# The Quest of the Bottleneck

## Controls of Bioreactive Transport in the Subsurface

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# Predicting Bioreactive Transport

In real aquifers a hopeless case?

- Spatial variability
- Temporal dynamics
- Interactions between transport & reactions
- Conceptually uncertain microbial behavior

⇨ Unifying theory about uncertainty and variability of „everything“ not attainable

…but also not necessary if primary controls of overall behavior are identified and addressed

# Microbiological Standpoint

„Most chemical transformations of contaminants in groundwater are catalyzed by microorganisms.“

⇨ Analyze how exactly the organisms do that:

- Which organisms are actually responsible?
- Degradation pathways?
- Genetic encoding? (molecular biology)
- How do the organisms interact in microbial communities?
- Which conditions are required by the microorganisms?
- How fast are they?
- …

# Counter-Standpoint by Systems Analysis

„If a chemical transformation yields energy, a microbial community catalyzing it will be established sooner or later.“

⇨ On the long run, microbial degradation is limited by abiotic processes.

⇨ These, rather than the microorganisms, determine the system behavior.

⇨ Search and analyze the bottlenecks!

# Control of Reactions by Mixing

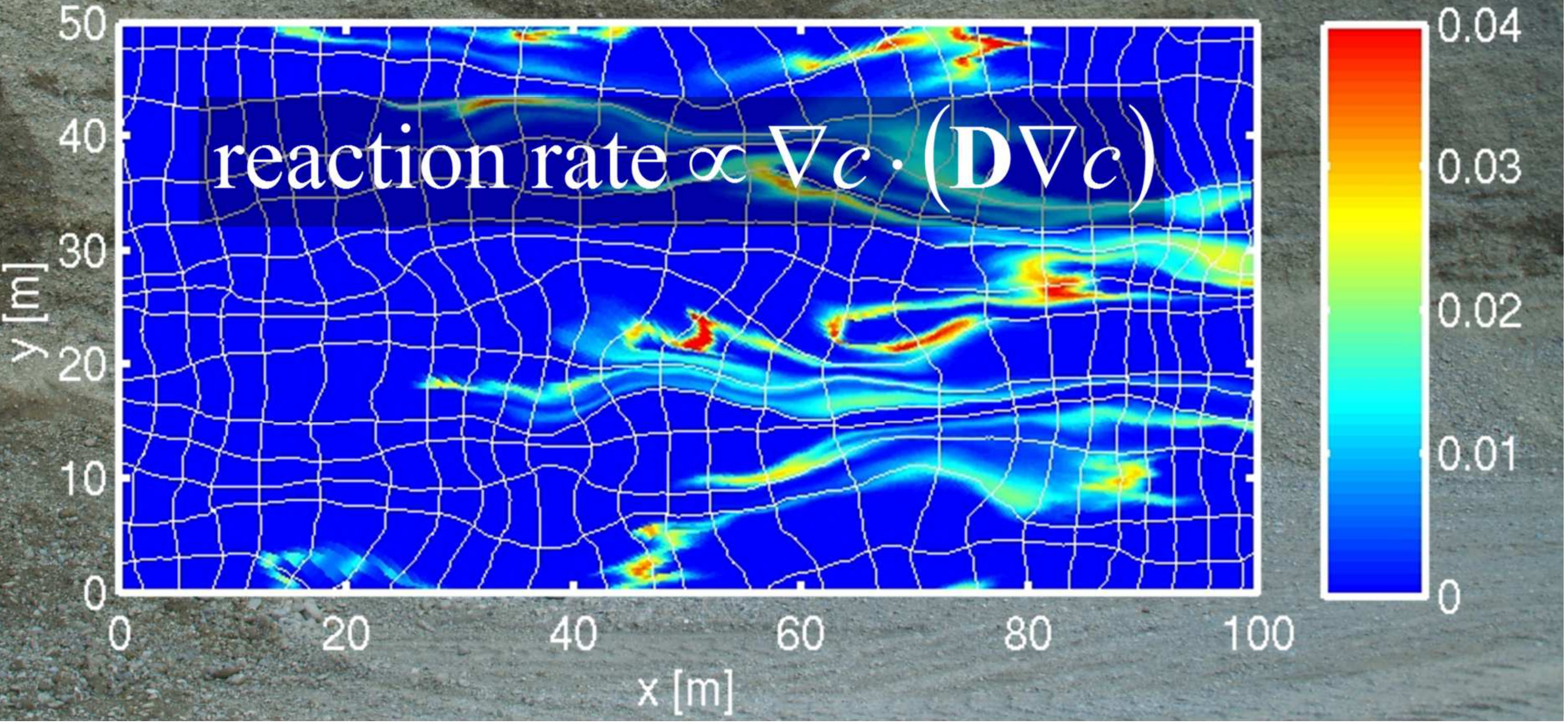
- Reactants (and microbes) must be at the same location at the same time

  (in individual pores!)
- Physical mixing in aquifers typically slower than the actual reaction ⇨ dominant control

  (Laws describing behavior of ensemble concentration don‘t describe mixing)
- Mixing in which direction?
- By which mechanism?

# Heterogeneity and Longitudinal Mixing

- Tremendeous progress made in recent years
  - Stretching and dilution of line sources
  - Balistic, (super)diffusive regimes of dilution
- What type of scenario does it reflect?



$$\text{reaction rate} \propto \nabla c \cdot (\mathbf{D} \nabla c)$$

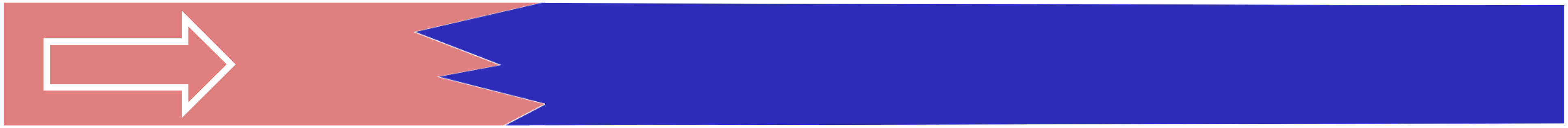
# Relevance of Dispersive Longitudinal Mixing in Bioreactive Transport

- Potential scenarios:
  - Cloud of one reactant surrounded by an ambient solution of the other reactant
  - Replacement of a solution, containing the first reactant, with a solution, containing the other ✓
- Bacteria must already be present at sufficient abundance (or grow very quickly) ✓

💣No sorption (differences) of the reactants

⇨Intriguing problem of limited practical relevance

# Longitudinal Mixing by Sorption

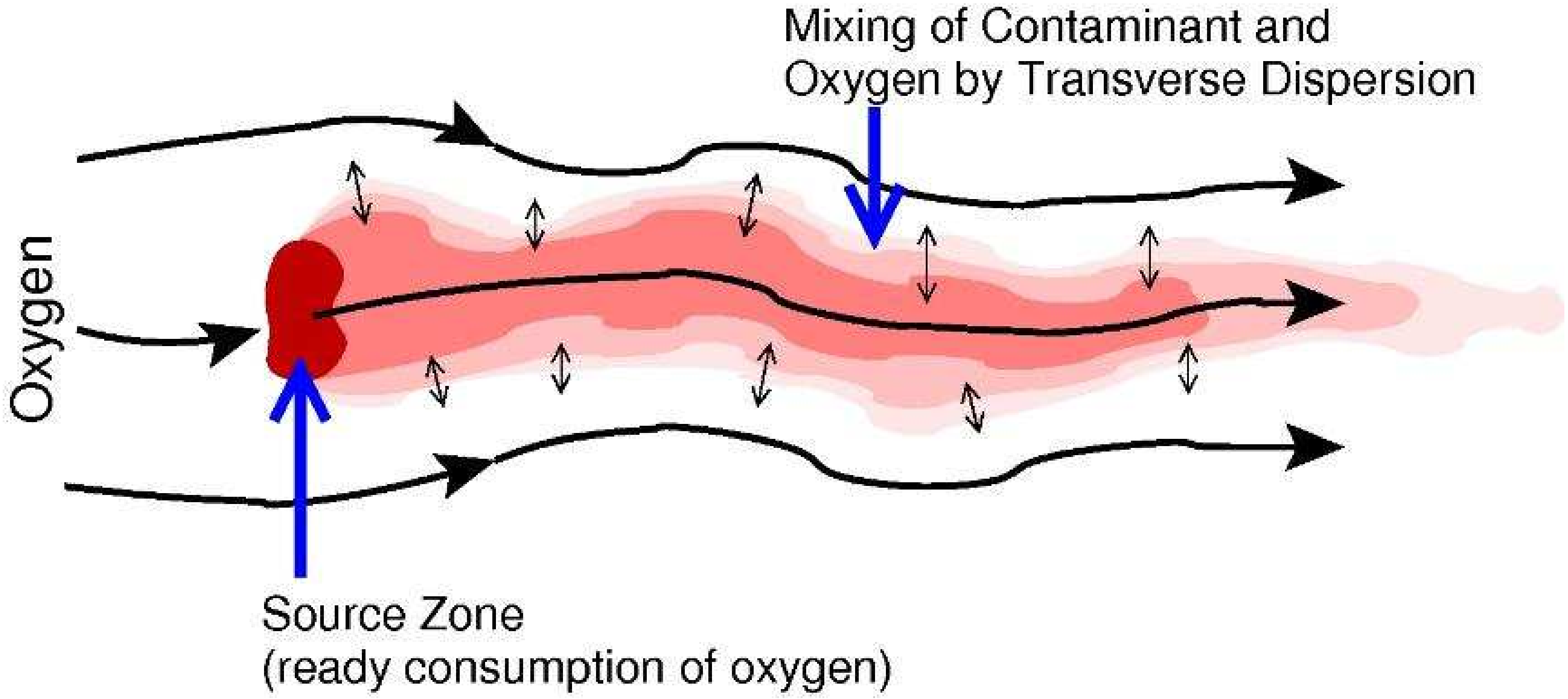


- Pink solution, containing the less sorbing reactant, replaces the blue solution, containing the more strongly sorbing one
- Classical application: oxygen-controlled biodegradation of petroleum-hydrocarbon compounds

