Biogeochemical Reactive Transport Modeling in the Subsurface

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REACTIVE TRANSPORT MODELING FRAMEWORK

Reactive Transport Modeling (RTM) has been developed in the past decades and used extensively to understand the coupling between fluid flow, diffusive and dispersive transport, and biogeochemical processes in the natural subsurface in a wide range of applications relevant to energy, water, and environment in earth sciences. The applications include , for example, geological carbon sequestration, nuclear waste disposal, chemical weathering, environmental (bio)remediation, and enhanced oil recovery.

Mass conservation equation:

$$\frac{\partial(\phi C_i)}{\partial t} = \nabla\bullet(\phi D_i \nabla C_i) - \nabla(\phi u C_i) - \sum_{r=1}^{N_r} \nu_{ir} R_r - \sum_{m=1}^{N_m} \nu_{im} R_m$$

Diffusion/Dispersion Advection Reactions

i = 1, n,
Ci: concentration of aqueous primary species

$$\frac{\partial \phi_{mi}}{\partial t} = \overline{V}_{mi} R_{mi}$$

mi = 1, mtot,
solid phase volume fraction

Property Evolution:

$$\phi_t = 1 - \sum_{mi=1}^{mtot} \phi_{mi,t}$$

porosity

$$\frac{perm_t}{perm_0} = \left(\frac{\phi_t - \phi_c}{\phi_0 - \phi_c}\right)^n$$

permeability

$$A_{mi,t} = A_{mi,0}\left(\frac{\phi_{mi,t}}{\phi_{mi,0}}\right)$$

Surface area

Main features:

- Process-based model
- Solves conservation equations of mass, momentum, and energy
- Partition between primary and secondary species
- Primary species: the basis species set defines the aqueous chemistry
  Secondary species: can be written in terms of primary species through laws of mass action
- Output: spatial and temporal evolution
  aqueous concentrations,
  solid phase composition,
  and properties, including porosity, permeability, and surface area
- Spatial scales: have simulated processes at spatial scales from within individual pores to kilometer scale
- Time scales: seconds to geological times (millenniums)

Tightly coupled reaction network:

Kinetics-controlled reactions:

- Mineral dissolution / precipitation
- Microbe-mediated redox reactions
- Biomass growth ....

Thermodynamics-controlled reactions:

- Sorption / desorption
- Surface complexation
- Ion exchange
- Aqueous speciation ....

[1,2] AN EXAMPLE: BIOGEOCHEMICAL COMPLEXITY IN THE HETEROGENEOUS SUBSURFACE

Rifle IFRC site:

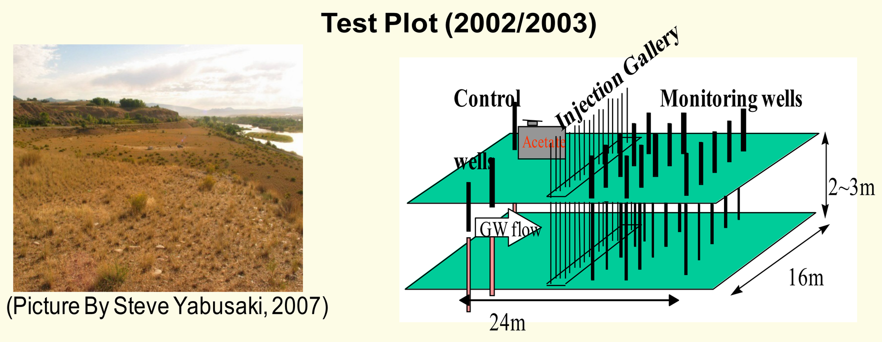


Fig. 1. The Rifle IFRC site is contaminated with micro-level U(VI). Field-scale experiments have been carried out to understand controls on U(VI) bioreduction and associated biogeochemical reactions upon the biostimulation of microbial community through the amendment of organic carbon.

Heterogeneous domain:

