Reach-scale modeling of reaction cascades and spatially-dependent reactions in the hyporheic zone

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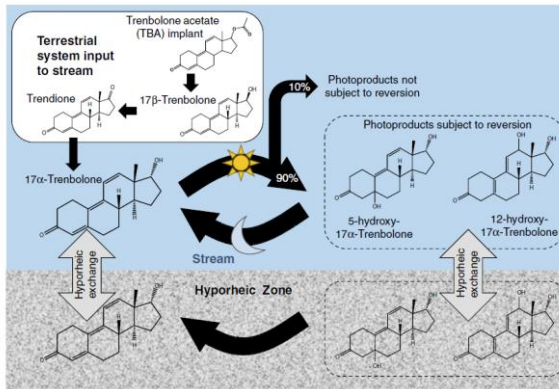
D522 | EGU2020-6057

May 5, 2020

HS10.7 Groundwater - Surface Water Interactions: Physical, Biogeochemical and Ecological processes, EGU General Assembly, 2020
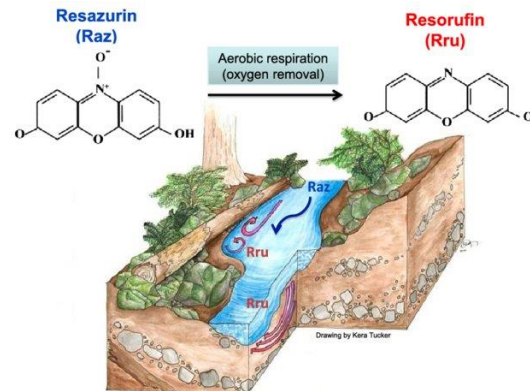
Background

Many reactions in natural systems occur in cascades, wherein the products of one reaction are the reactants of a subsequent one.
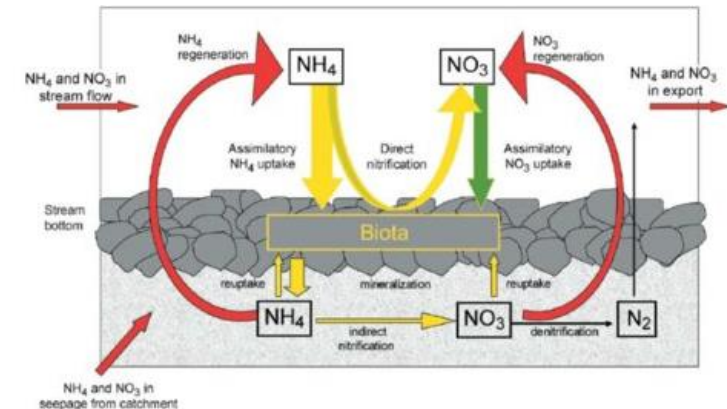
Pharmaceuticals

Ward et al., 2015

Tracers

González-Pinzón et al., 2012

Redox Reactions

Wymore et al., 2019

Modeling reaction cascades: haves & needs

- We *have* a general analytical framework for describing...
  - In-stream mass transport coupled with hyporheic exchange, under reasonable assumptions (e.g., separation of velocity scales between the stream and the hyporheic zone).
  - Independent, first-order degradation reactions for *one* constituent in the mobile and/or immobile zones.
  - Ability to model parent-to-daughter cascade reactions under some assumptions about immobile-zone residence times (e.g., Knapp et al., 2018 *WRR*).

- We *need* a general analytical framework for describing...
  - Zone-specific reaction cascades in a stream with an *arbitrary* residence time distribution
  - Reactions that vary spatially in the hyporheic zone, as is observed in the field.

Ideally, this framework will allow us to describe the evolution of solute concentrations, making it applicable to field experiments (e.g., breakthrough curves).

A generalized model framework

We address these needs by…

Point 1: generalizing existing mobile-immobile models to account for a cascade of first-order reactions (e.g., A → B, B → C, etc.)