⇨Chromatographic mixing with advective scaling
⇨Larger than dispersive mixing at late times

- Comparably simple laws for reaction fronts

# Plume-Fringe Concept



- Permanent input of a degradable contaminant
- Oxygen in the source zone limited, but present in ambient flow

⇨Late times: Reaction along the plume fringe, controlled by transverse dispersive mixing (not affected by sorption)

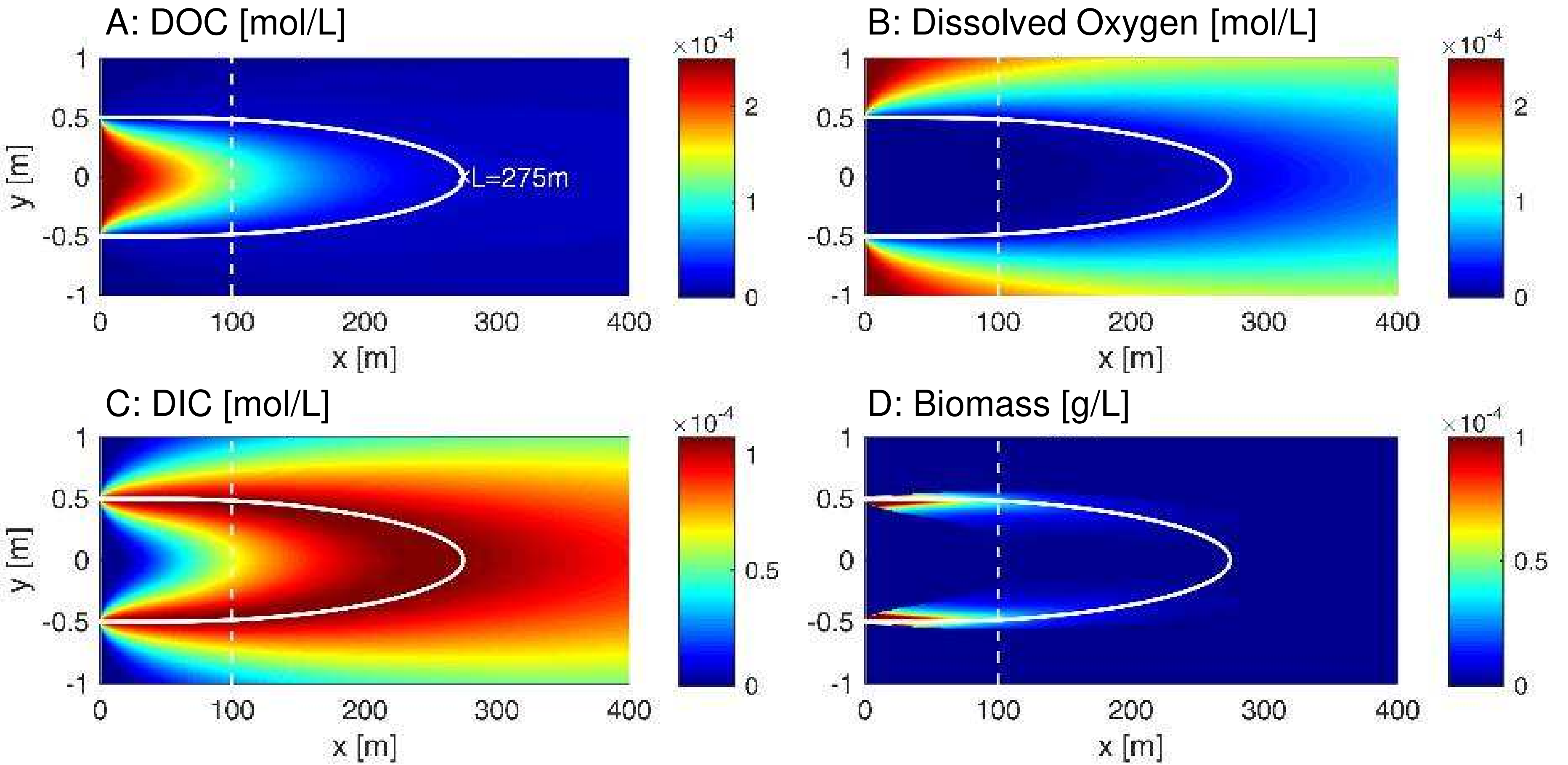
# Steady-State, Mixing-Controlled Plume

- Concentrations of reactive species depend on mixing ratio of plume-borne and ambient water.
- Mixing is provided by transverse dispersion.
- 2-D analytical solution: plume length is inversely proportional to transverse dispersivity

$$L = \frac{w^2}{16\left(\mathrm{inverf}\left(X_{crit}\right)\right)^2} \times \frac{v}{D_t}$$

