Coupled Flow and Multicomponent Biogeochemical Reactive Transport Modeling: In Situ Biostimulation at the Rifle Site

Steve Yabusaki

Yilin Fang

Phil Long

Pacific Northwest National Laboratory

April 17, 2007

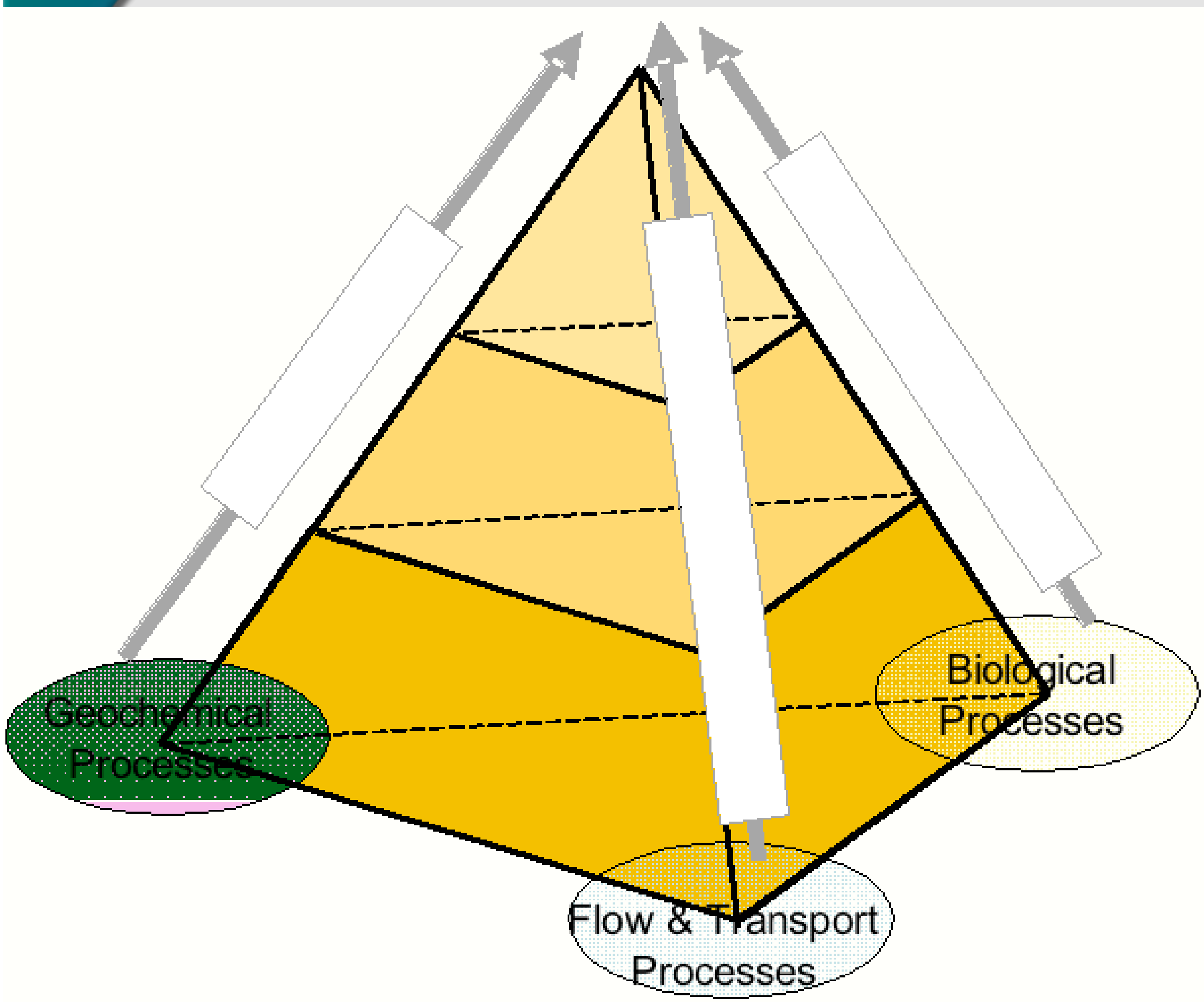
2007 ERSP PI Meeting
Lansdowne, Virginia, USA

Field-Scale Modeling: Understand, Predict, and Control

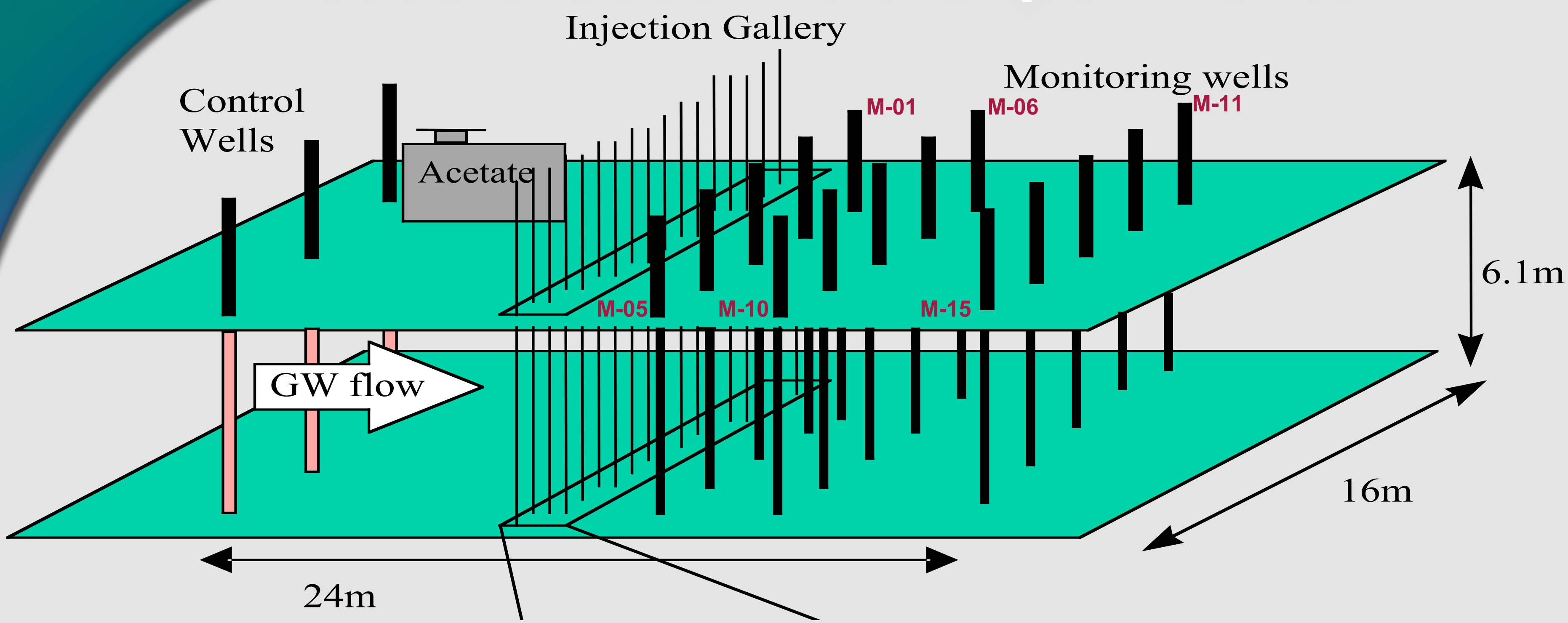
- Engineering bioremediation for site-specific conditions will require a ***quantitatively predictive understanding*** of the dominant processes and properties controlling contaminant behavior
- Complex natural environments make the reliable prediction of field scale behavior a scientific challenge
  - Many field-scale issues are difficult to address at the lab scale
  - Many processes and properties are difficult to monitor in the field
  - Need to develop a quantitatively mechanistic understanding of field-scale behaviors by addressing the relevant range of scales and multiple interacting processes
- In the context of temporally and spatially variable conditions at the site, use ***modeling to develop understanding*** of the interplay between the dominant flow, transport, and biogeochemical processes