Point 2: demonstrating model fidelity to physical parameters by comparing to Lagrangian particle tracking simulations

Point 3: identifying conditions under which a spatially varying reaction profile can be described with an effective (constant) reaction rate in the hyporheic zone

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Point 1: A generalized model framework

The model takes a familiar form of a generalized advection-dispersion-reaction equation, describing the mobile concentration of constituent *j*.
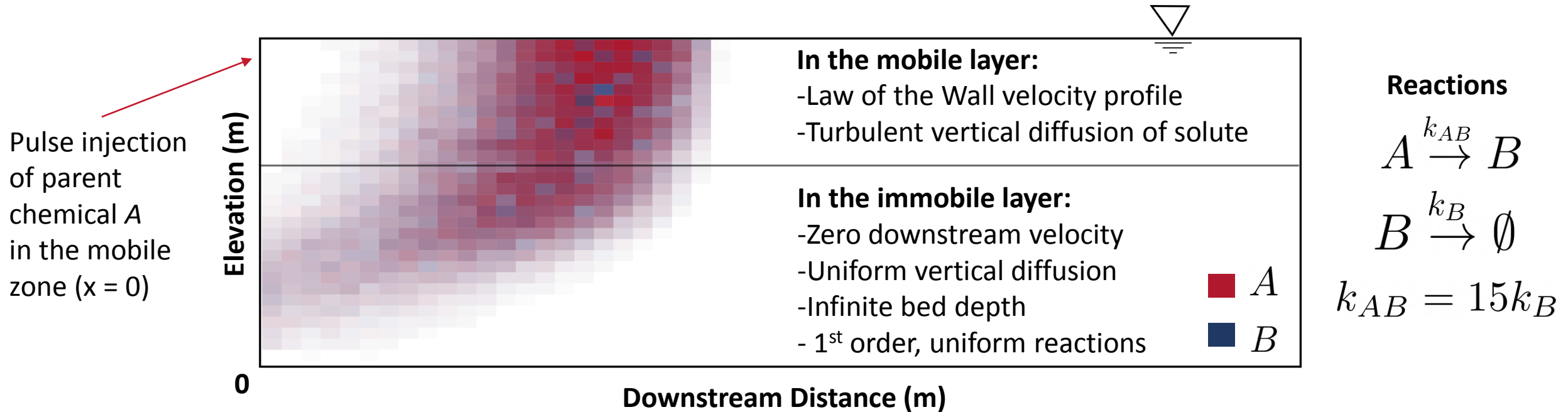
$$\frac{d}{dt}C_{m,j} + f_{im,j} = A_m C_{m,j} - R_m C_{m,j}$$

Immobile zone forcing of chemical constituent *j*, **which accounts for the time history of mass retention in the immobile zone** *and* **the time history of constituent *j* creation via reaction of its parent.**

Spatial operator, describing advection and dispersion in the mobile zone.

Mobile-zone reactions, if applicable (not used in this presentation)

Point 2: Validation using particle tracking simulations

Pulse injection of parent chemical A in the mobile zone (x = 0)

In the mobile layer:
-Law of the Wall velocity profile
-Turbulent vertical diffusion of solute

In the immobile layer:
-Zero downstream velocity
-Uniform vertical diffusion
-Infinite bed depth
- 1st order, uniform reactions

Reactions

$$A \overset{k_{AB}}{\rightarrow} B$$

$$B \overset{k_B}{\rightarrow} \emptyset$$

$$k_{AB} = 15 k_B$$

■ A
■ B

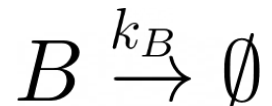Elevation (m)

0

Downstream Distance (m)

- Solute is conceptualized as an ensemble of infinitesimal particles each undergoing a random walk.