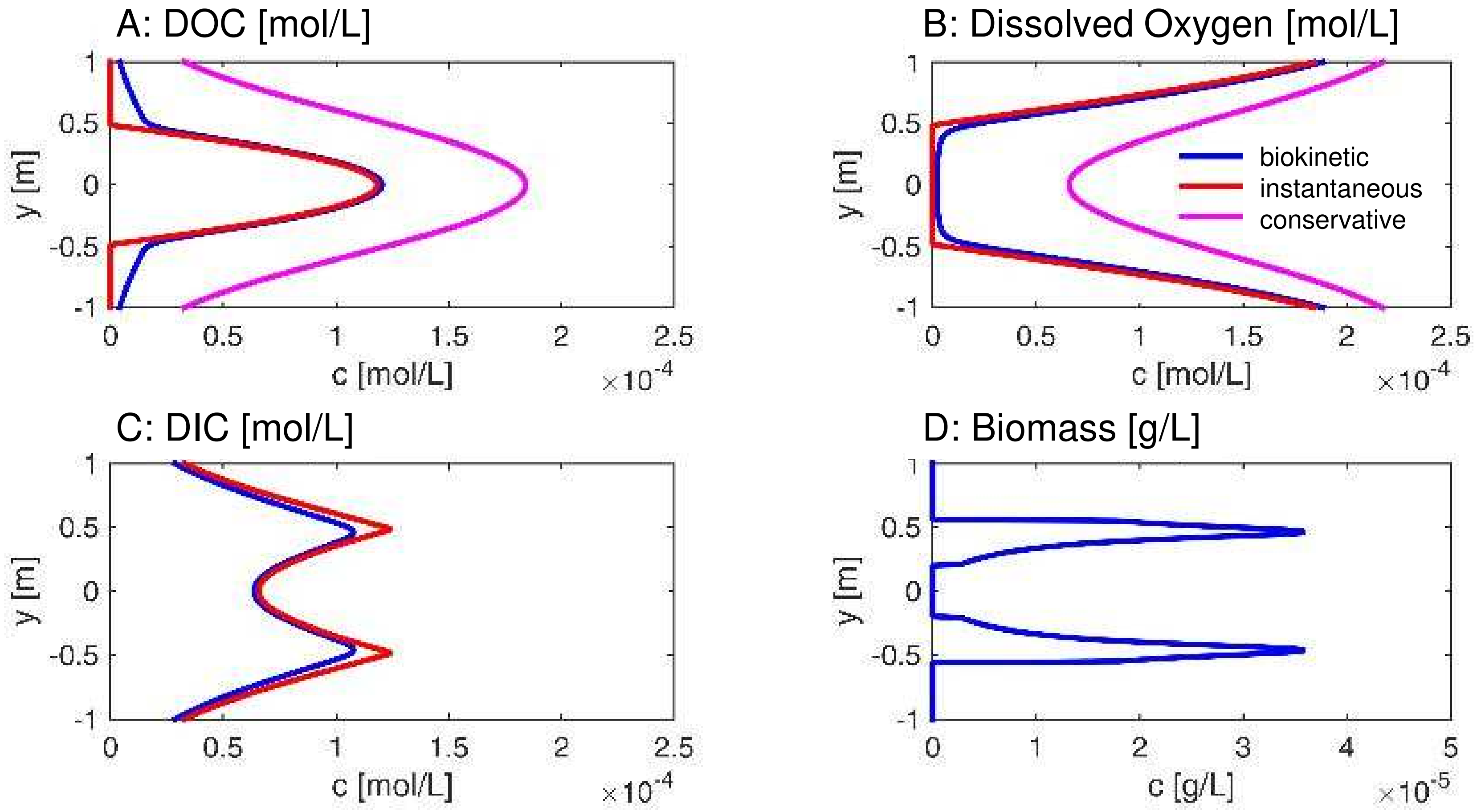
Cirpka et al., 2006

# Steady-State, Mixing-Controlled Plume: Planviews



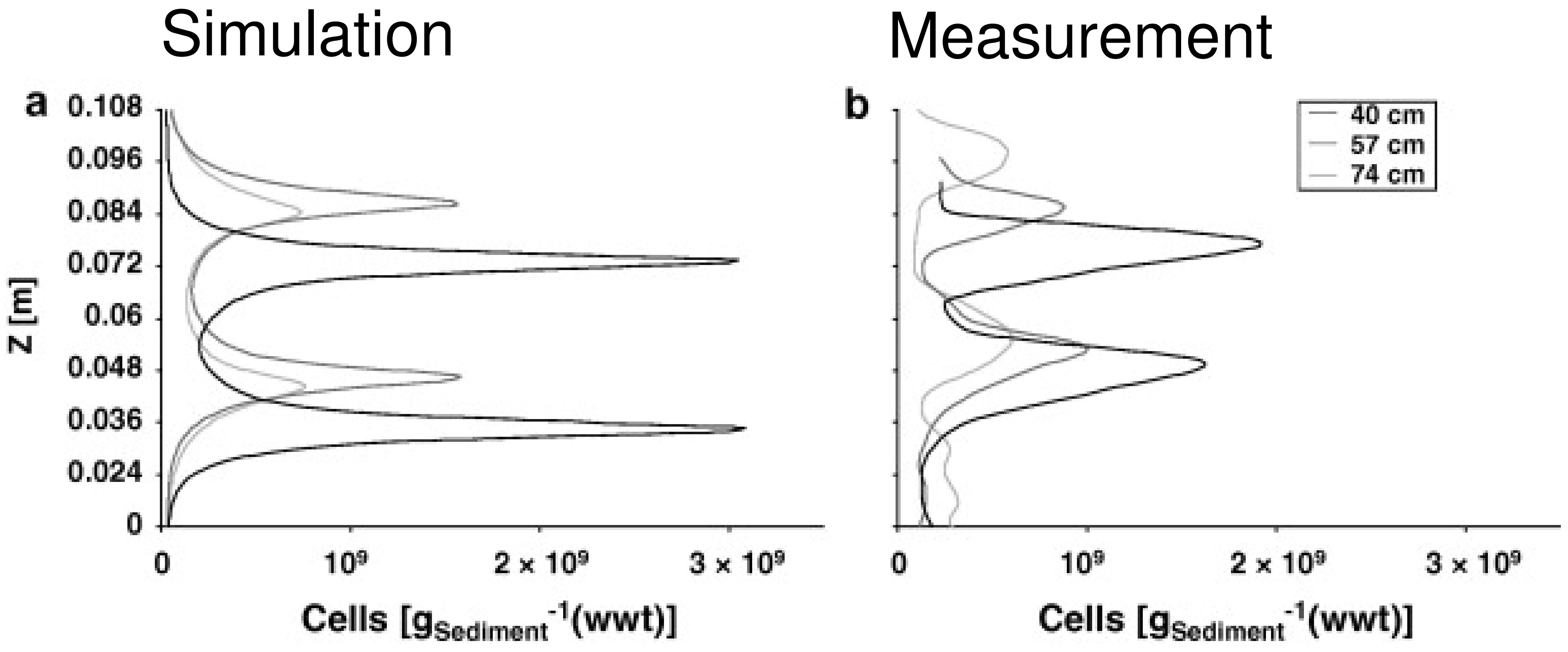
Cirpka & Valocchi, 2007, 2009

# Steady-State, Mixing-Controlled Plume: Vertical Profiles



Cirpka & Valocchi, 2007, 2009

# Accumulation of Biomass at the Fringe of a Steady-State, Mixing-Controlled Plume

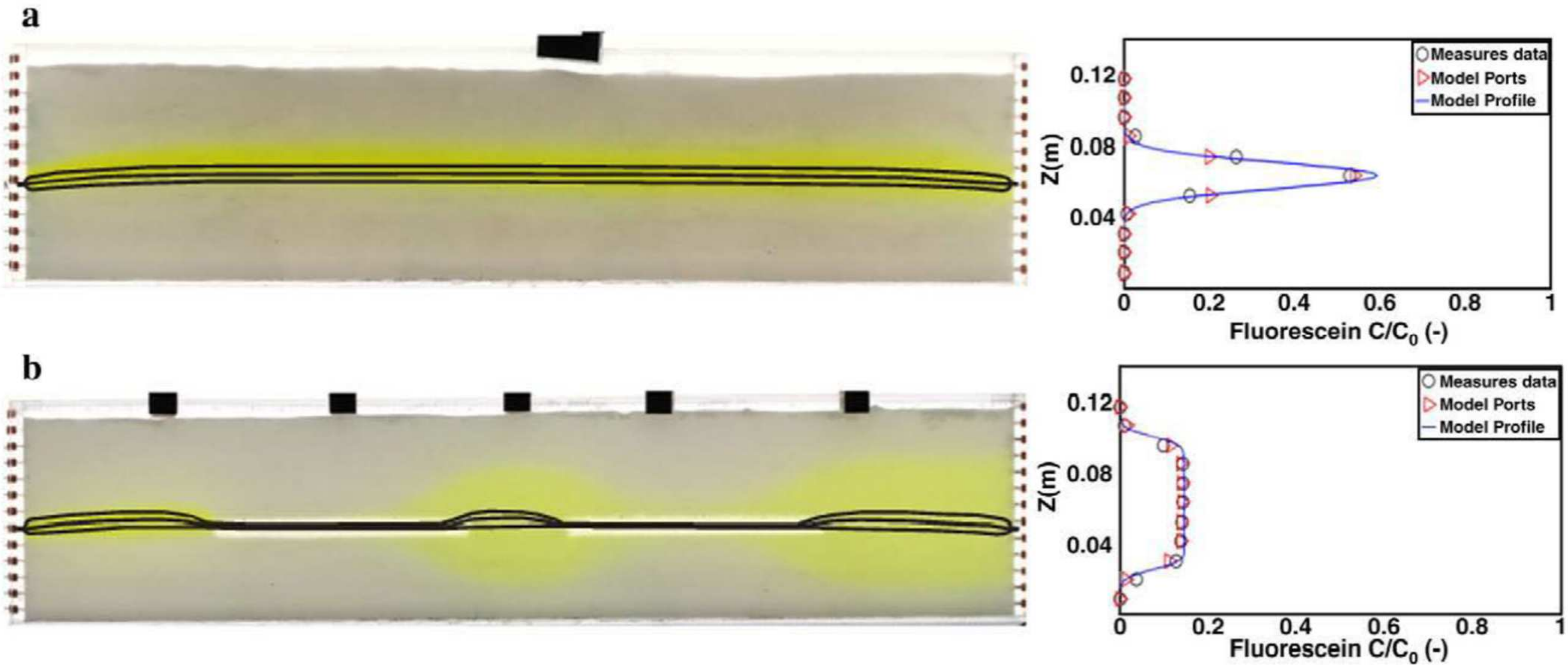


Simulation

Measurement

Bauer et al., 2009

# Effect of High-Conductivity Inclusions

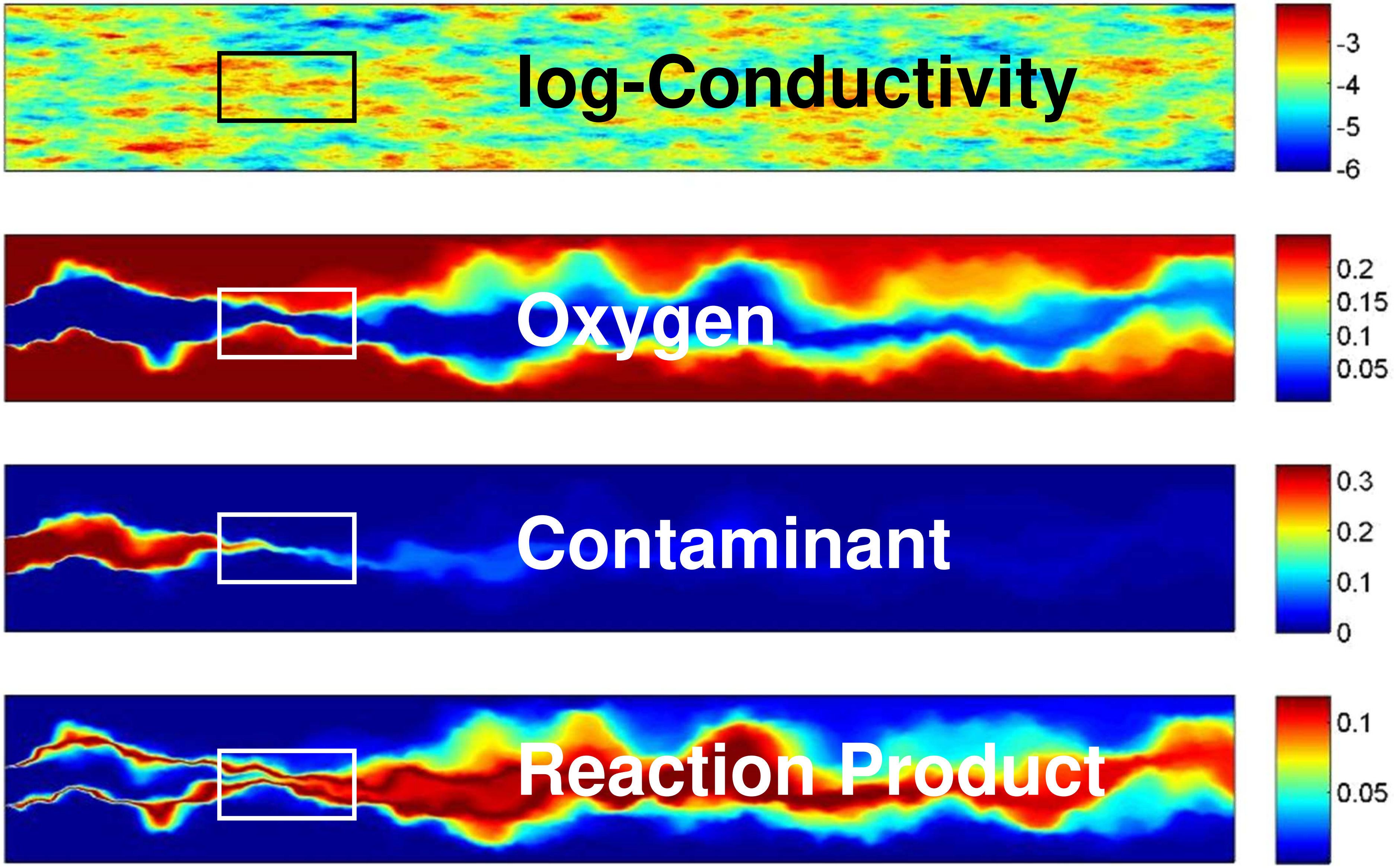


- High-conductivity inclusions squeeze the plume
- But they come out wider!