Presentation Outline

- Previous modeling
- gaps & issues
- d

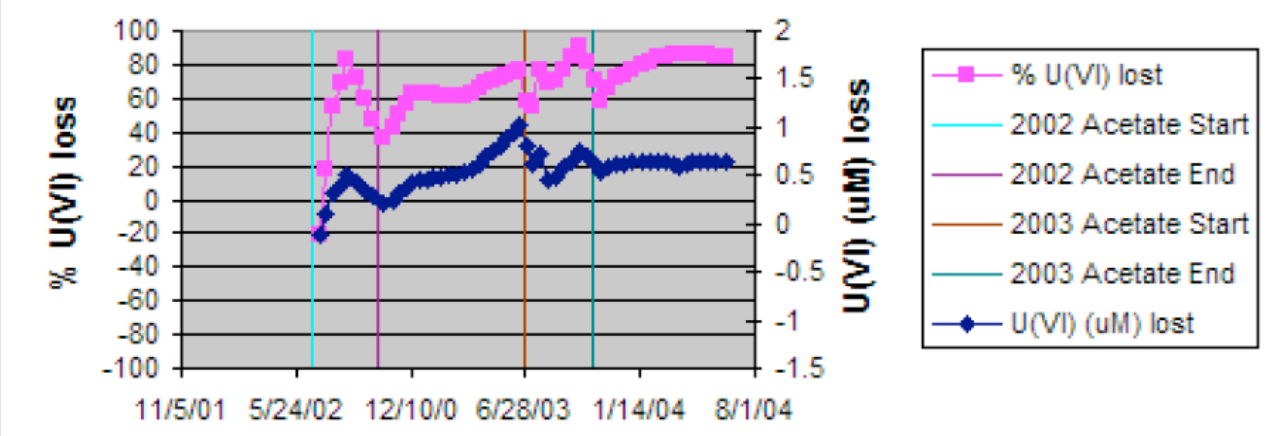


2002 & 2003 Field Experiments



- Hypothesis: Dissimilatory metal-reducing bacteria grown on acetate can be used to immobilize U(VI) in a field setting
- Continuous influx of elevated uranium (140 to 350 ug/L)
- 2002: Initial biostimulation
  - 123-day release period
  - 100 mM acetate, 10 mM bromide
  - average rate ~70 L/d (range 0 to 120 L/d)
- 2003: 2nd biostimulation
  - 109-day release
  - 300 mM acetate, 10 mM bromide
  - Average rate ~80 L/d (range 0 to 400 L/d)

Observations from Old Rifle Biostimulation Experiments



<u>Proof of Principle</u>

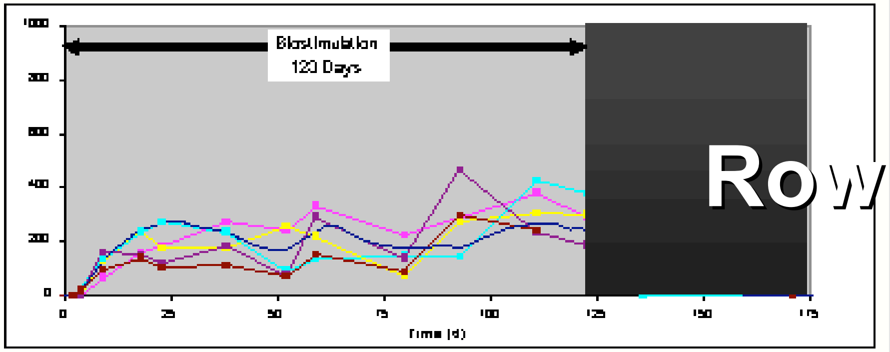
- Acetate stimulated growth of microbial populations that reduced aqueous U(VI) to U(IV), effectively removing uranium from groundwater through the precipitation of U(IV) mineral
- Initial bioreduction of aqueous U(VI) was 75 to 85 percent efficient and attributed to iron reducing bacteria (*Geobacter sp*.)
- Subsequent onset of sulfate reduction, coincided with less efficient U(VI) removal from groundwater

