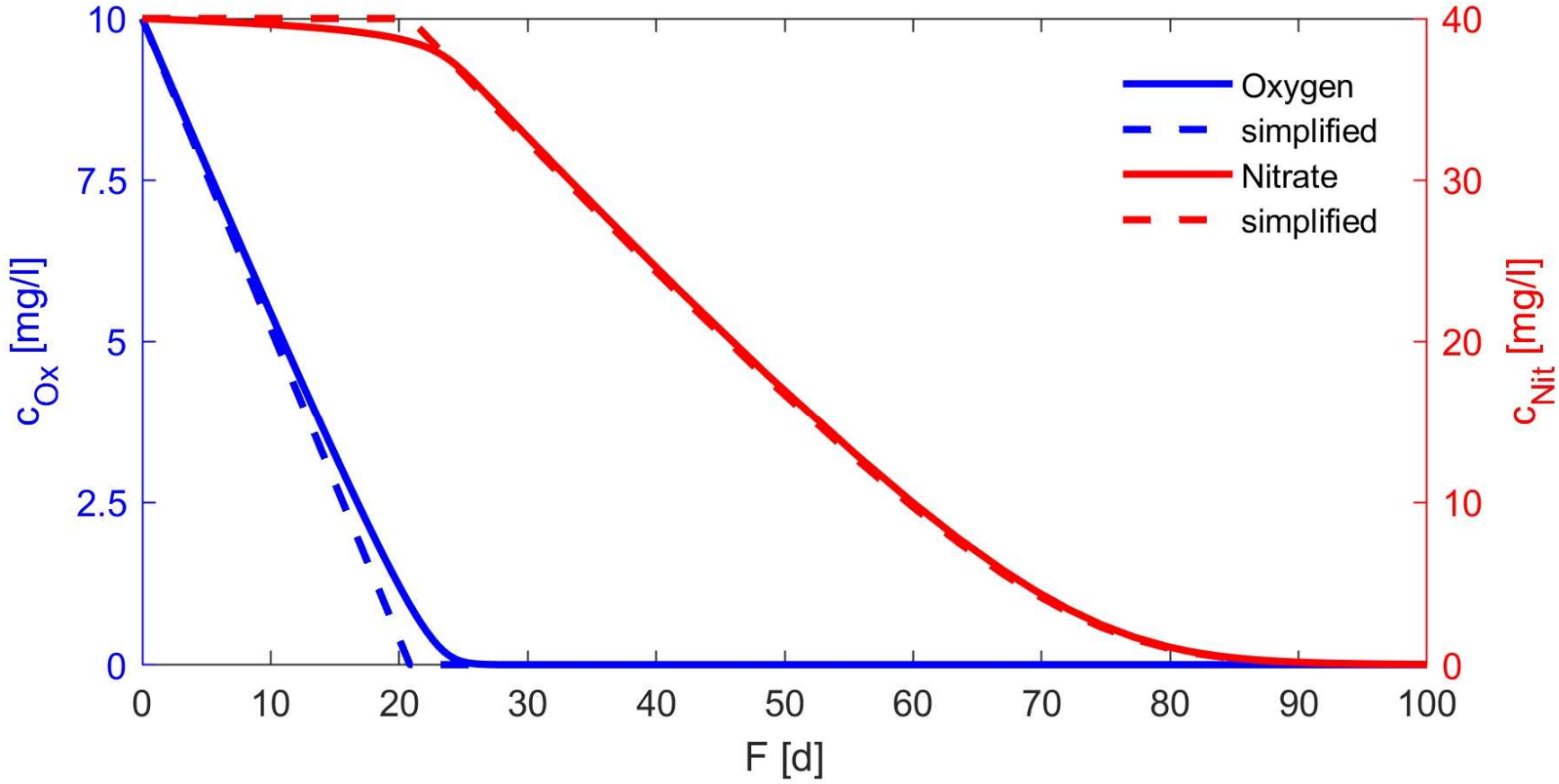
$$\frac{D\mathbf{c}}{DF} = \mathbf{r}_0(\mathbf{c})$$

⇨ Single ODE-system for one set of initial concentrations !