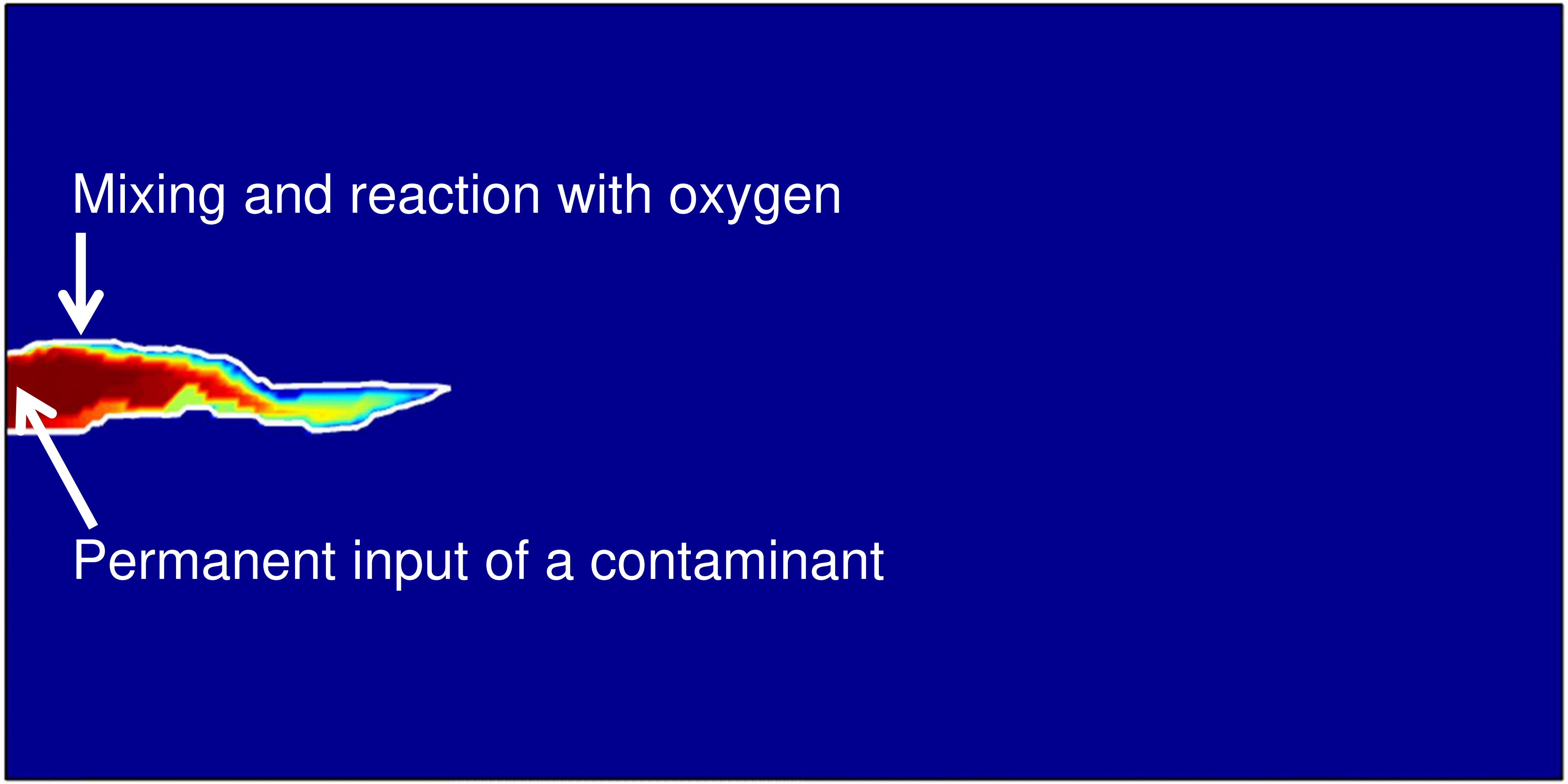
⇨ Enhanced transverse mixing!

Rolle et al., 2009

# Mixing-Controlled Steady-State Reactive Plume in a Heterogeneous Aquifer



# Contaminant Plume in Monte-Carlo Simulations



Mixing and reaction with oxygen

Permanent input of a contaminant

⇨ Uncertain length of contaminant plume

# You can do this analytically, too…

$$\xi_1^{\textcircled{I}} = \frac{\alpha_t}{\Theta}\left\langle \Delta\psi\Big|_{-W/2}^{W/2} \int_0^L K q_x \, dx \right\rangle - \frac{\alpha_t}{\Theta} K_G^2 J (1+\sigma_Y^2) L \underbrace{\left\langle \Delta\psi\Big|_{-W/2}^{+W/2} \right\rangle}_{\langle q_x \rangle W_{sz}}$$

$$= \frac{\alpha_t}{\Theta}\left\{ \left\langle \Delta\psi\Big|_{-W/s}^{W/s} \int_0^L K q_x \, dx \right\rangle - K_G^2 J (1+\sigma_Y^2) L \underset{\boxed{K_G J}}{\underset{\parallel}{\langle q_x \rangle}} W_{sz} \right\}$$

$$\xi_1^{\textcircled{I}} = \frac{\alpha_t}{\Theta}\left\{ \Gamma_1 - K_G^2 J L (1+\sigma_Y^2) W_{sz} K_G J \right\}$$

$$\xi_1^{\textcircled{I}} = \frac{\alpha_t}{\Theta}\left[ \Gamma_1 - K_G^3 J^2 L W_s (1+\sigma_Y^2) \right] \tag{18}$$

# Contaminant Plume in Monte-Carlo Simulations

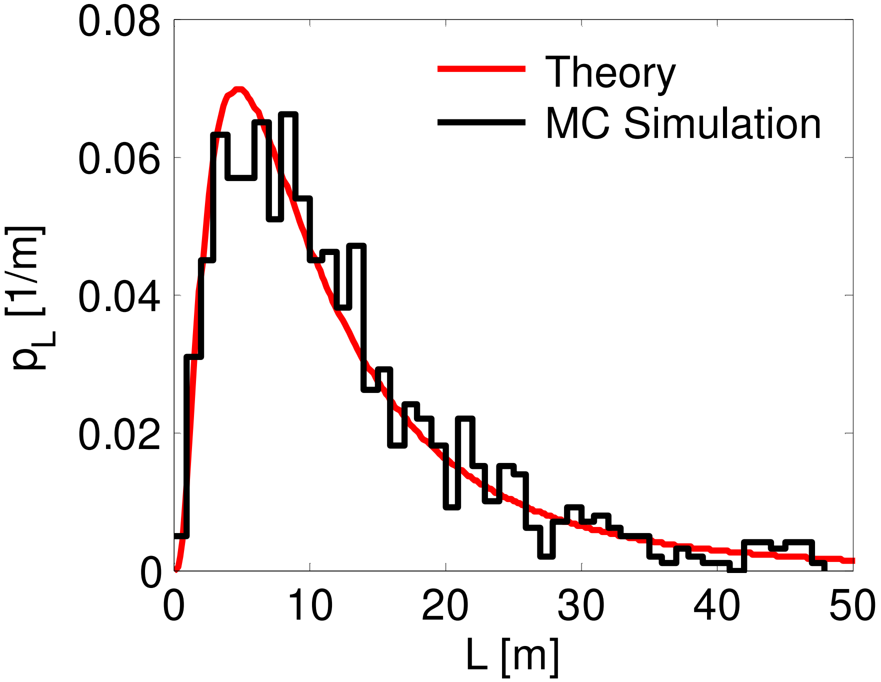
- Uncertain spatial variability

⇨ Uncertain discharge through the source zone

⇨ Uncertain length of contaminant plumes

- Predictable uncertainty…

…which is horribly high.