Modeling Approach

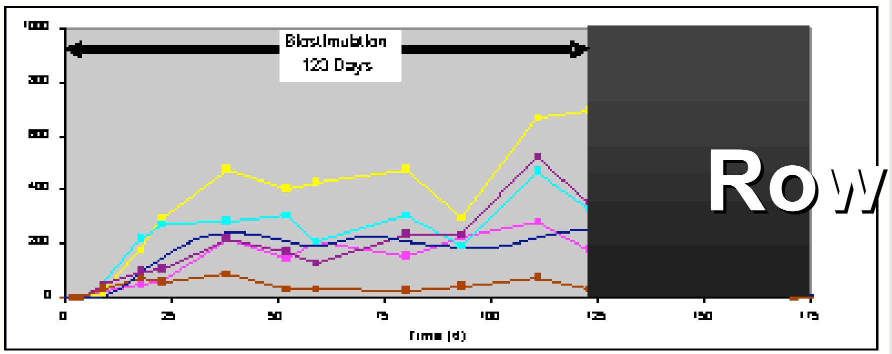
- Use mechanistic coupled process simulators as a systematic framework to
  - gain insight on the dominant processes and properties responsible for observed behaviors in the field
  - identify knowledge gaps that need to be addressed
- Philosophy
  - Start simple to isolate major behaviors
  - Systematically add process complexity and detail
- Field-scale flow and biogeochemical reactive transport simulation of biostimulation experiments
  - consistent gradient direction and magnitude: 1-D steady flow
  - iron and sulfate reducers: Fe(III), U(VI), and sulfate TEAPS
  - 2002 field experiment data set: calibrate flow, transport, and biogeochemical reaction parameters
  - 2003 field experiment: strict application of 2002 calibrated parameters