(Cumulative) Relative Reactivity

- Relative reactivity:
  - How strong is the electron-donor source in comparison to reference conditions?
  - Depends on the type and amount of electron-donor source in the matrix
- Cumulative relative reactivity
  - How much (relative) reactivity has a water parcel seen on its way to an observation point?
  - Units of time: The clock ticks more quickly in zones of high reactivity than in lowly reactive zones
  - Can easily be evaluated by particle tracking

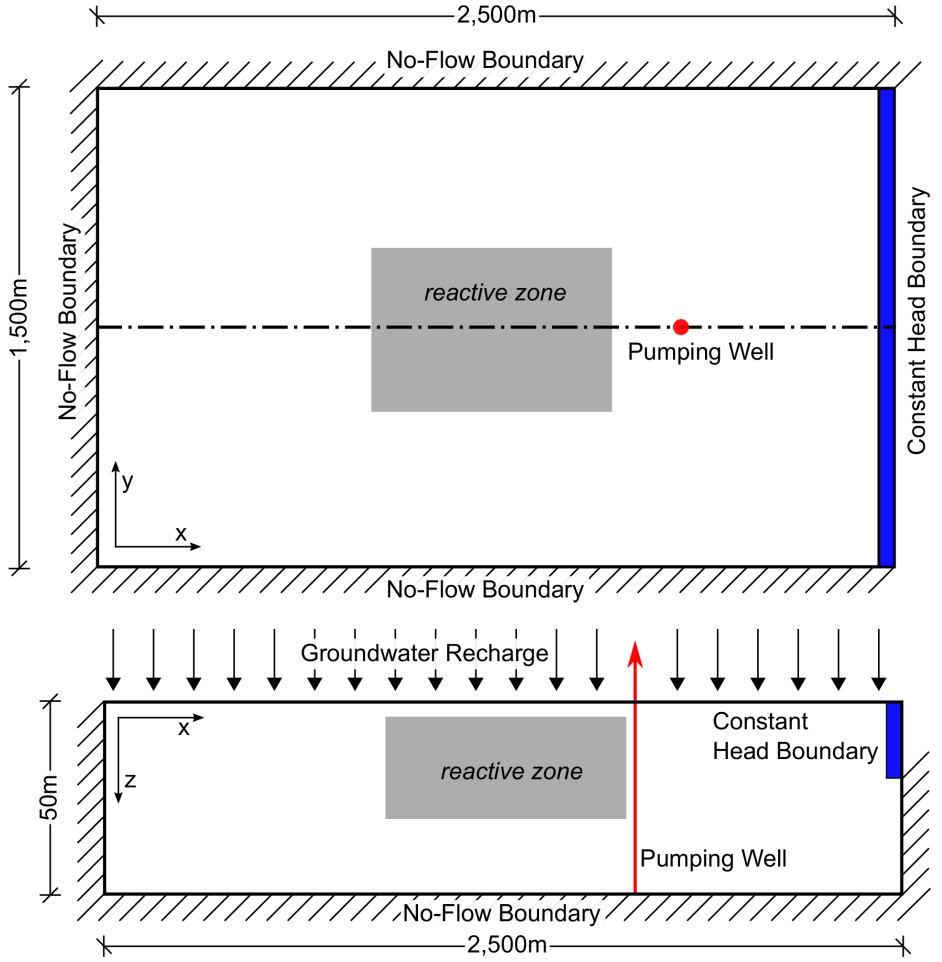
Ageing of a Water Parcel Causes Decrease in Oxygen and Nitrate Concentration