- **Under these assumptions, the simulation can be fully described by a mobile-immobile model parameterized with a fractal memory function (i.e., zero degrees of freedom) .**
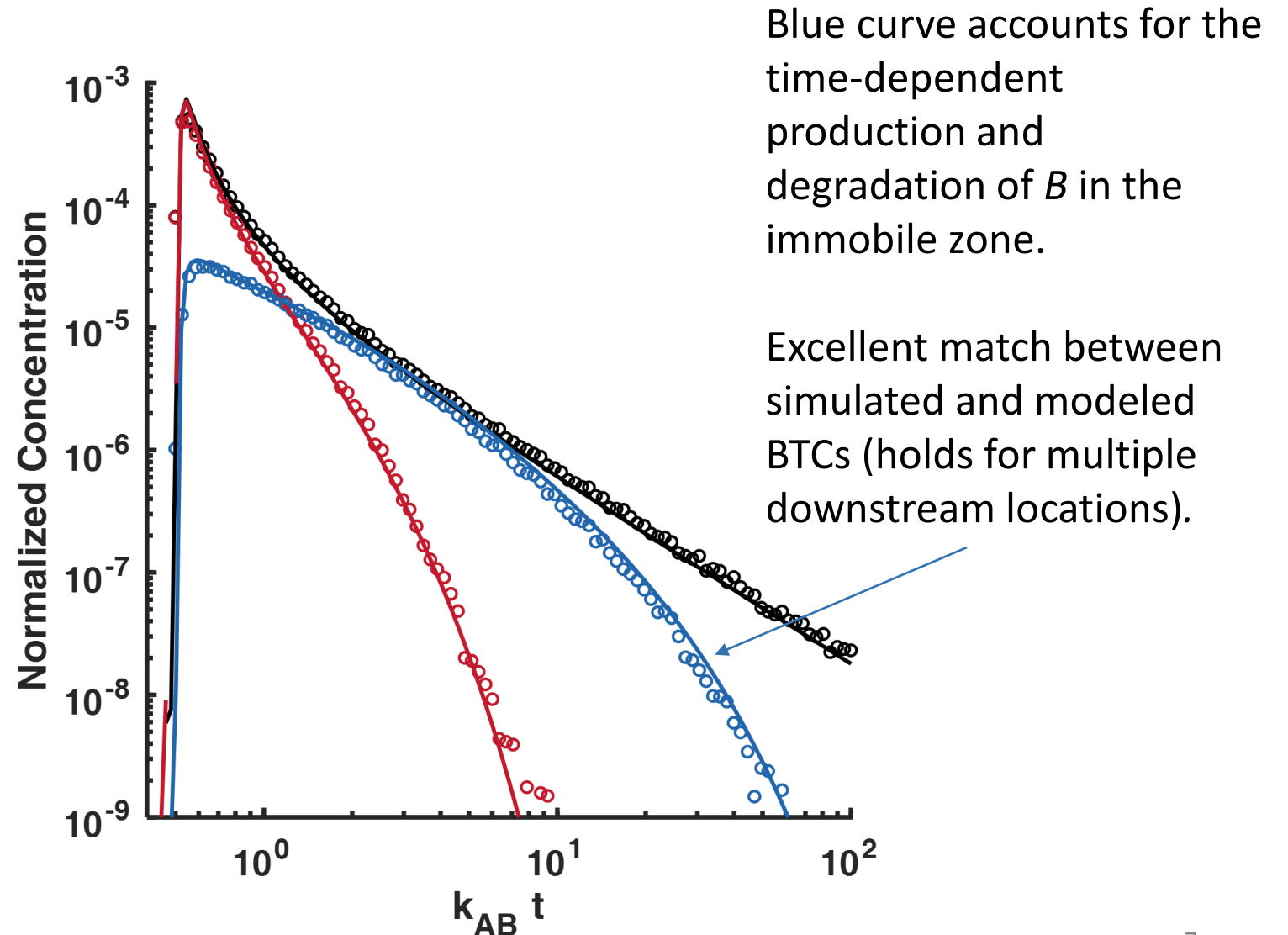
Point 2: Breakthrough curves, 500 m

Sim Model

○ —— Conservative Solute

○ —— A Parent Chemical

○ —— B Daughter Chemical

Pulse injection of parent chemical A

$$A \xrightarrow{k_{AB}} B$$

$$B \xrightarrow{k_B} \emptyset$$

$$k_{AB} = 15k_B$$

Blue curve accounts for the time-dependent production and degradation of B in the immobile zone.

Excellent match between simulated and modeled BTCs (holds for multiple downstream locations).

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Point 3: Spatially dependent reactions

Recent field experiments show evidence of a benthic biolayer in the hyporheic zone, where reactions are strongest near the sediment-water interface.

We approximate this behavior using a reaction rate that decays exponentially with depth.