Flow and Transport Modeling

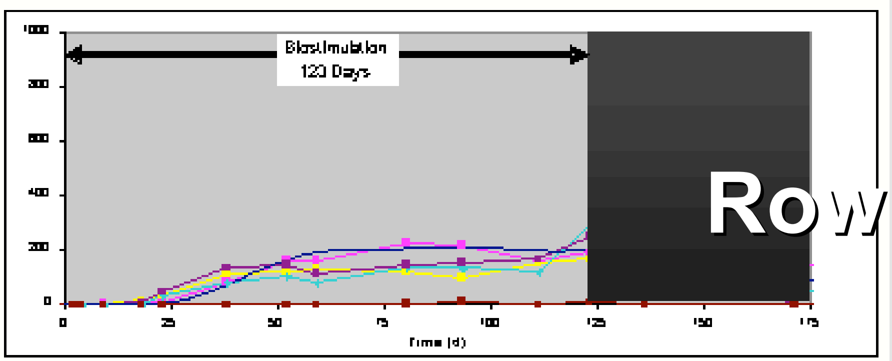
2002



Row 1

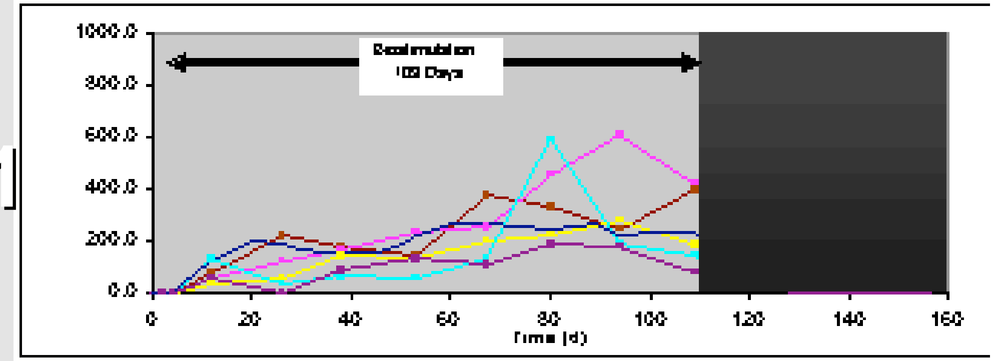


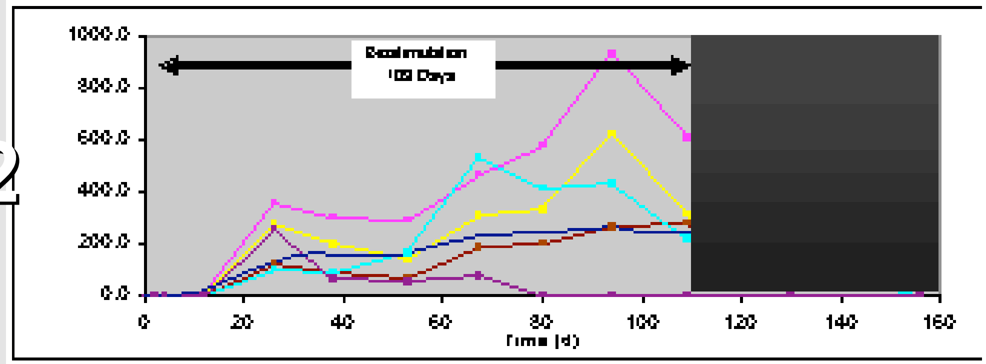
Row 2

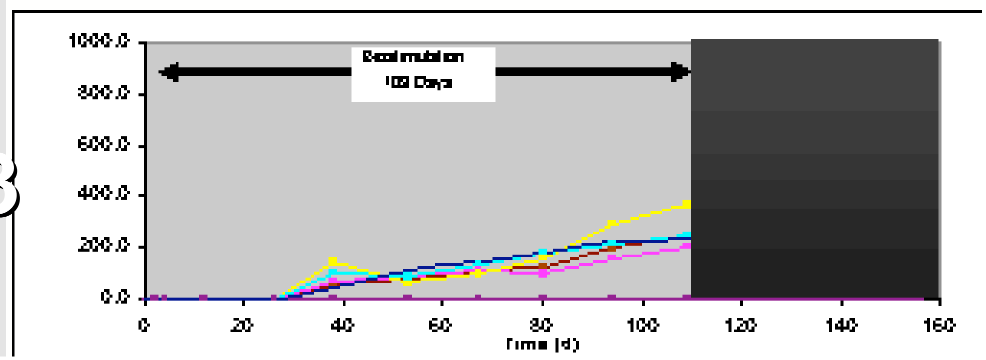


Row 3

2003



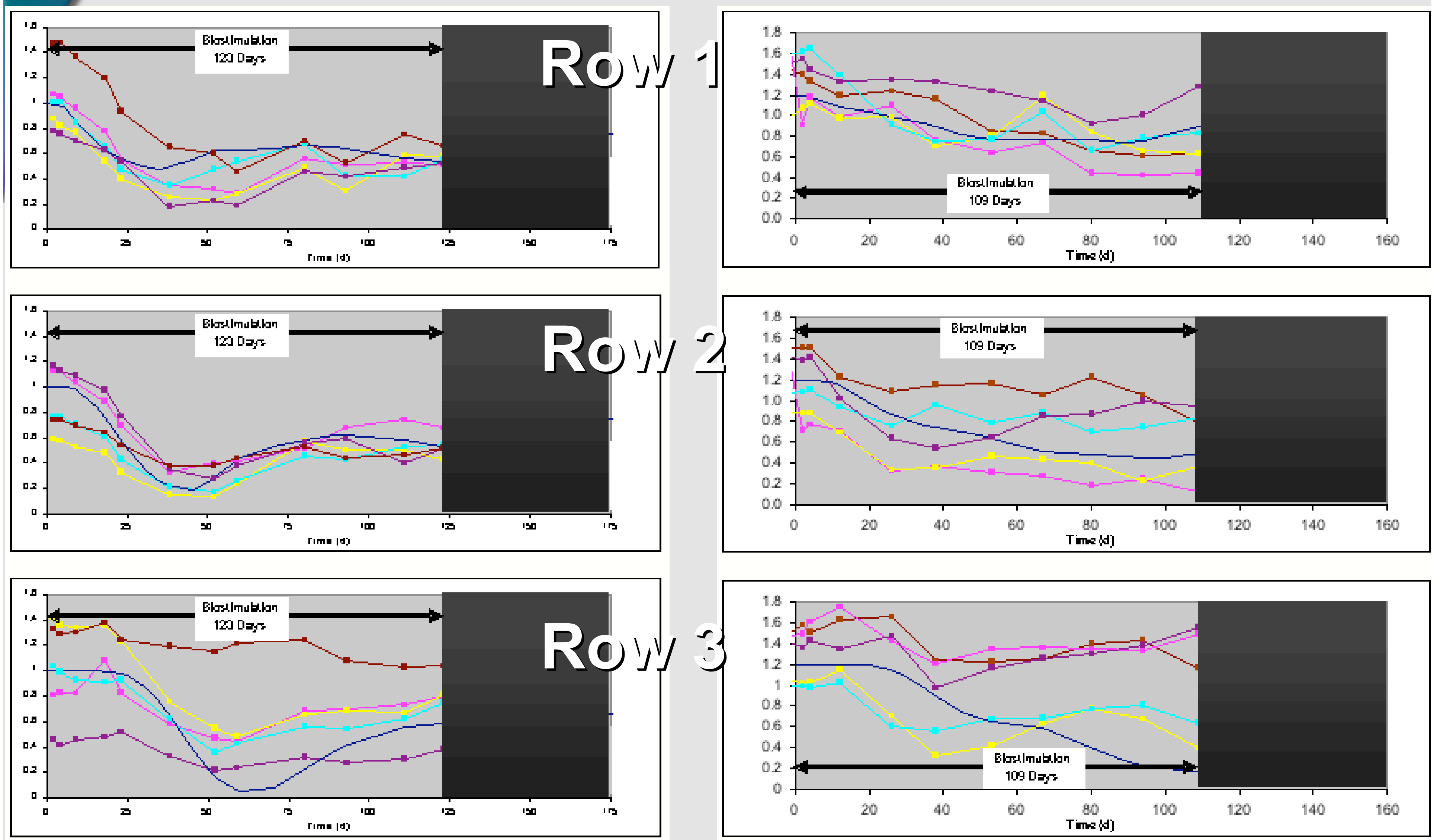




Uranium

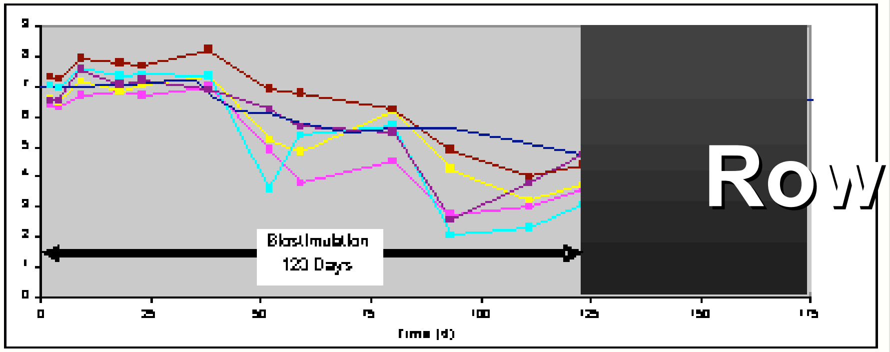
2002

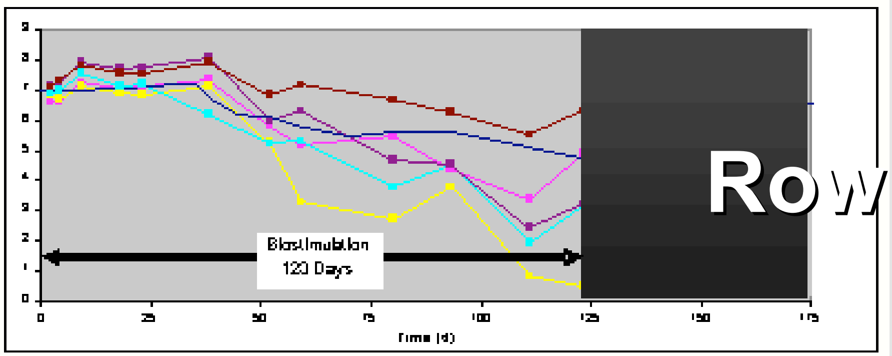
2003

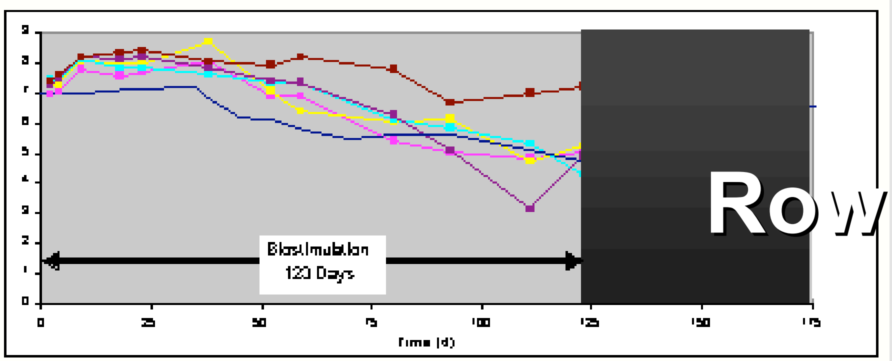


Sulfate

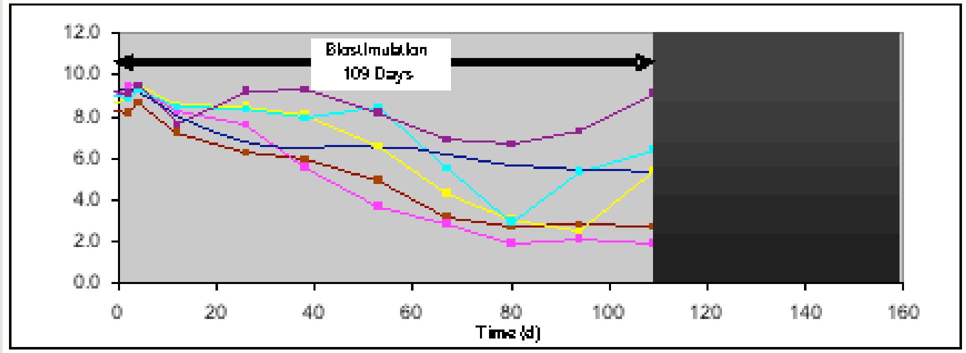