Closed-form solution for simplified Michaelis-Menten kinetics

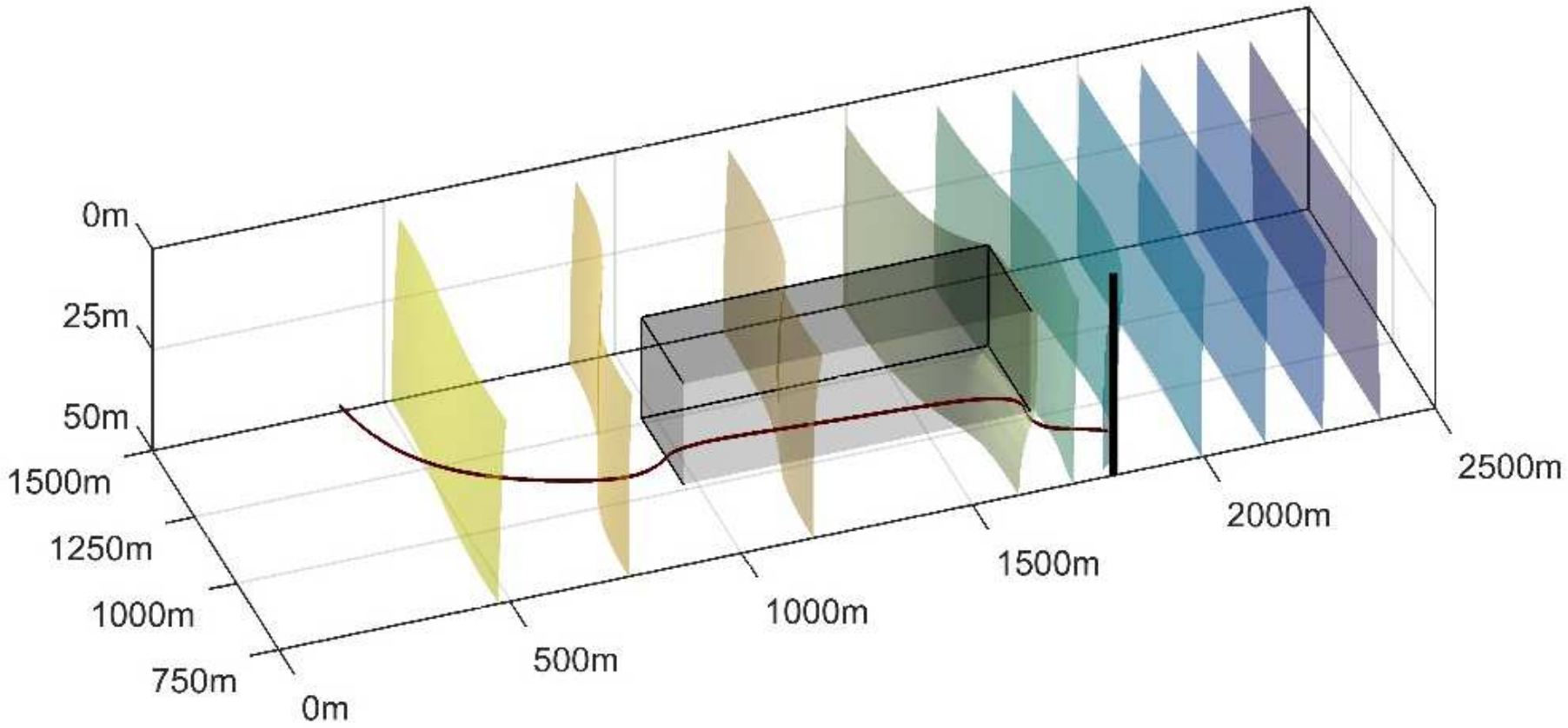
Proof-of-Concept Application

- 1.5 Mio. cells
- Groundwater recharge contains nitrate and oxygen
- using MATLAB, MODFLOW-NWT, CUDA GPU Particle Tracking
- Computing time: 12min (mostly MODFLOW)