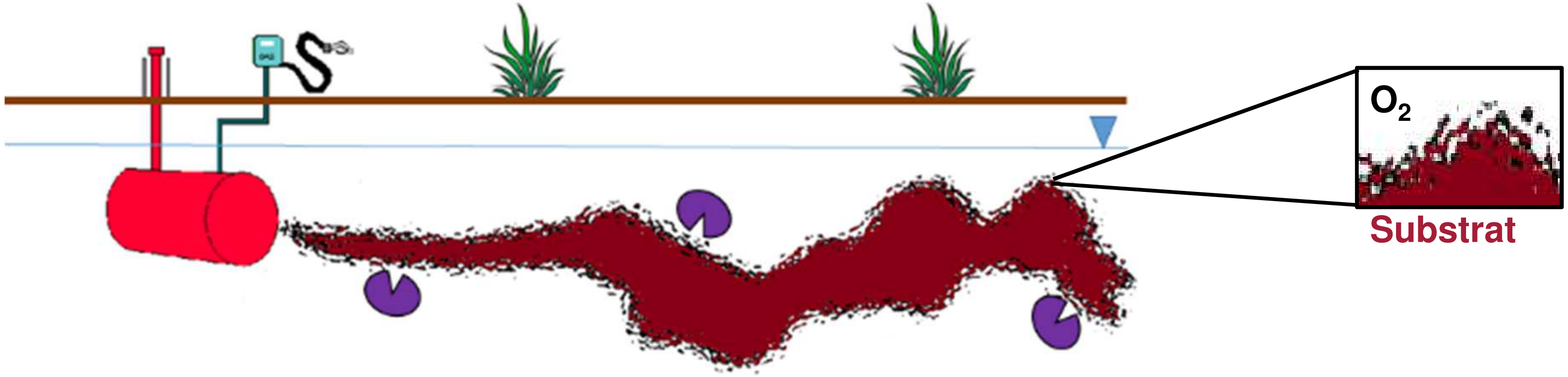


Cirpka et al., 2011, 2012

# Intermediate Conclusions

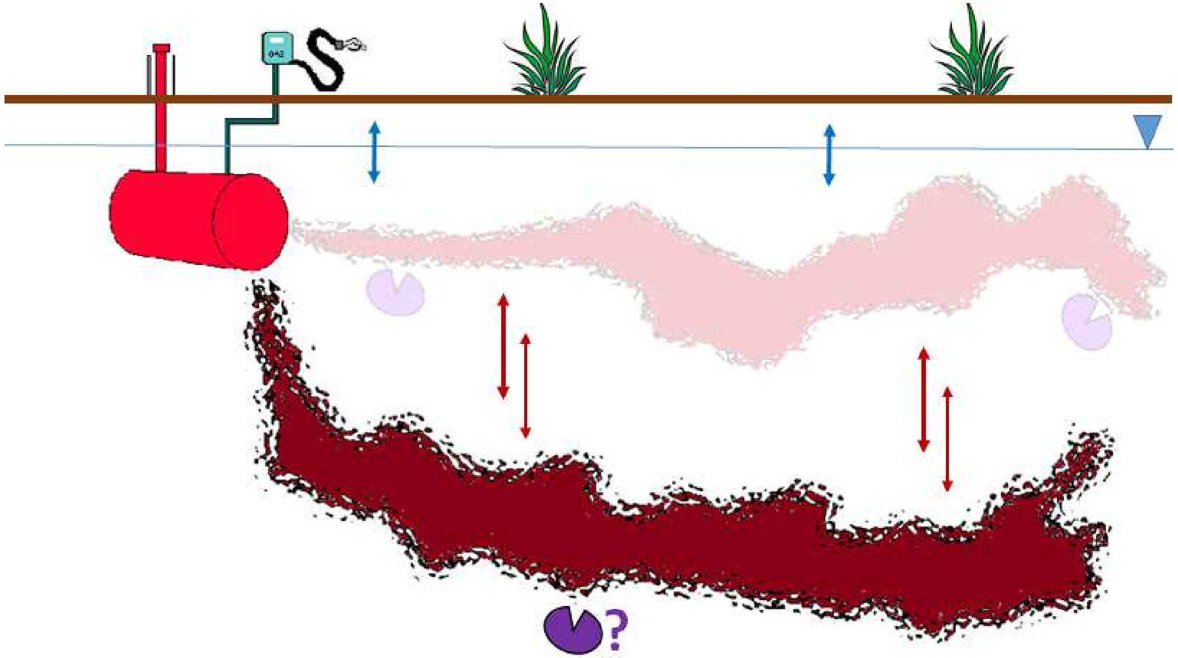
- In steady-state plumes, the degradation of contaminants is limited by insufficient mixing of the reactants.
- Microbial kinetics determine only how long it takes to reach the steady state.
- Spatial variability of hydraulic conductivity causes slight enhancement of mixing and tremendous uncertainty.

# Moving Plumes caused by Dynamic Groundwater Flow



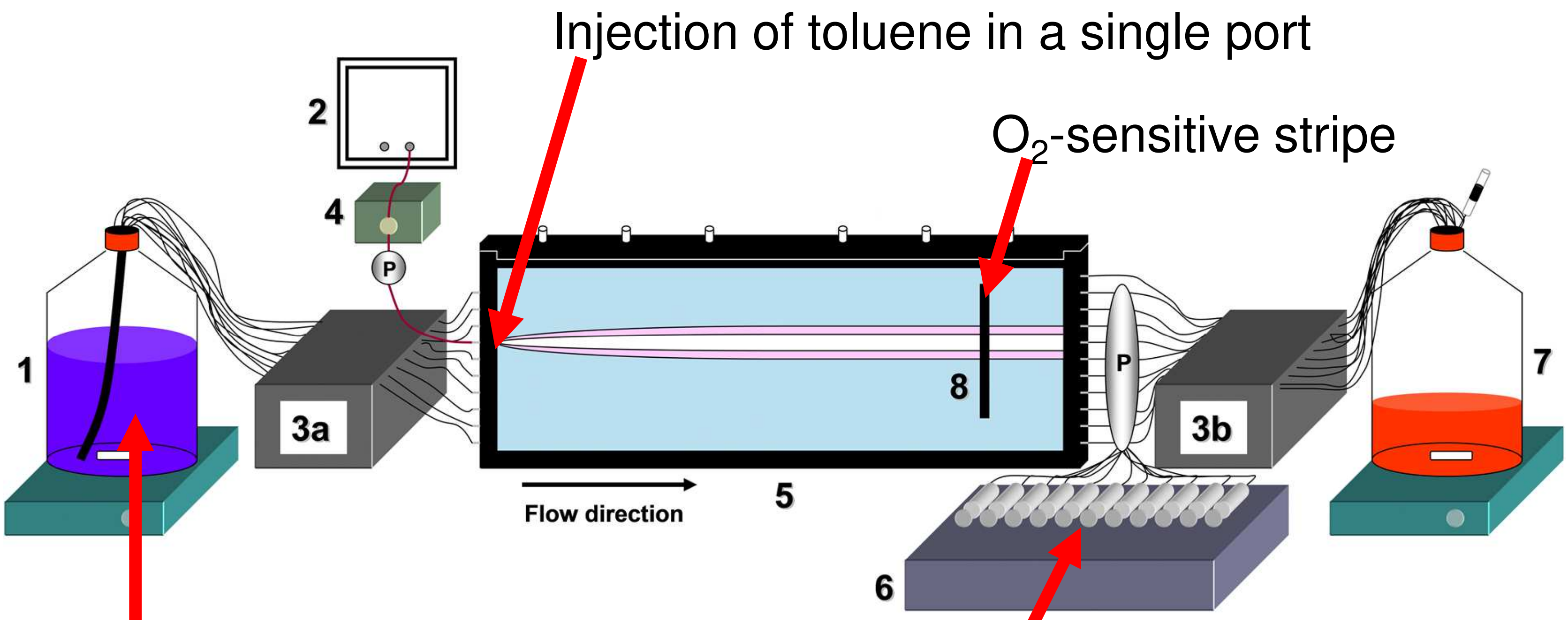
- Biomass accumulates at plume fringe.

# Moving Plumes caused by Dynamic Groundwater Flow



- Biomass accumulates at plume fringe.
- When the plume moves, the sessile bacteria are at the wrong place.
- Does this control the overall degradation?

# 2-D Sandbox Experiment

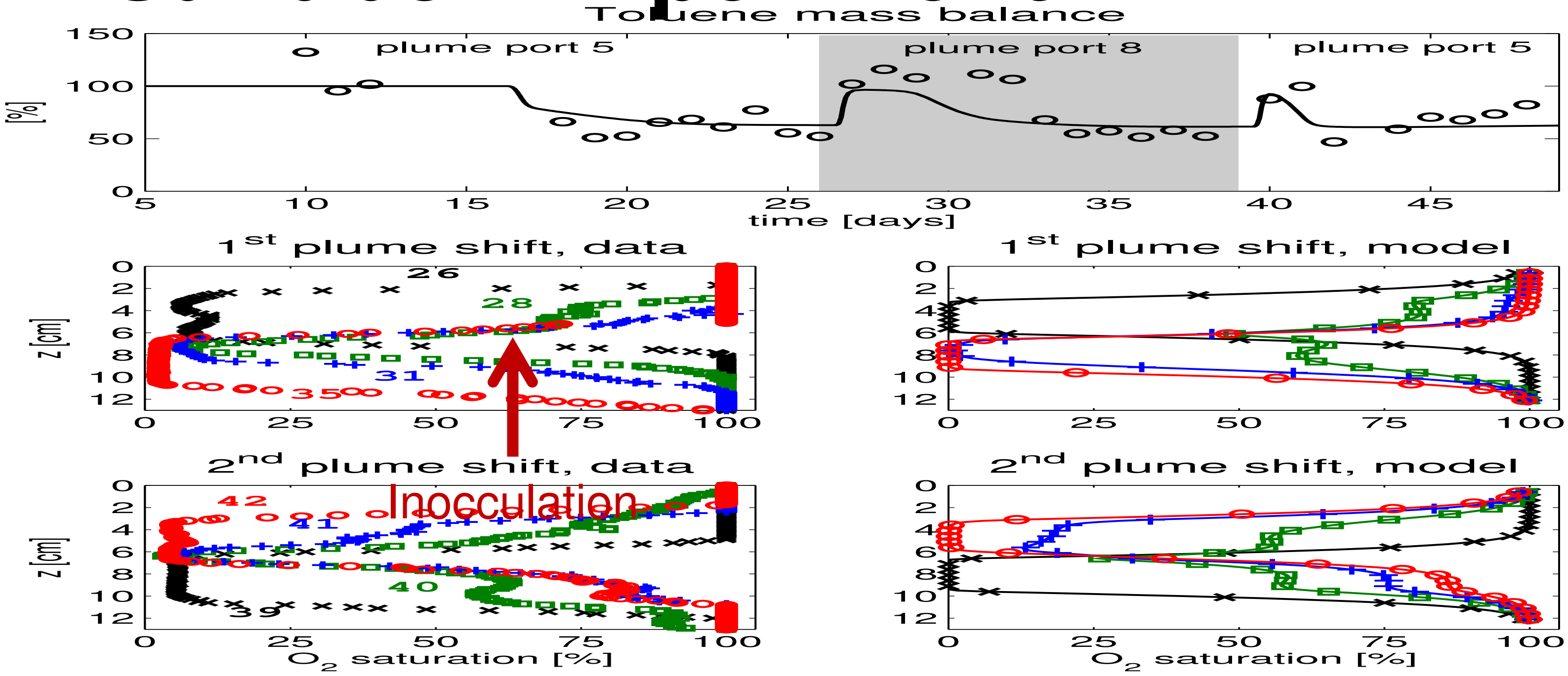


Injection of toluene in a single port

$O_2$-sensitive stripe

- Inocculation with *Pseudomonas putida* F1 on day 16
- Shift of toluene port on day 26
- Shift back on day 39

# 2-D Sandbox Experiment



- After inoculation, recovery of toluene drops.
- After shift of plume, toluene comes back until biomass is established at the new fringe.
- After the backward shift, the disturbance is shorter.