2002

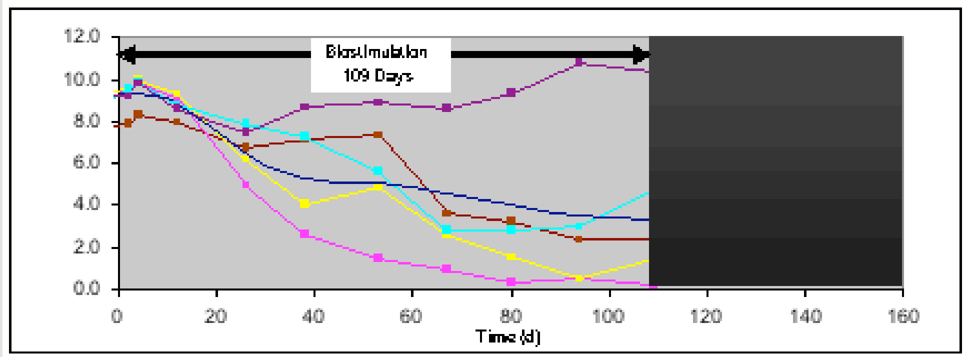


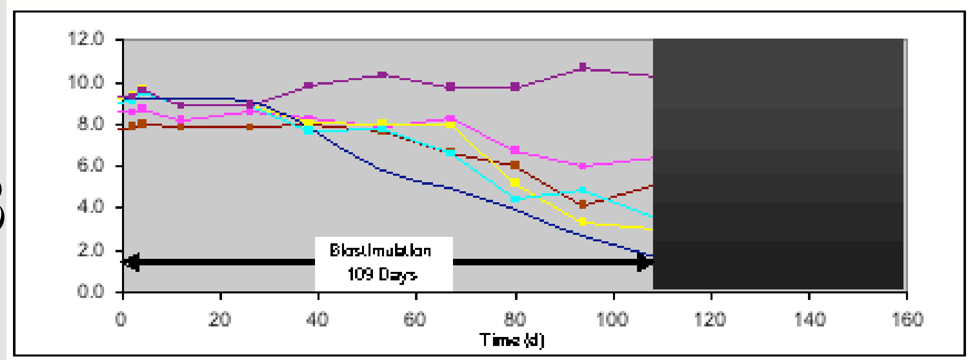




2003







Row 1

Row 2

Row 3

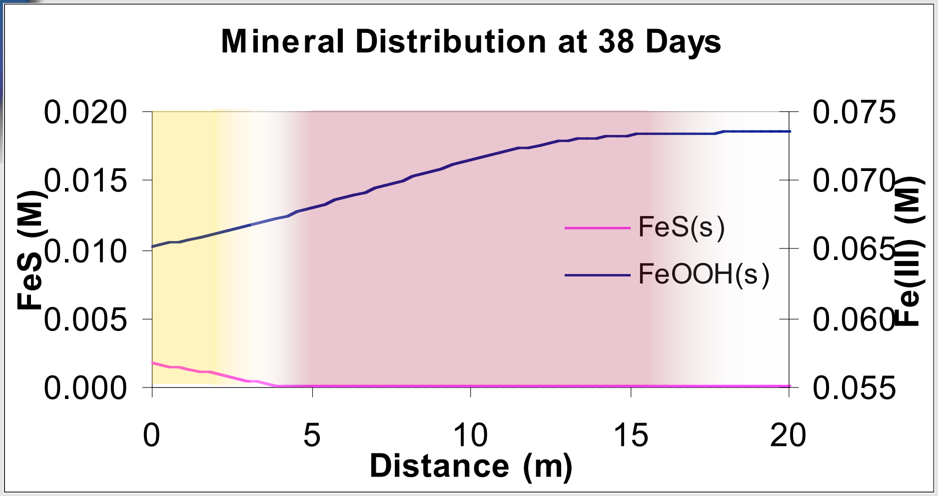
Summary of Results

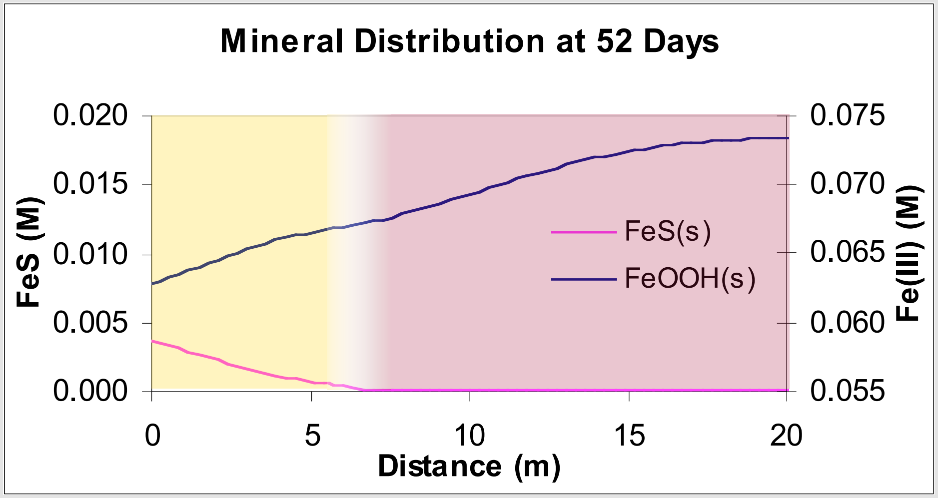
Observations during 2002 & 2003 biostimulation experiments are consistent with:

- 2 dominant microbial populations: iron reducers (i.e., *Geobacter*) and sulfate reducers
- 3 TEAPs: Fe(III) mineral, U(VI), sulfate