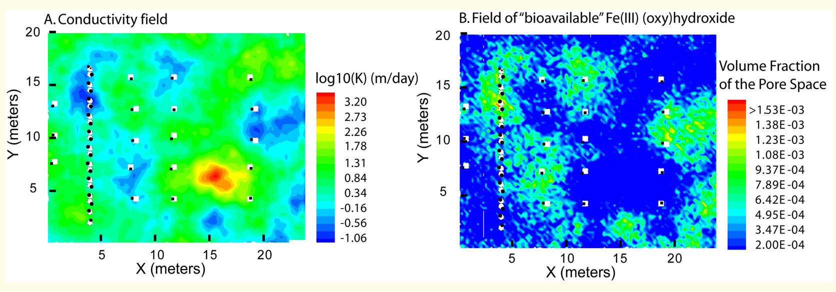
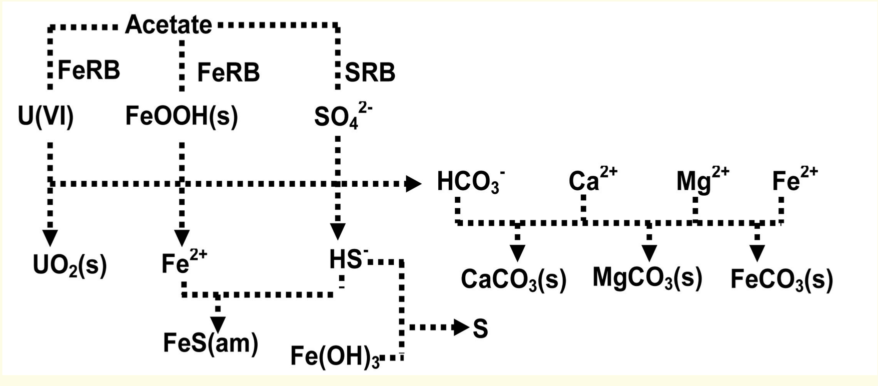


Fig. 2. Heterogeneous distribution of hydraulic and geochemical properties were generated using field data and physical-chemical relationships.

Fig. 3. Three major bioreduction reactions occur as the driving force of the system: iron, sulfate, and U(VI) reduction. The reaction products results in other secondary reactions.

Reaction Network and Rate Laws:



$$R_s = -k_{\max} X_S(x,t) \frac{C_S}{K_{M,S} + C_S} \frac{C_{TEA}}{K_{M,TEA} + C_{TEA}} \frac{K_I}{K_I + C_I}$$

Fit to field data:

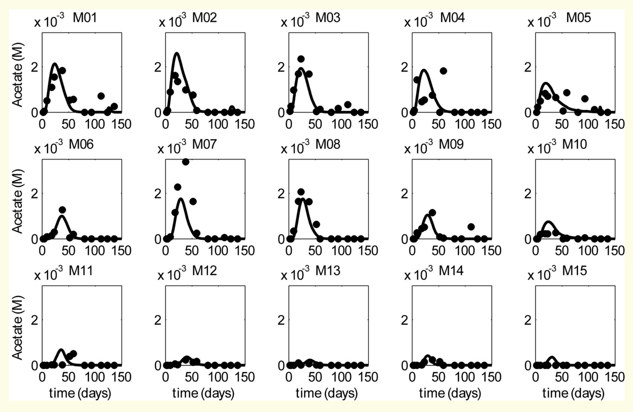


Fig. 4. The model was constrained by fitting the field data of bromide, acetate, sulfate, and U(VI) from monitoring wells.

SUMMARY: With data as constraints, RTM can be a powerful tool to mechanistcally and quantitatively understand the coupling among flow, transport, and biogeochemical reactions.

Spatial and Temporal Evolution:

Aqueous species:

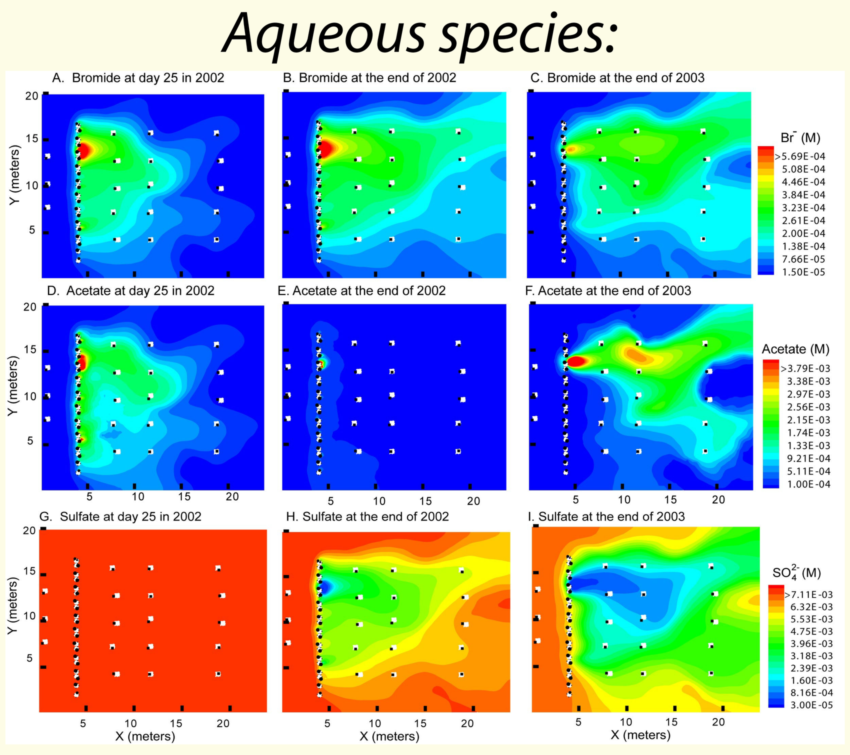


Fig. 5. The model regenerated the spatial-temporal evolution of bromide, acetate, and sulfate.
1. The distribution of hydraulic conductivity dictates the that of non-reactive bromide.
2. The plume of acetate is controlled by both the physical and geochemical heterogeneities.