⇨ Cells can cope with hunger periods.

Eckert et al., 2015

# Insights of Experiments and their Modeling

- Required components in modeling the dynamics of the biomass:
  - biomass growth
  - biomass decay
  - endogeneous respiration (living on internal reserves)
  - transport of microorganisms
  - attachment and detachment of biomass
  - maximum density of attached cells (carrying capacity)
  - dormancy = „sleeper cells“ (under bad conditions, „cells fall asleep“ and can be reactivated upon improvement of conditions)

# How Important is Dormancy?

- Dormant cells require less maintenance energy in hunger periods.
- Rapid reactivation of contaminant degradation after the end of hunger periods

☞ Bactera can cope with dynamic environmental conditions.

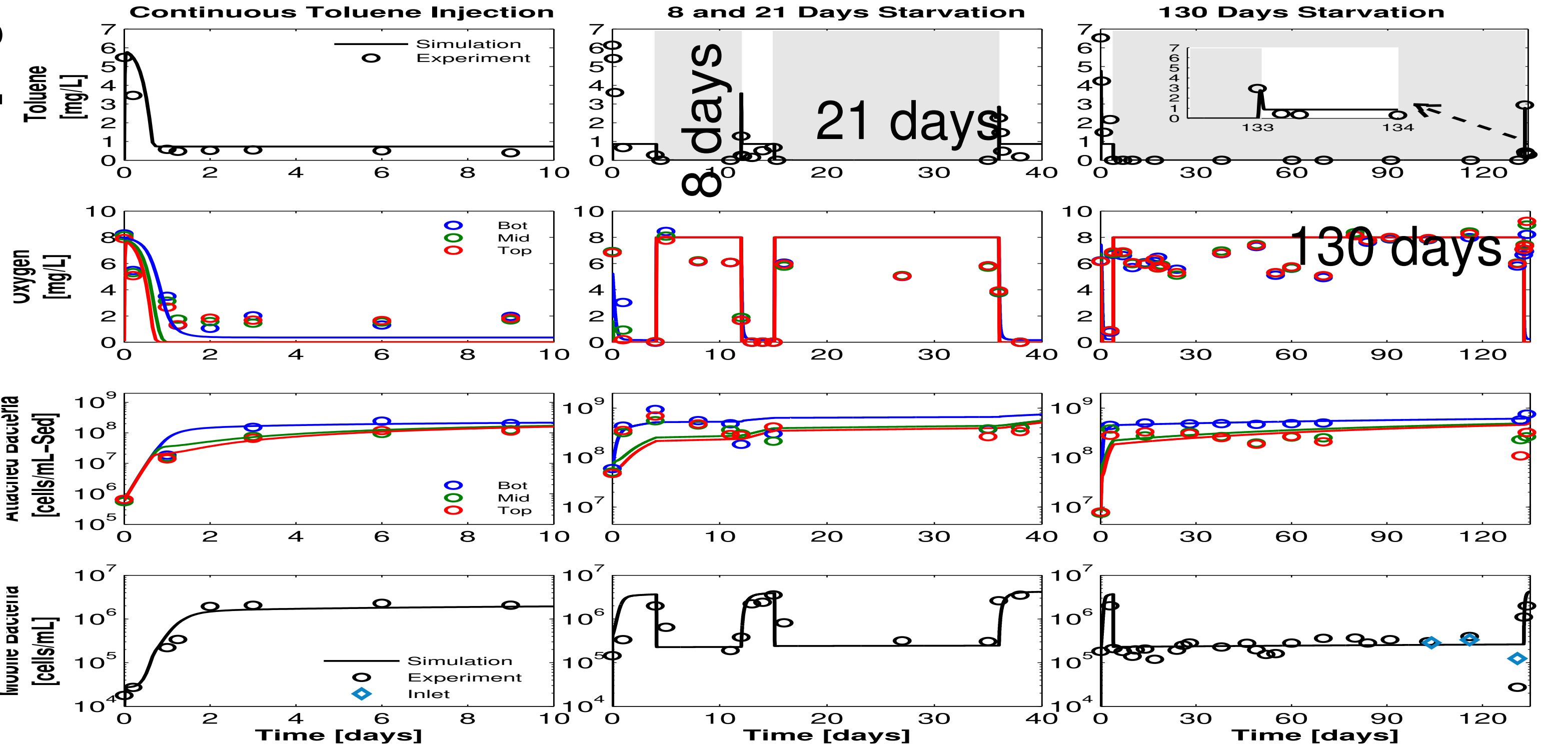
☝ Microbial community needs to be established only once. Later, it can always be reactivated.

# „Hunger Games“ in Mini-Columns (1.6cm)

Continuous Injection Short Hunger Phase Long Hunger Phase

Toluene [mg/L]

$O_2$ [mg/L]



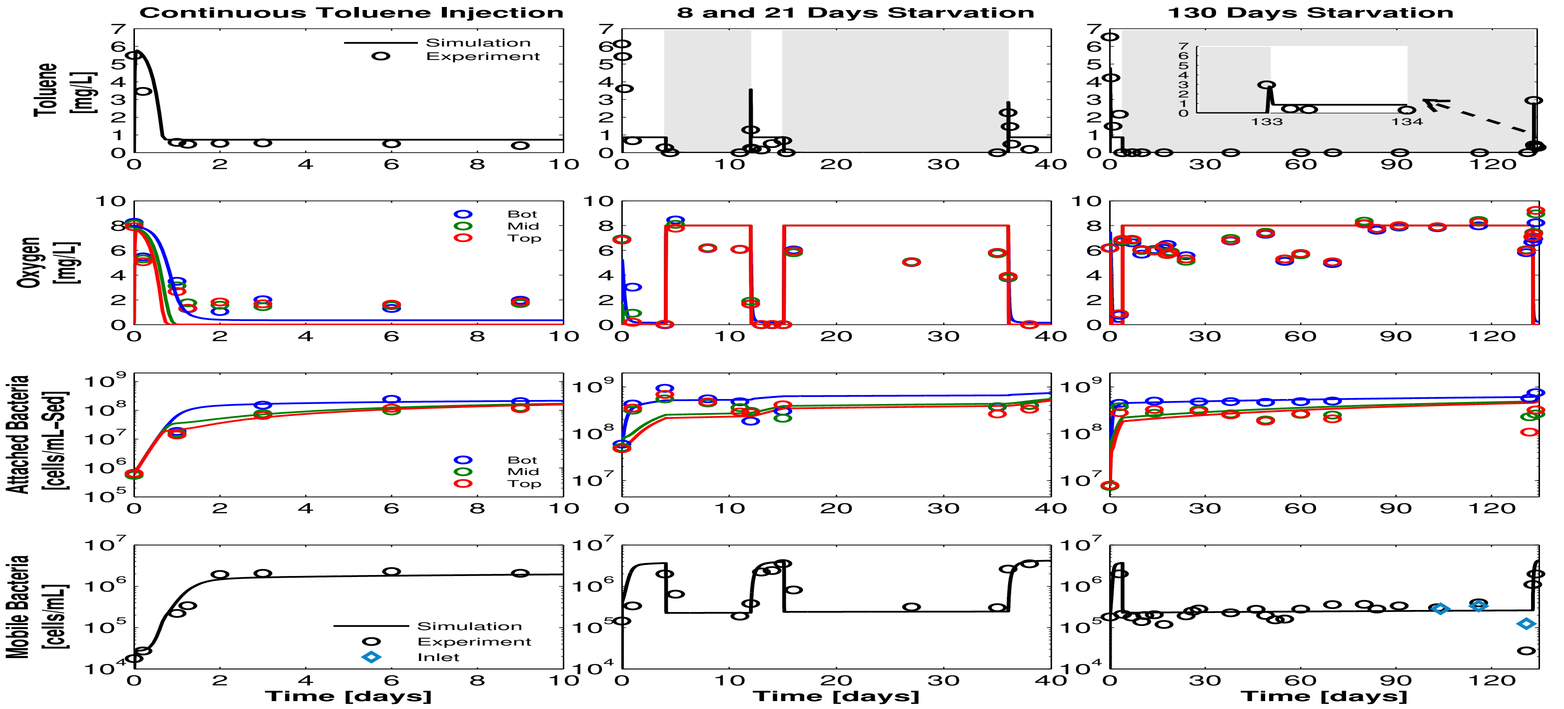
Time (days) Time (days) Time (days)

- Even after 130 days of hunger, the bacteria were reactivated within hours.

Mellage et al., 2015

# „Hunger Games“ in Mini-Columns (1.6cm)

Continuous Injection Short Hunger Phase Long Hunger Phase



Time (days) Time (days) Time (days)

- Attached cells hardly disappear in hunger phases.
- Mobile cells occur only in growth phases.