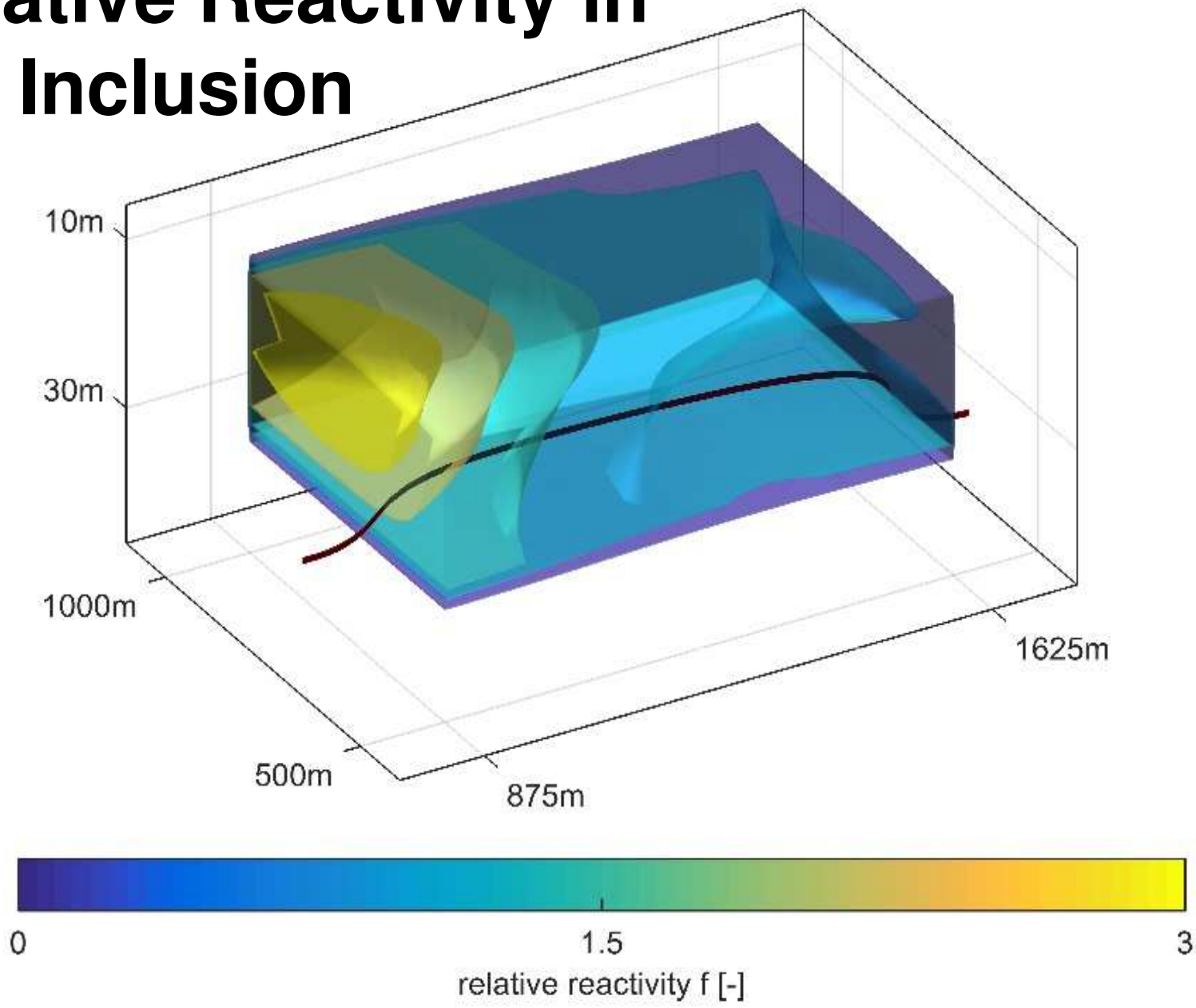


Loschko et al. (2016)