Biomass:

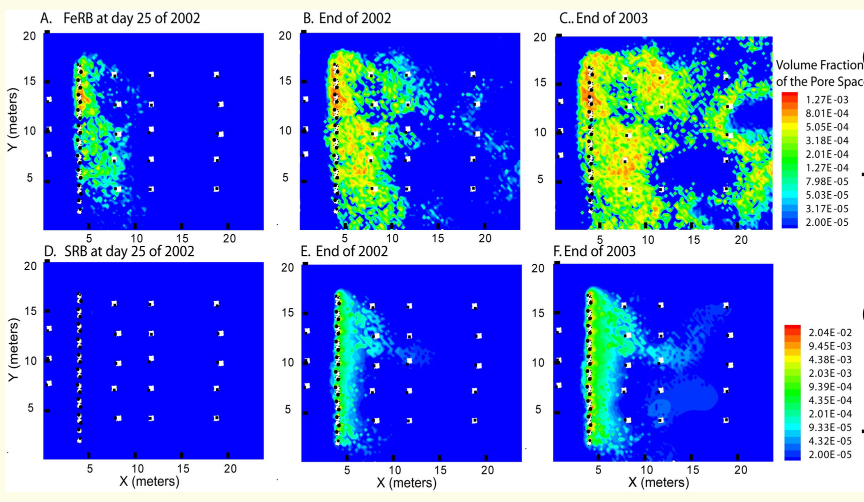


Fig. 6. The model also regenerates the distribution of the Fe-reducing bacteria controlled by the geochemical heterogeneity. Sulfate -reducing bacteria, however, mostly accumulates close to the injection wells.

Solid phases:

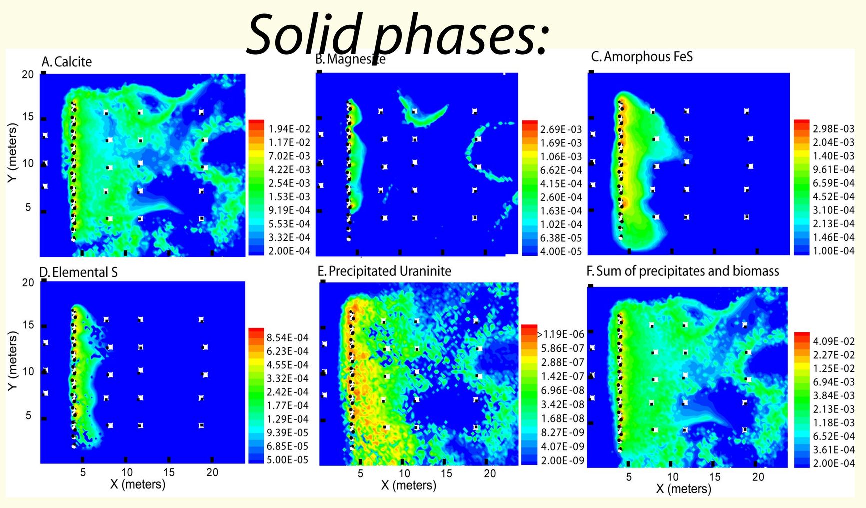


Fig. 7. The model regenerated the distribution of secondary mineral phases, including calcite, magnesite, FeS(am), elemental S, U(IV).

A VISION FOR THE FUTURE: RTM APPLICATION TO CRITICAL ZONE SCIENCES

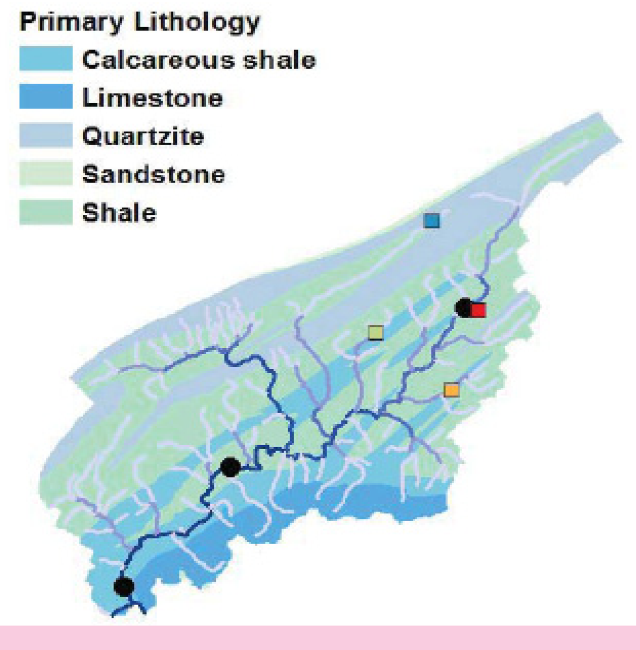


Fig. 8. Lithogy map of Shavers creek watershed.