# Next Set of Conclusions

- Microbial kinetics are horribly complicated…

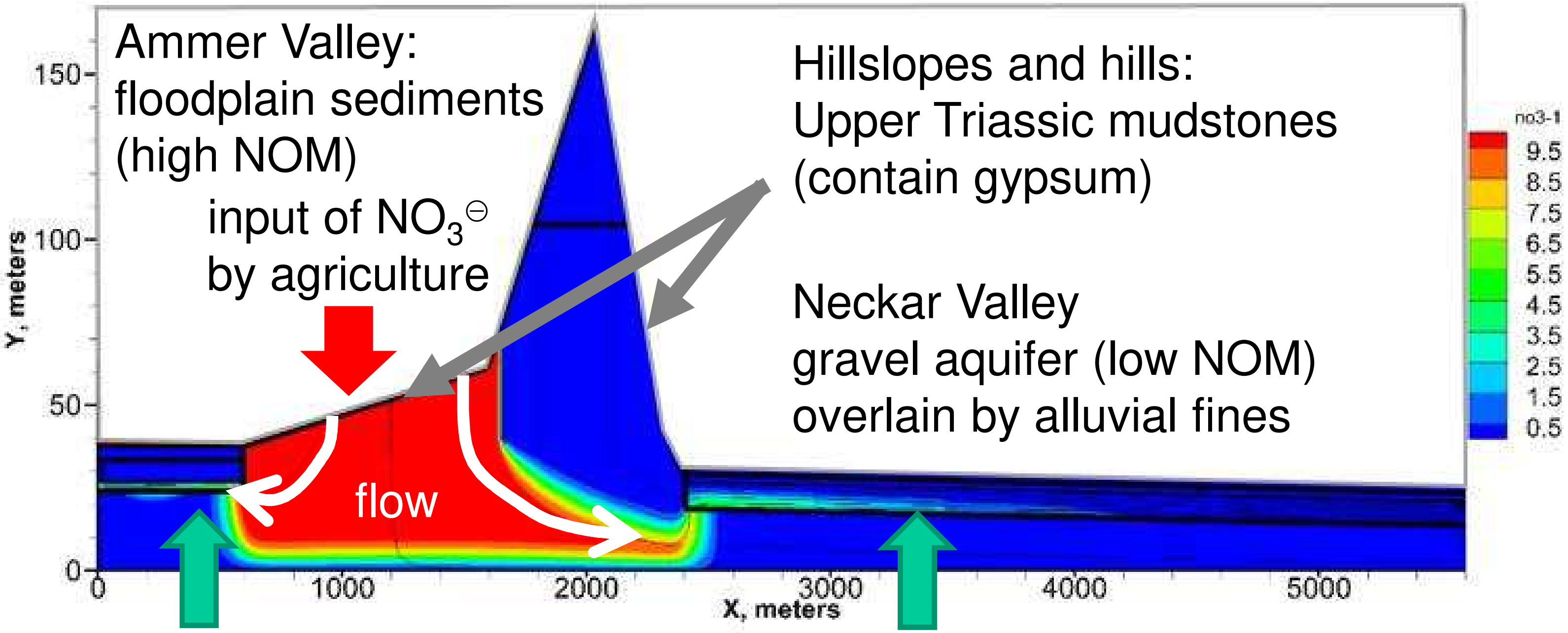
…but often irrelevant for system behavior.

- A microbial community that was established in the past can rapidly be reactivated in the future.
- At the first occurrence of a contaminant, biomass growth controls degradation,…

…until abiotic processes become limiting.

# ATale of Two Valleys

## Fate of Nitrate in a 2-D Vertical Cross-Section Connecting Two Valleys



Ammer Valley:
floodplain sediments
(high NOM)

input of $NO_3^{\ominus}$
by agriculture

Hillslopes and hills:
Upper Triassic mudstones
(contain gypsum)

Neckar Valley
gravel aquifer (low NOM)
overlain by alluvial fines

Denitrification as soon as nitrate reaches NOM-rich sediments

- ⇨ Controlled by e-donor release
- ⇨ May be modelled by the approach discussed in the lecture

Denitrification upon mixing with DOC-rich water from recharge

- ⇨ Controlled by vertical dispersion (discussed in previous slides)
- ⇨ Requires 2-D model

(Evgenii Kortunov)

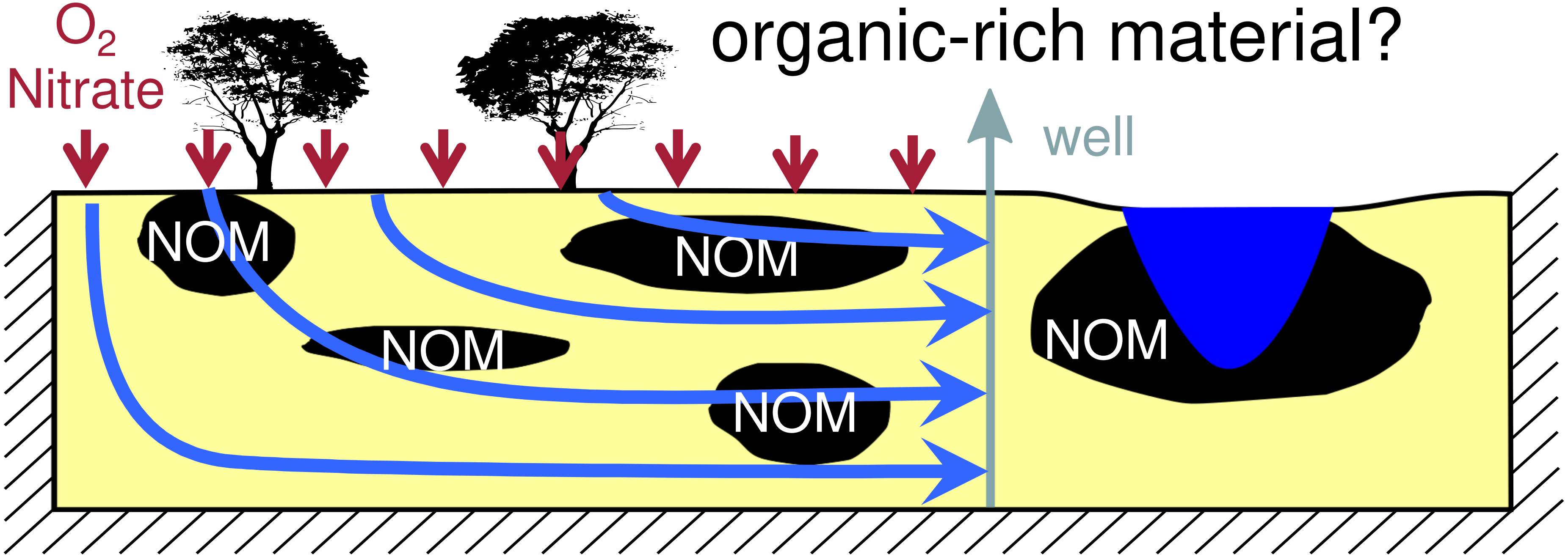
# Control by Inter-Phase Mass Transfer

- Reactions between immobile and mobile phases in the plume core or at an invading front:
  - Dissolution of NAPLs
  - Release of e-donors (DOC from NOM, ferrous iron/sulfide from pyrite,…)
  - Release of e-acceptors (ferric iron from iron (hydr)oxides, sulfate from gypsum,…)

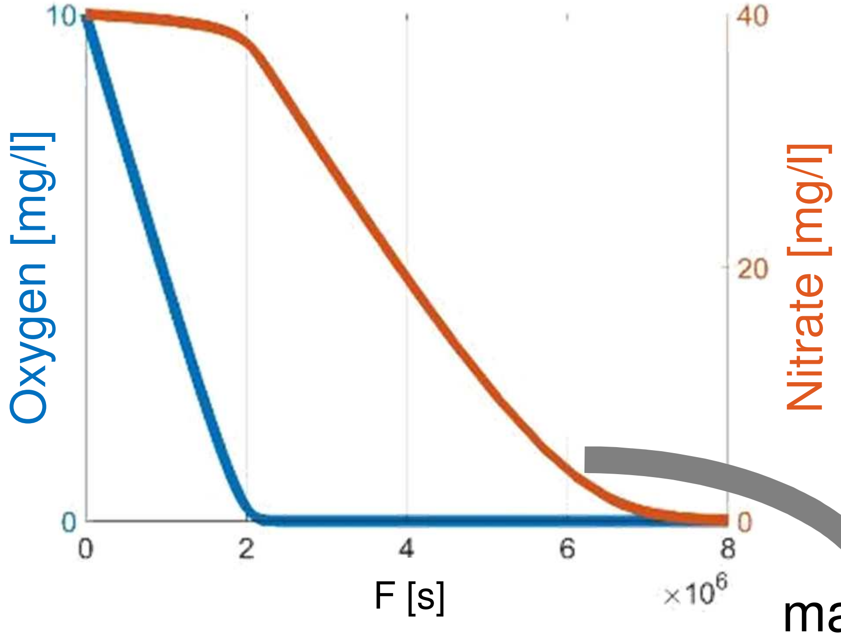
☝ Macroscopic dispersive mixing irrelevant

# Reactions Controlled by Release from the Matrix

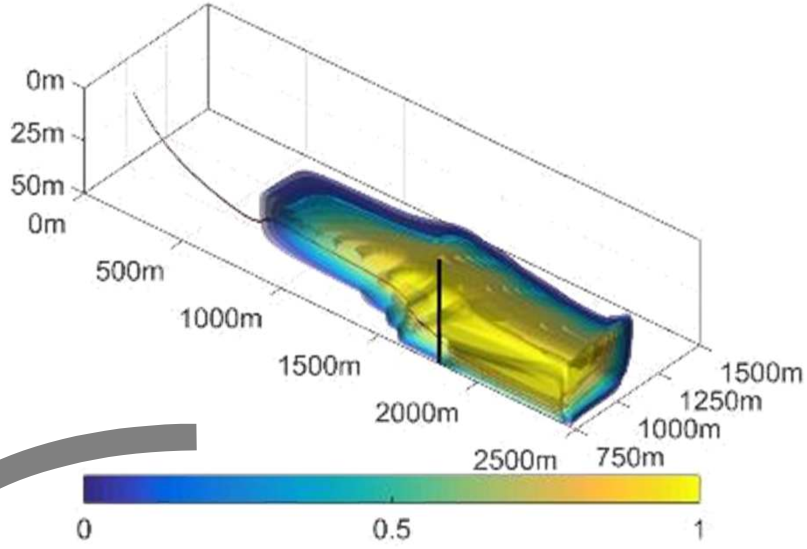
- Nitrate and oxygen introduced by recharge
- DOC released from organic-rich sediments
- Decisive: How long has a water parcel seen organic-rich material?