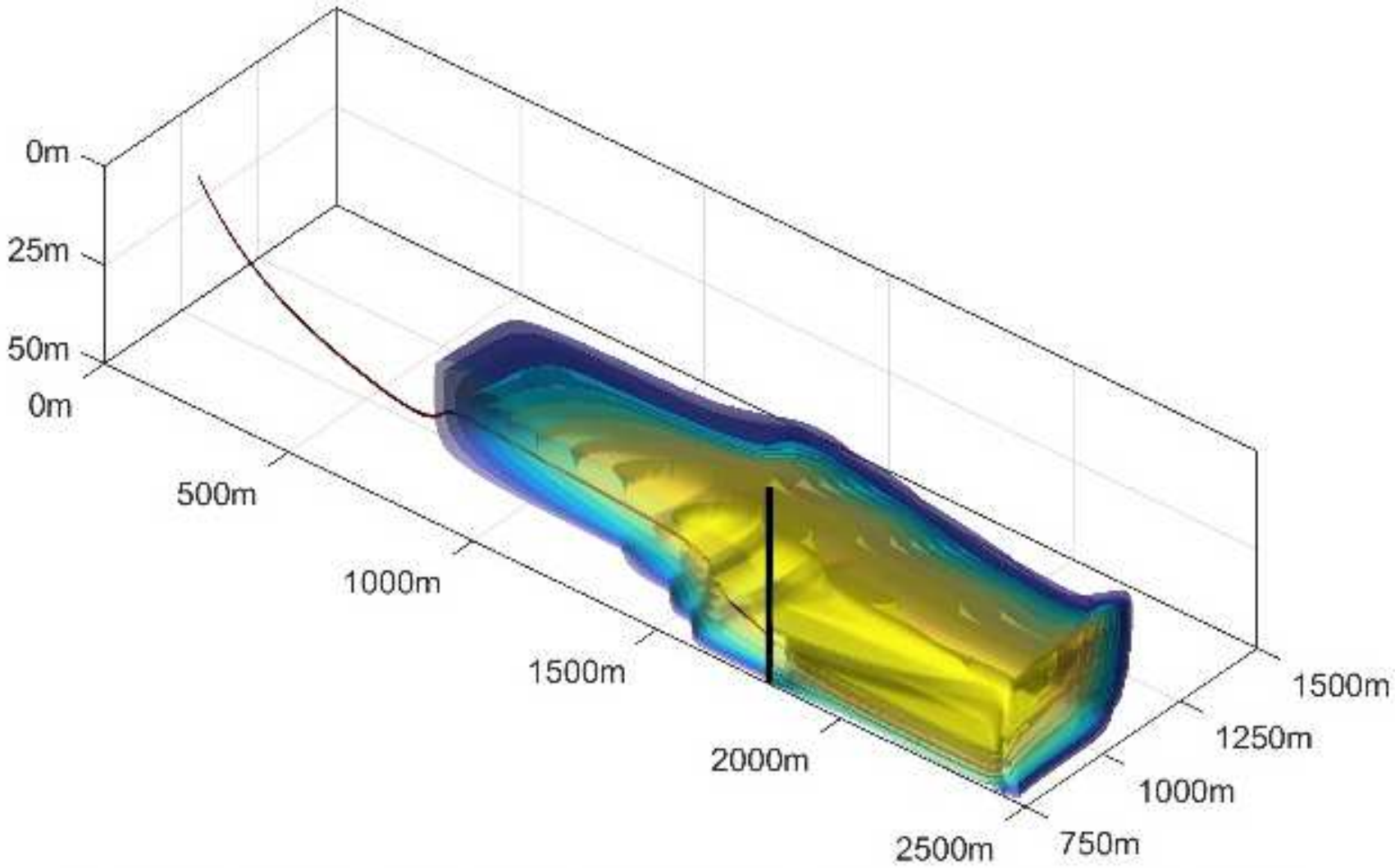
Hydraulic Heads



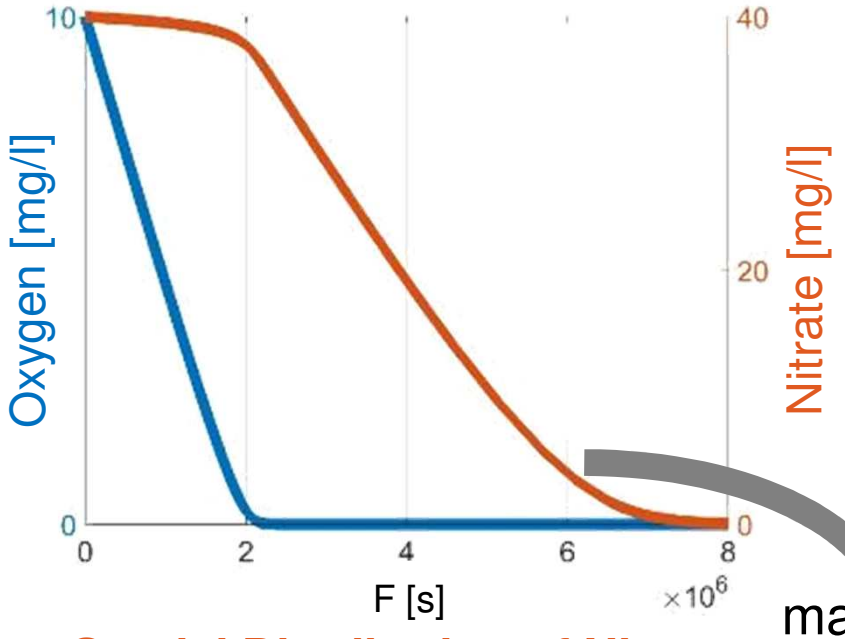
Relative Reactivity in the Inclusion



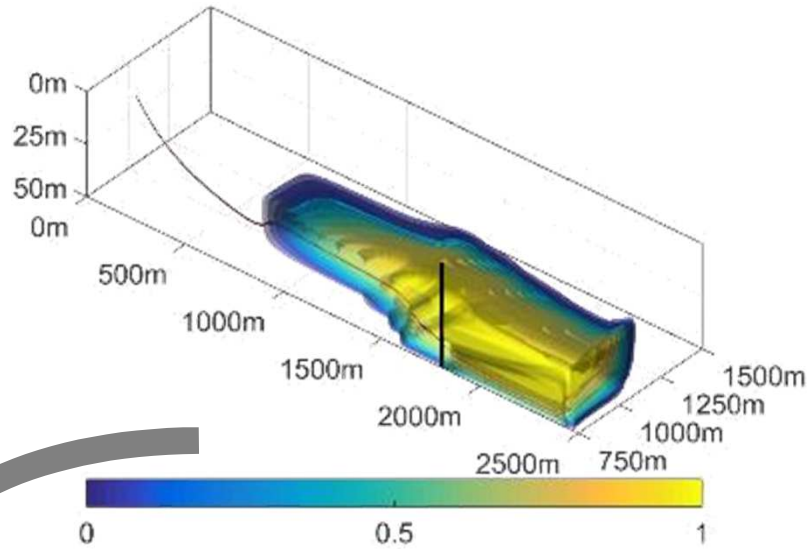
Cumulative Relative Reactivity



Concentrations as Function of Cumulative Relative Reactivity

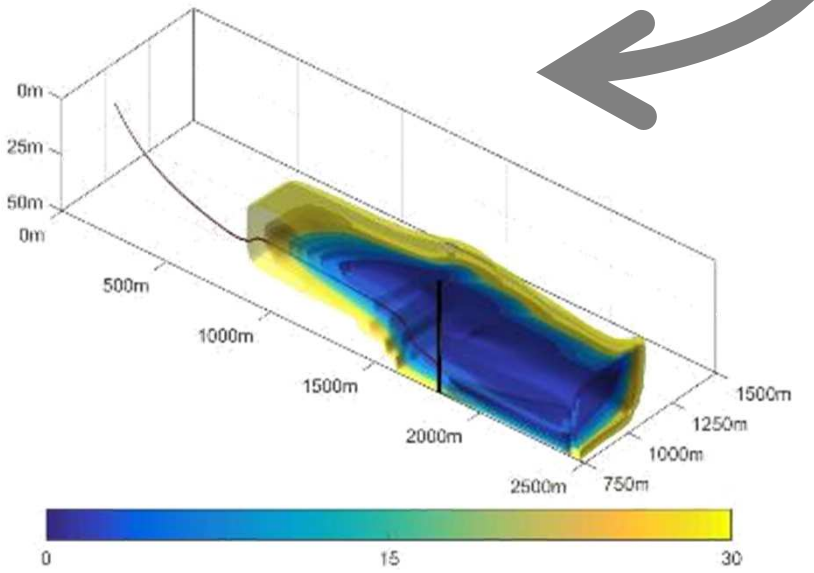


Spatial Distribution of Cumulative Relative Reactivity