- Iron reducers concomitantly responsible for U(VI) reduction
- Onset of sulfate reduction triggered by consumption of threshold amount of Fe(III) mineral by iron reducers
- Lower U(VI) removal rate during sulfate reduction due to competition for acetate

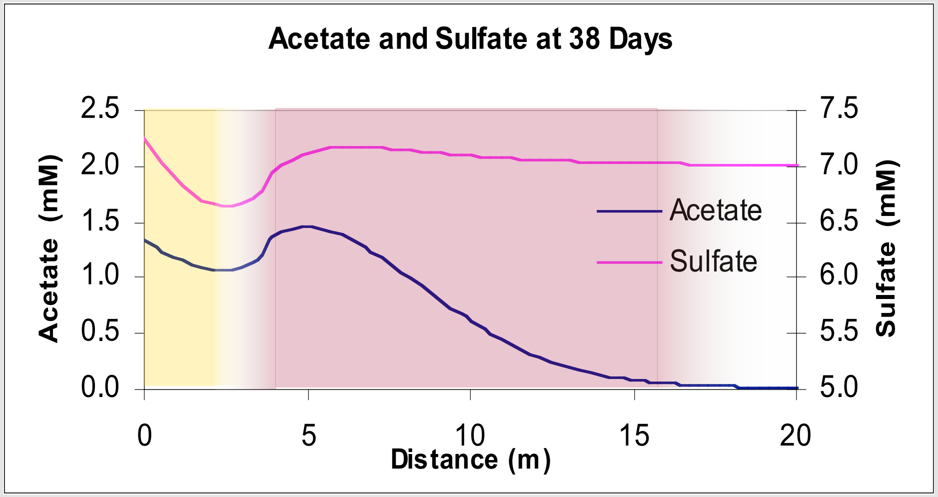
2002 Simulation: Day 38, 52

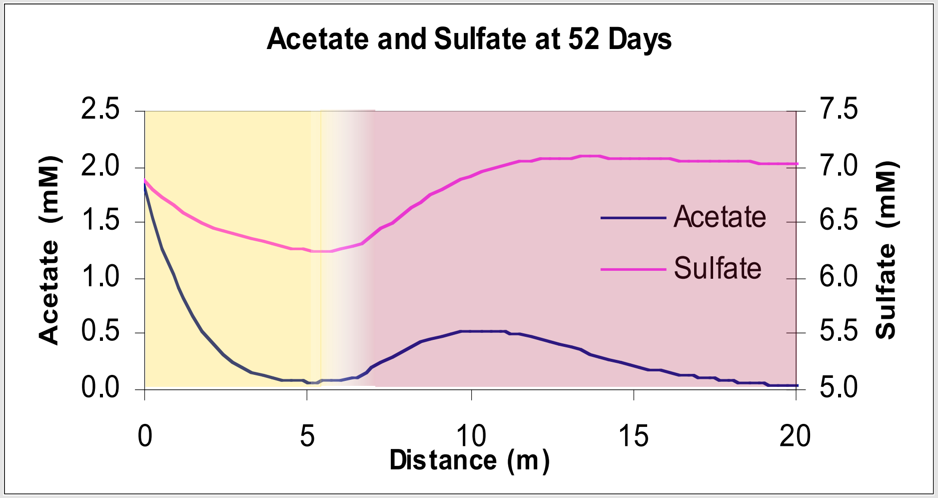
SOLID PHASE





AQUEOUS PHASE





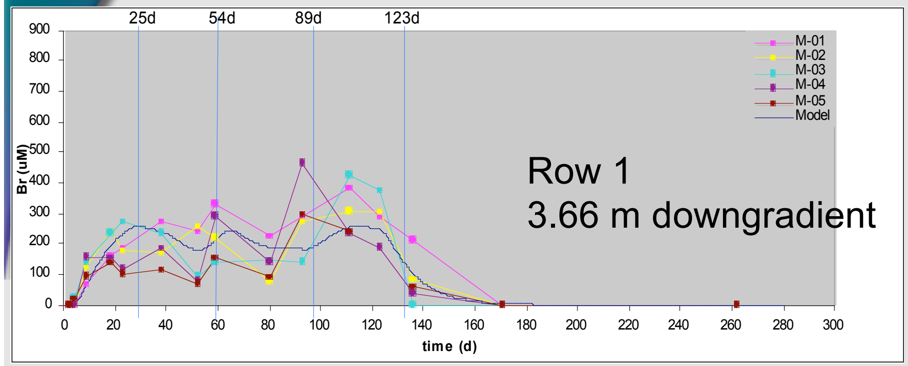
Principal Knowledge Gaps: Processes and Properties