We will develop models in earthcasting the Critical Zone.

-- Over short timescales (days and months) and large spatialextents (tens of kms) , we will use an atmosphere-land surface model (PIHM) that couples meteorological and ecological processes with hydrological and biogeochemical processes in regolith.

-- Over long timescales (tens of thousands years) and smaller spatial extent (meters), we will develop models that will reproduce and predict the regolith evolution as a function of geological and climatological history.

PIHM-RT will expand existing capabilities to understand the coupling among different forces and how that forces control short-term and long-term chemical and biological processes at multiple spatial scales.

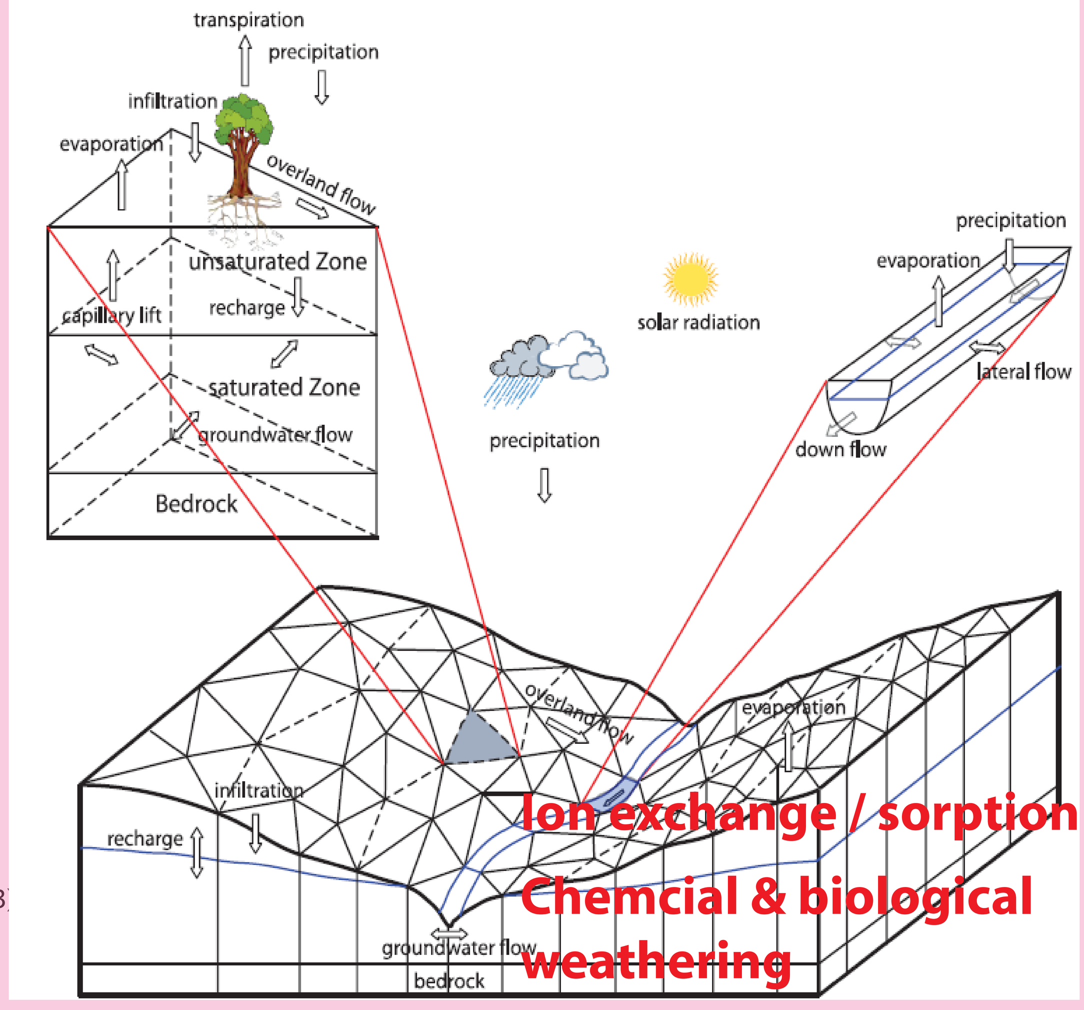


Fig. 9. PIHM-RT conceptual model3

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