Assume a constant background decay of daughter *B*.

$$A \xrightarrow{k_{AB}} B$$

$$B \xrightarrow{k_B} \emptyset$$

$$k_{AB}(z) = k_0\, e^{\alpha\, z}$$

Depth (m)

$-1/\alpha$

k_{AB}

k_B
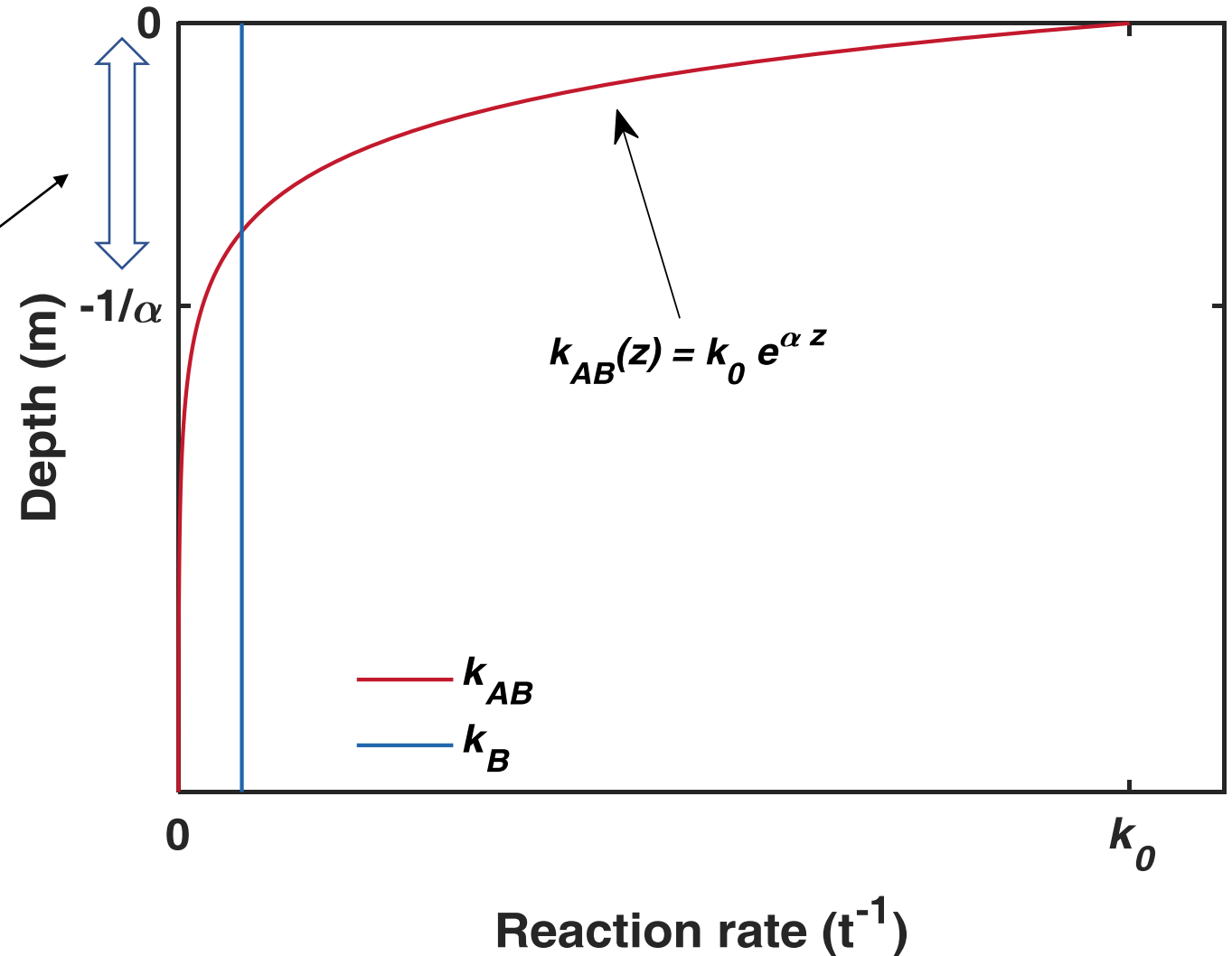
0

k_0
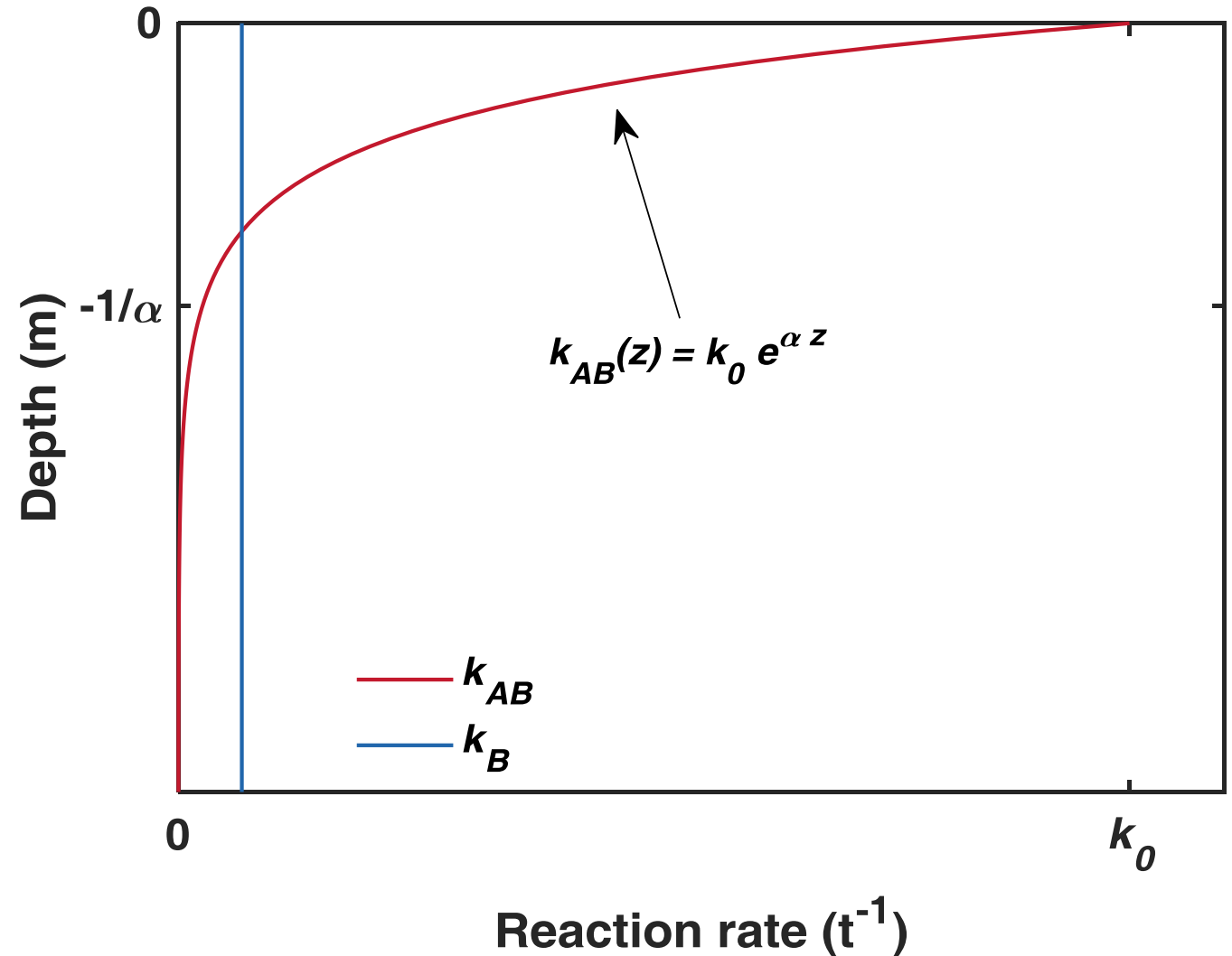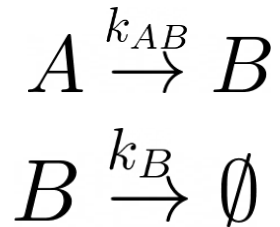
Reaction rate (t^{-1})

Point 3: Spatially dependent reactions

It turns out we can upscale this problem assuming a constant, *effective* reaction rate, $k_{AB}(z) \approx k_{AB,eff}$, when reactions are fast, i.e., when…

$$\tau_R \ll \tau_{Dr}$$

characteristic reaction time

diffusion time over the benthic biolayer

$k_{AB}(z) = k_0\, e^{\alpha z}$

Depth (m)

$-1/\alpha$

0

k_{AB}

k_B

0

k_0

Reaction rate (t^{-1})

Point 3: Breakthrough curves, 500 m, $\tau_R \ll \tau_{Dr}$

When $\tau_R \ll \tau_{Dr}$, simulated breakthrough curves can be predicted by the model parameterized with a constant, effective reaction rate, $k_{AB}(z) \approx k_{AB,eff}$.

Here, reaction dynamics are dominated by the high reactivity in the upper region of the bed. The majority of parent chemical A is transformed rapidly to B and hardly makes it below the benthic biolayer.