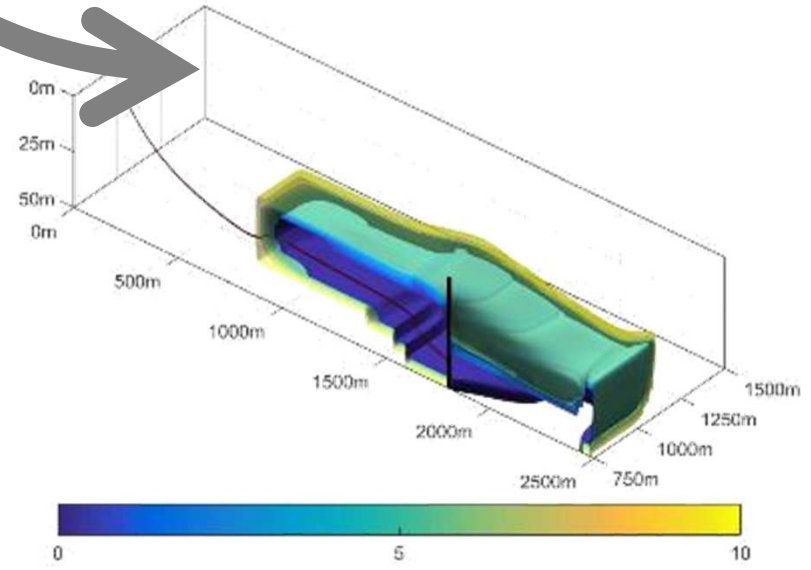


mapping

Spatial Distribution of Nitrate



Spatial Distribution of Oxygen



Accounting for Decreasing Denitrification Potential of the Aquifer Matrix

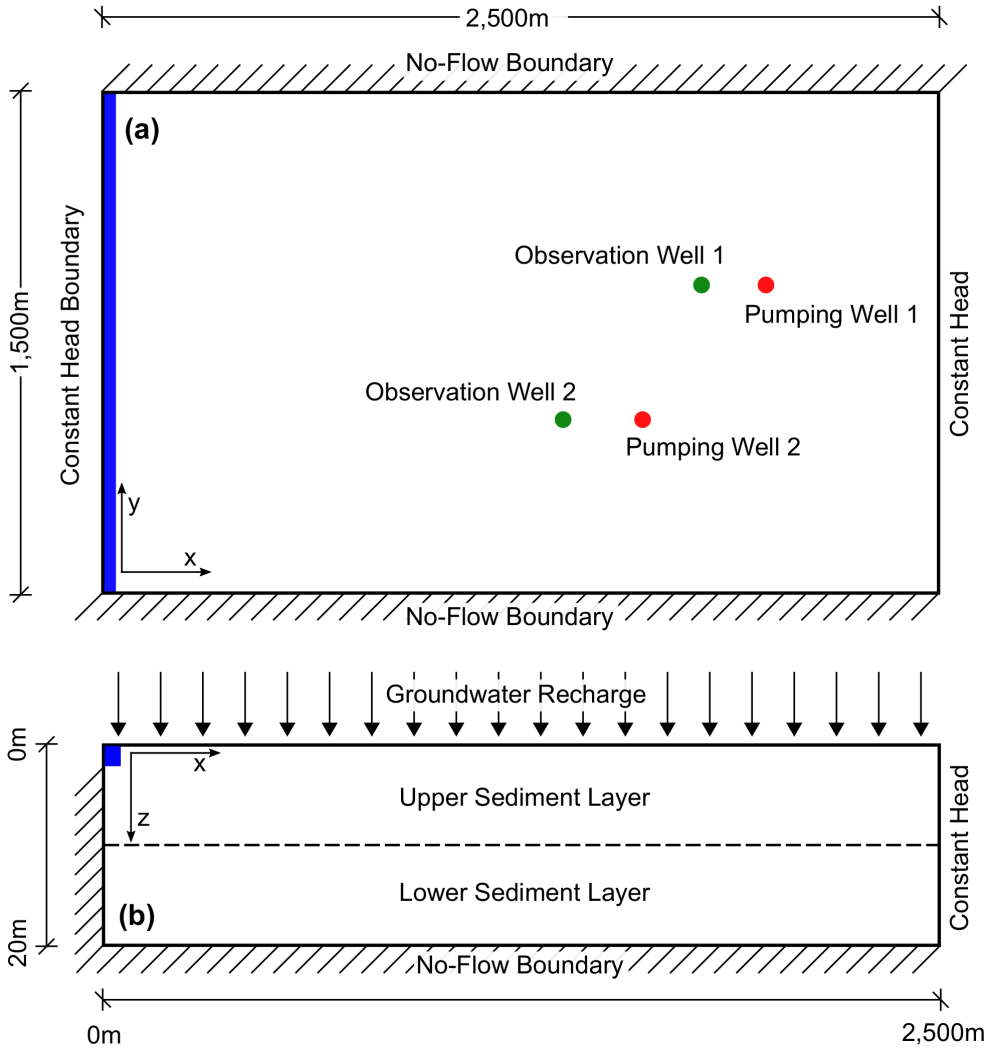
- Stoichiometries: $1O_2{:}1C_{org}$ & $1NO_3^{\ominus}{:}1.25C_{org}$
- Need a functional dependence of relative reactivity f on NOM-content of the matrix