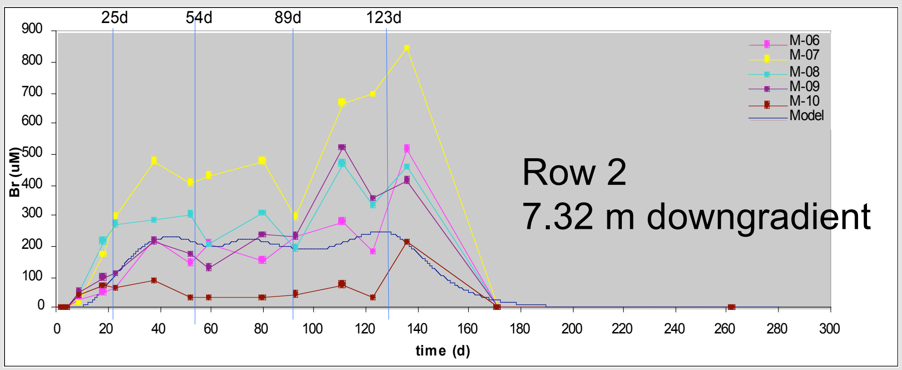
- Large gap ("THE GAP") between fundamental research in geochemistry, microbial ecology and molecular biology, and field-scale reactive transport modeling
  - Need development of detailed biogeochemical reaction network models
  - Need to link new knowledge of cell reactions/metabolism to kinetics and constraints of enzymatic processes
- Need for 3-D characterization of spatially-variable model parameters
  - controls flow paths, sediment reactivity, rate-limited mass transfer between pore domains, gas entrapment during water table fluctuation
  - simulation will play a key role in characterizing spatially variable parameters
    - testing and linking process models
    - accommodating a variety of data types from different scales
    - joint inverse modeling approaches

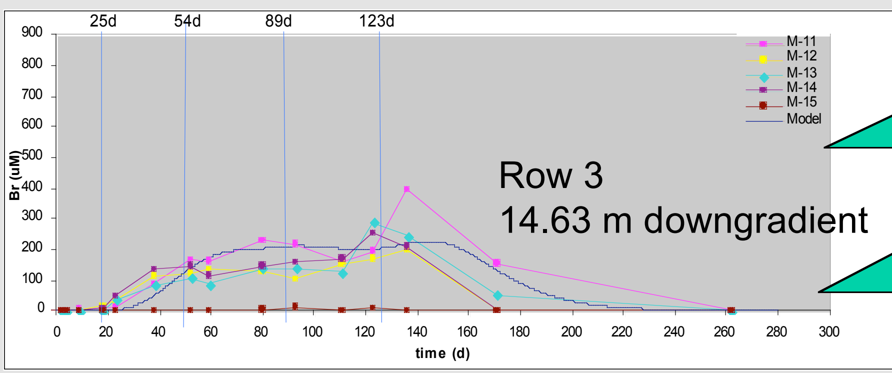
Biogeochemical Issues

- Are there other microorganisms consuming acetate?
- What factors control the stoichiometry and rates for TEAP reactions?
  - nutrient limitations
  - water chemistry
  - mineral form
- What factors control the onset of sulfate reduction?
  - "bioavailable" iron (e.g., poorly crystalline iron)
  - redox potential
  - metabolic lag
- What is the role of biomass in controlling U mobility?
  - production/consumption/decay
  - attachment/detachment
  - contribution to microbial reaction rates
  - effect on reactivity of mineral surfaces
  - sorption effects
- What is the role of U surface complexation before, during, and after biostimulation?