Slight deviation due to finite bed effects
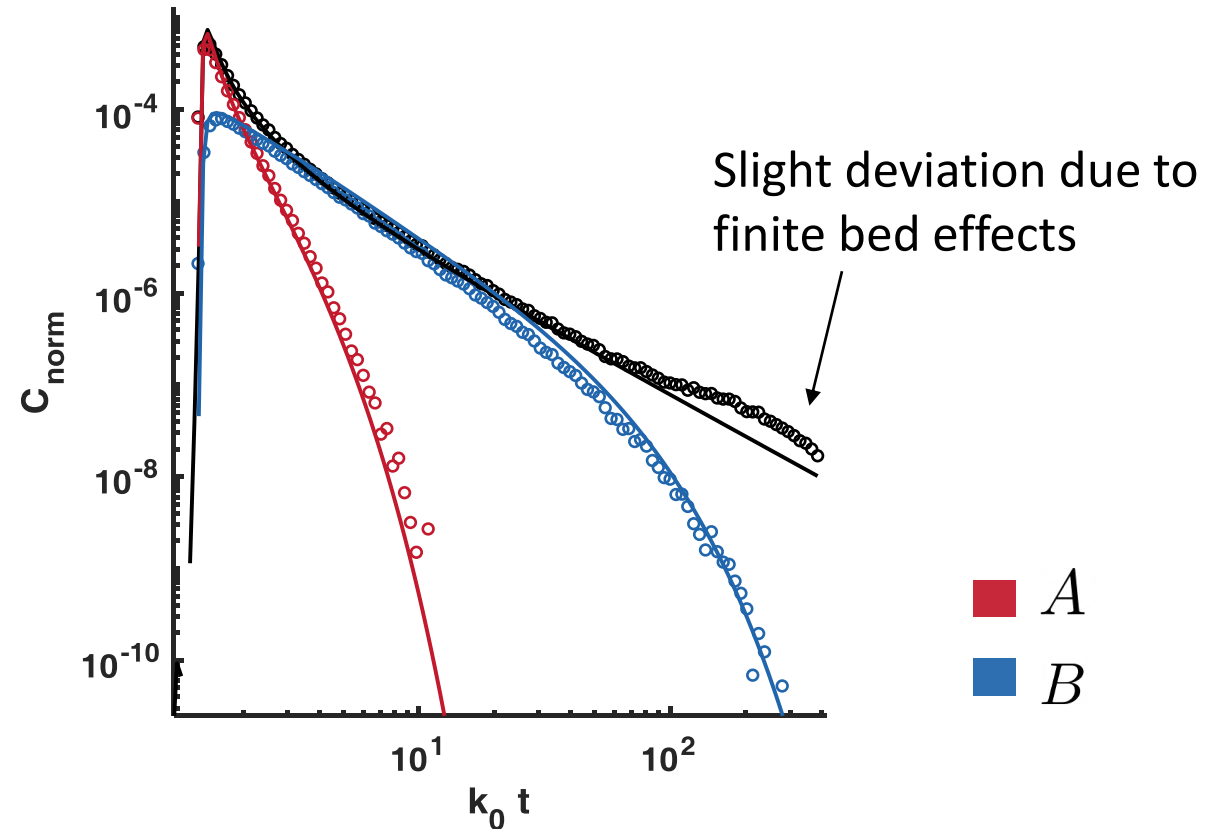
Point 3: Breakthrough curves, 500 m, $\tau_R \approx \tau_{Dr}$

When $\tau_R \approx \tau_{Dr}$, a constant *effective* k_{AB} fits the simulated BTCs well **prior to the reaction time**, $\boldsymbol{k_0^{-1}}$. During this time, most of the reactive solute leaving the reach has only sampled the upper-most section of the immobile layer. Daughter chemical *B* is slightly under-predicted.

Beyond the reaction time, $\boldsymbol{k_0^{-1}}$, the benthic biolayer is depleted of solute. Reaction of the parent chemical *A* (red circles) is limited by chemical *A*'s diffusion into the benthic biolayer. Here, a time-invariant, effective k_{AB} cannot describe the dynamics of parent chemical *A*.