- Consumption of NOM in the matrix reduces cumulative relative reactivity F along trajectories

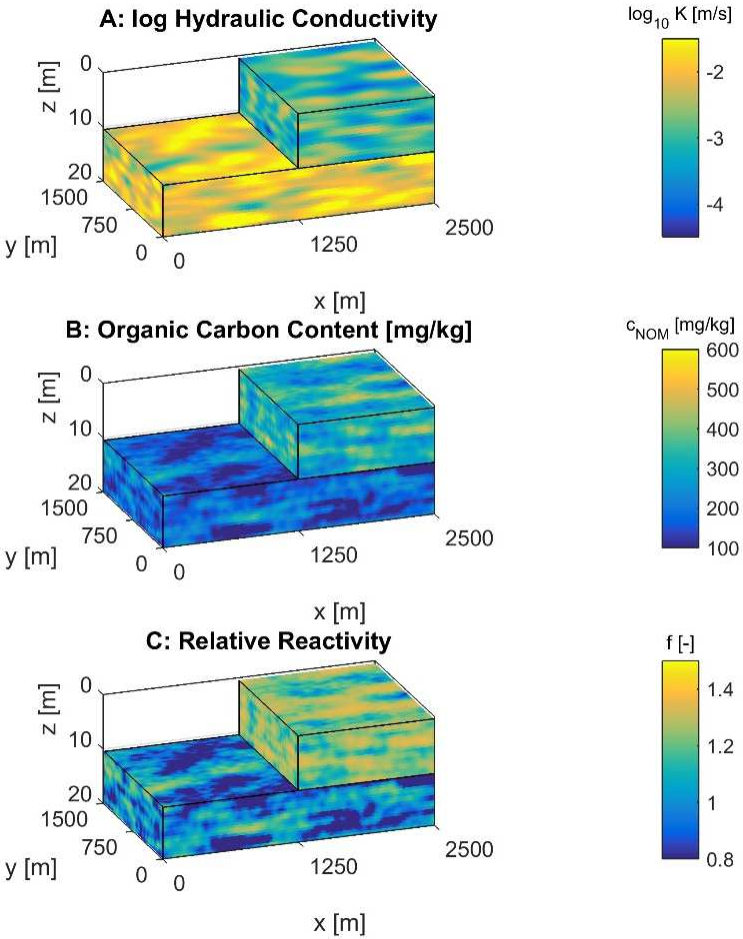
⇨ Regular update needed

⇨ Spatially explicit problem, solved along pathlines that are discretized in travel-time increments

3-D Monte-Carlo Simulations

750‘000 Cells, 200 Realizations





Loschko et al. (2018)