## Concentrations as Function of Cumulative Relative Reactivity

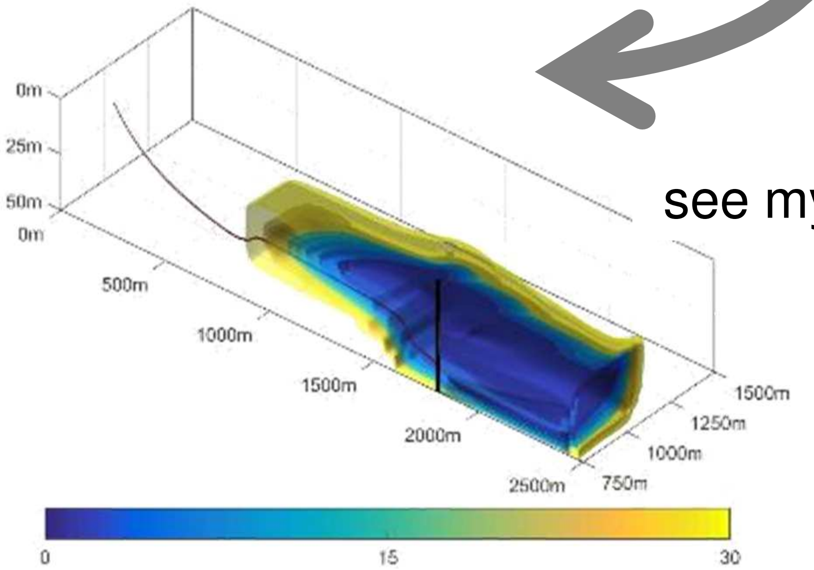


## Spatial Distribution of Cumulative Relative Reactivity



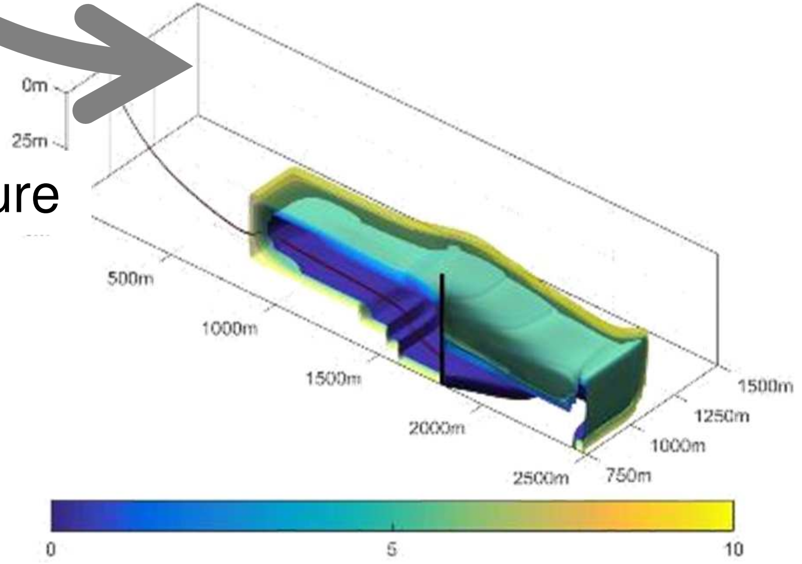
mapping

## Spatial Distribution of Nitrate



## Spatial Distribution of Oxygen

see my lecture

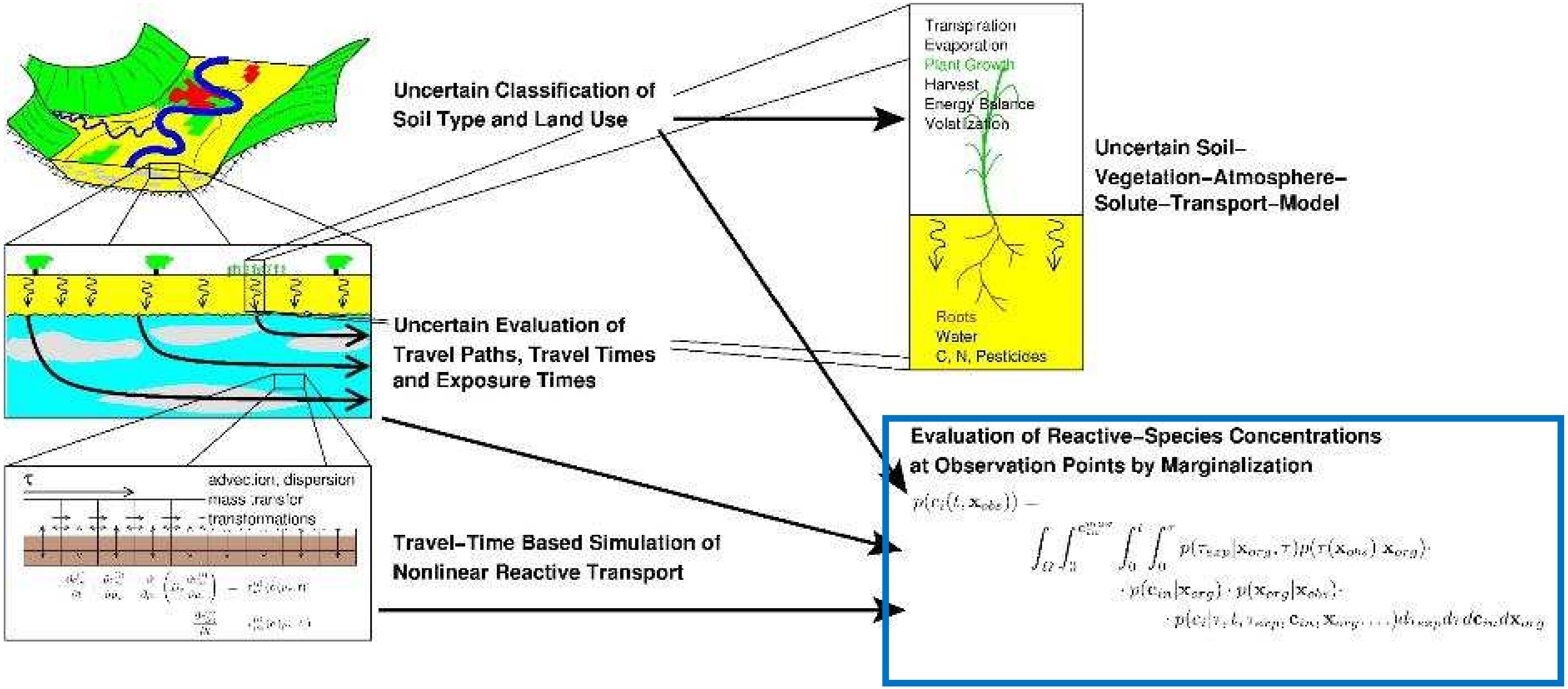


# CRC CAMPOS: Catchment-Scale Stochastic Modeling Framework

- Classification of the land-surface
- 1-D land-surface models for each class
- 3-D classification of subsurface units
- 3-D groundwater flow model & particle tracker
- Reactive transport with cumul. relative reactivity

- mechanistic
- yet efficient

⇨ allows ensemble-based calibration & uncertainty analysis



$$p(c_i(t, \mathbf{x}_{obs})) = \int_\Omega \int_0^{c_{in}^{max}} \int_0^t \int_0^\tau p(\tau_{exp} | \mathbf{x}_{org}, \tau) p(\tau(\mathbf{x}_{obs}) | \mathbf{x}_{org}) \cdot p(\mathbf{c}_{in} | \mathbf{x}_{org}) \cdot p(\mathbf{x}_{org} | \mathbf{x}_{obs}) \cdot p(c_i | \tau, t, \tau_{exp}, \mathbf{c}_{in}, \mathbf{x}_{org}, \ldots) d\tau_{exp} d\tau d\mathbf{c}_{in} d\mathbf{x}_{org}$$

# Is Microbially Mediated Solute Transport Exclusively Controlled by Abiotic Processes?

- The examples were based on the assumption, that the solute transformations facilitate microbial growth.
- Contaminant hydrogeologists are biased, because they love contaminant plumes:
  - High concentrations of pollutants = stacked buffet for specialized bacteria

(Also most microbiologists love to study turnover under growth conditions)

☹Natural turnover often at the energetic limit

# Control by Microbial Dynamics

Microbial dynamics are rate limiting when …

- a new community must be established (first-time exposure to a reactant) …

& little energy is to be gained by the reaction.

⇔ In comparison, reactivation of dormant bacteria is quick.

- What if there is no obvious benefit for the organisms?

…or if the capabilities of the degraders lack important factors?

# Degradation of Micropollutants

- Pharmaceuticals, artificial sweeteners, personal care products etc. occur in ng/L concentrations in the environment
- There is no way that organisms can live on degrading exclusively these compounds
- Why are they sometimes degraded and sometimes not?

# Degradation of Micropollutants

- Some micropollutants are better degraded when there is less „good food“ around
- Potential mechanism: Organisms activate all pathways when they are hungry

  (like spoiled kids eating even vegetables when there is defnitely no icecream available)

…They do this even with pathways that currently don‘t gain enough energy

(just to be ready for anything passing by)

# Degradation of Micropollutants

- Alternative mechanism: Degradation of micropollutants depend on structurally similar substrates from which they can gain energy („cometabolism“)
- Has been used in the stimulation of aerobic TCE degradation by adding aromatic compounds or isoprene as primary substrates

Suitable modeling framework = research topic

# Presumably Wise Words of an Old Man

- The behavior of contaminants in the environment is
  - neither pure chemistry
  - nor pure microbiology
  - nor pure physics

Transformation!

Bio-Degradation!

Transport!

- System = Interplay of processes!

# Personal Advice of the Old Geezer

- Perform a (preliminary) system analysis of reactive transport in each application
- Identify the bottleneck in the specific situation
- Be accurate in the prediction of the controling factor!
- You may introduce simplifications of the non-controling processes
- Mind your professor‘s personal pet problem

# Acknowledgements

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## Bioreactive Transport Experiments:

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