Slight deviation due to finite bed effects

A

B

Good fit before the reaction time

Poor fit beyond the reaction time

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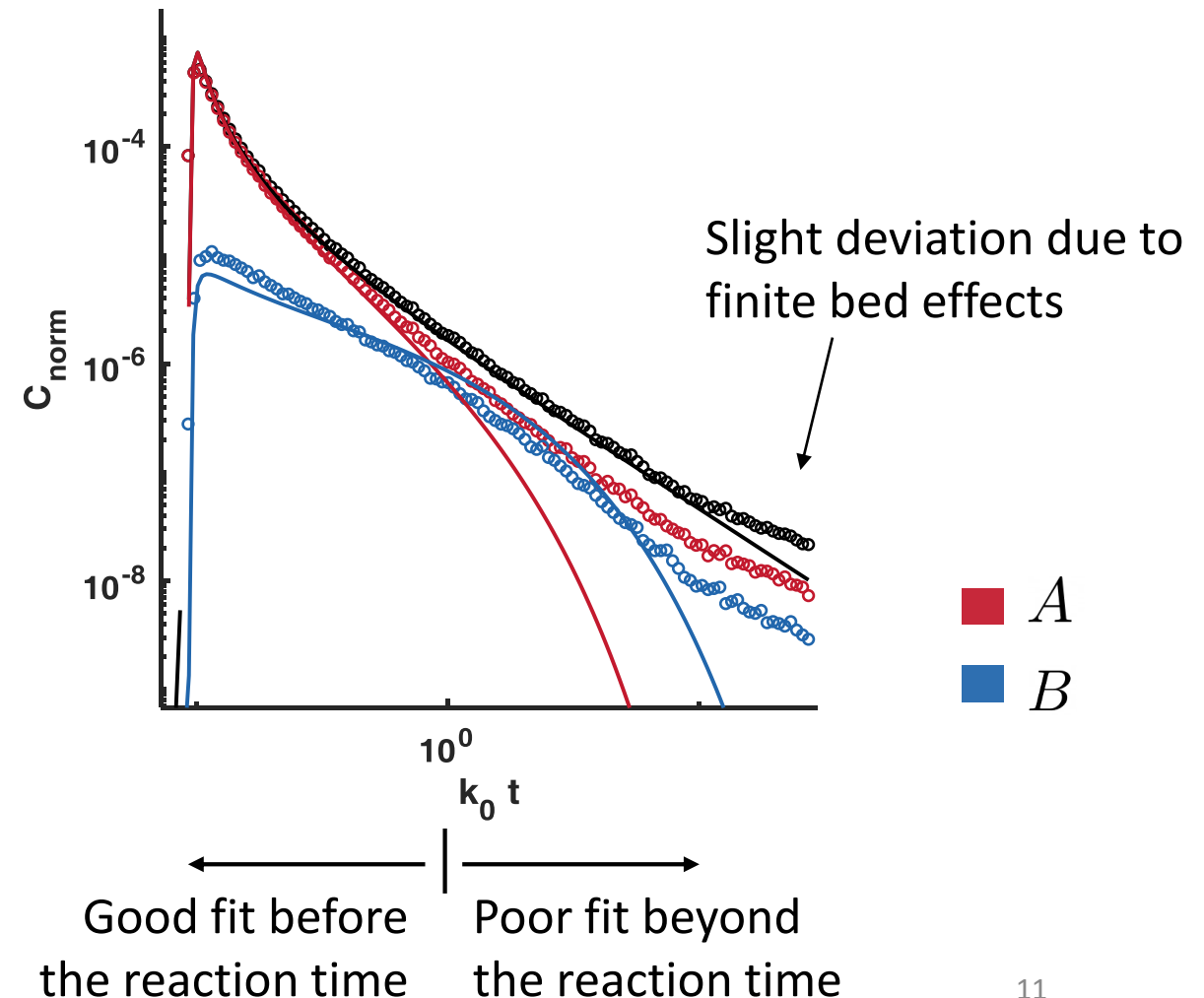
Summary

- We have generalized a classical mobile-immobile modeling framework to account for parent-to-daughter reactions.

- We demonstrated the model's fidelity to physical measures using a physically-based particle tracking simulation.

- We have identified conditions for which spatially variable reactions can be approximated with a uniform reaction rate.

Future work

- Advance model to capture the time-evolution of effective reactivity when a benthic biolayer is present (see Slide 11).

- Simultaneously model mobile zone and immobile concentration time series.

- Application to field data (*please contact me if you have an interesting dataset!*)

Thank you from a distance

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p.s. I am looking for graduate students interested in reactive transport (experiments and modeling). Click here for more info, and please spread the word.

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