Breakthrough Curves

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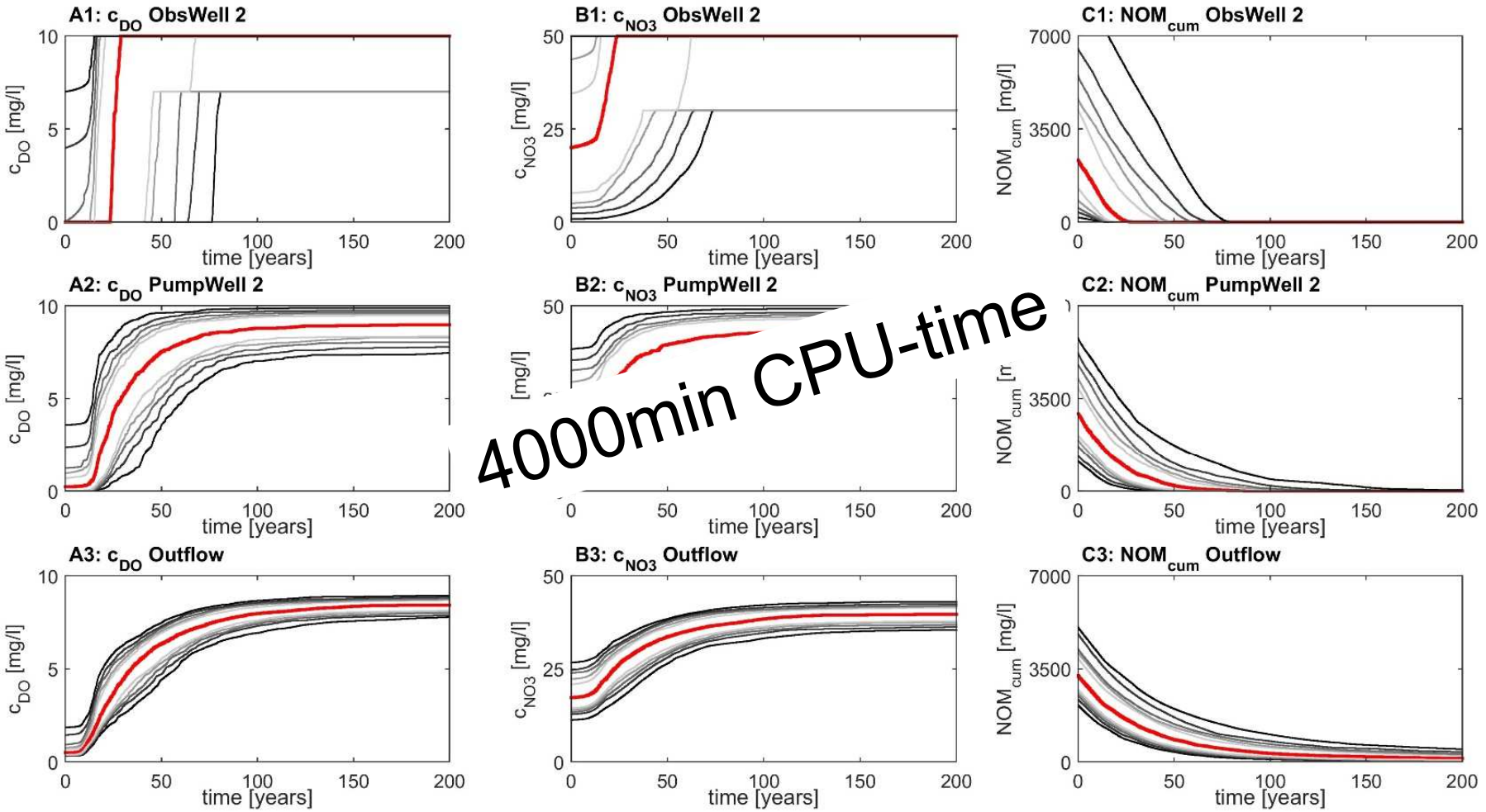
Dissolved Oxygen | Nitrate | Bioavailable NOM



Loschko et al. (2018)

Carry-Home Messages

- Travel-time based approaches conceptually simplify reactive transport simulations
- Not the golden bullet for all setups...

…but suitable under specific conditions

- A model does not need to include all processes and properties that you know of

…but those that control the system.

- If chosen wisely, you can reduce the computational effort dramatically

Practical Challenges

- Inference of travel times from „age tracers“ is less straightforward than many believe
- Chemical heterogeneity (e.g., spatial distribution of NOM) exists but is less frequently assessed than physical heterogeneity
- Catalogue of geological structures with typical sizes, hydraulic and reactive parameters?
- Relationship between NOM content and aquifer reactivity?