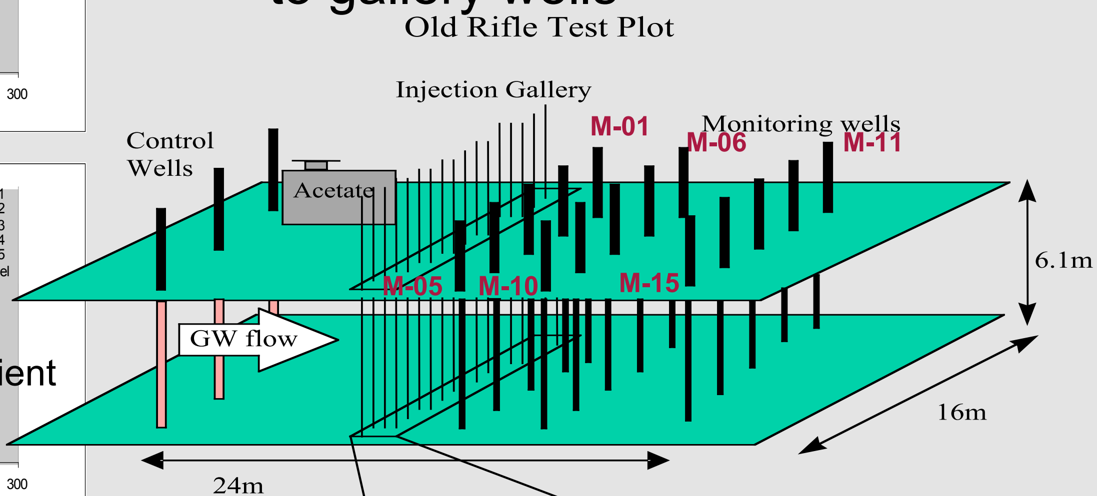
Preferential Flow and Transport Paths





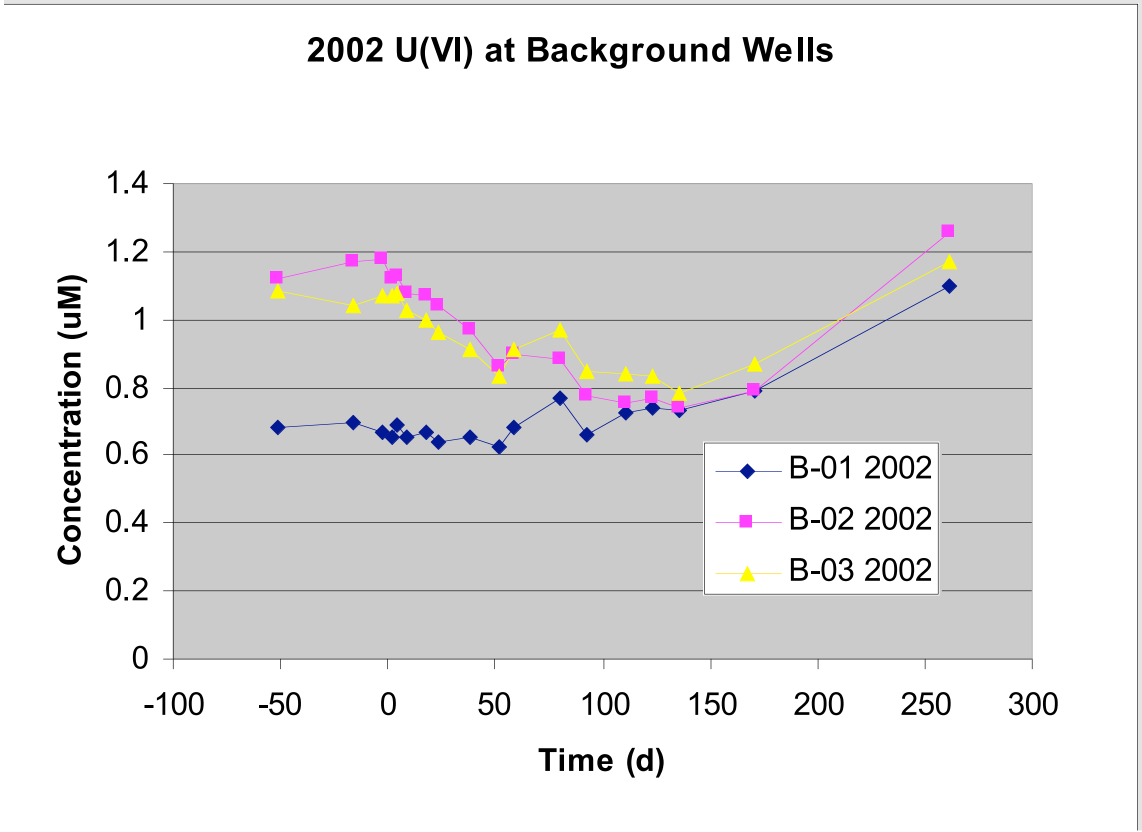


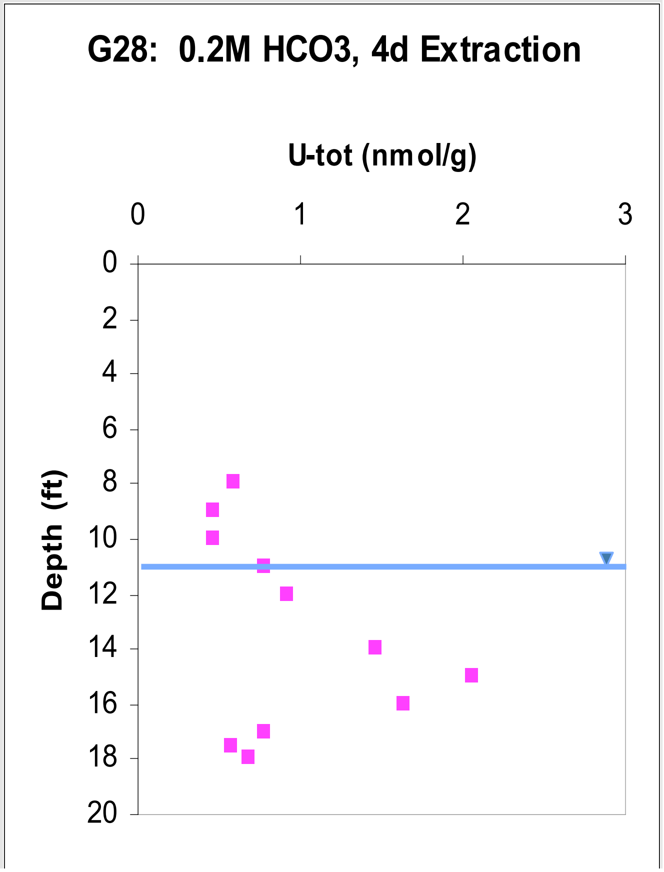
- Considerable variability in bromide concentrations in the same row
- Row 2 has highest concentrations and maximum variability
- Some wells bypassed
- Issues
  - Heterogeneous sediments
  - Nonuniform metering of injectate to gallery wells



Spatially & Temporally Variable Uranium

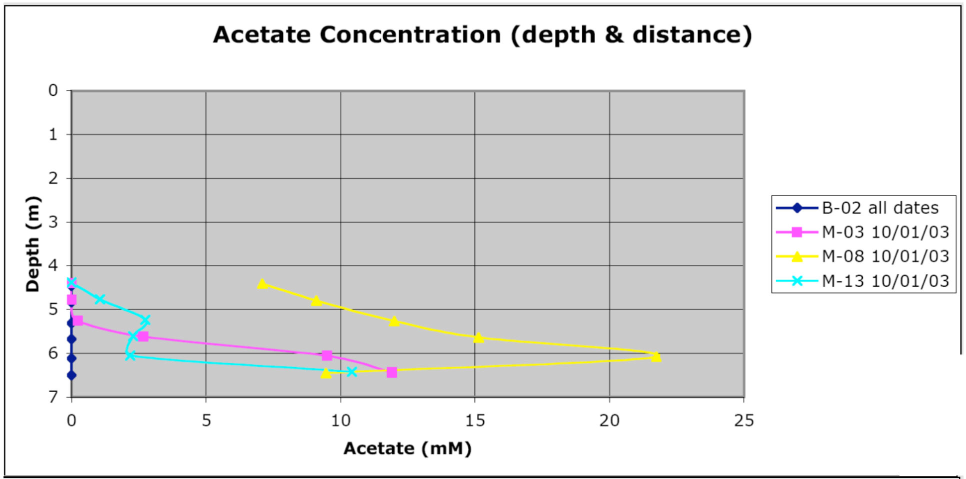
- Spatially variable pre-biostimulation aqueous concentrations in 2002
  - U ranged from 0.3 to 1.5 uM
  - Fe(II) ranged from 18 to 250 uM
- Initial uranium distribution in G-28 sediments is strongly depth dependent

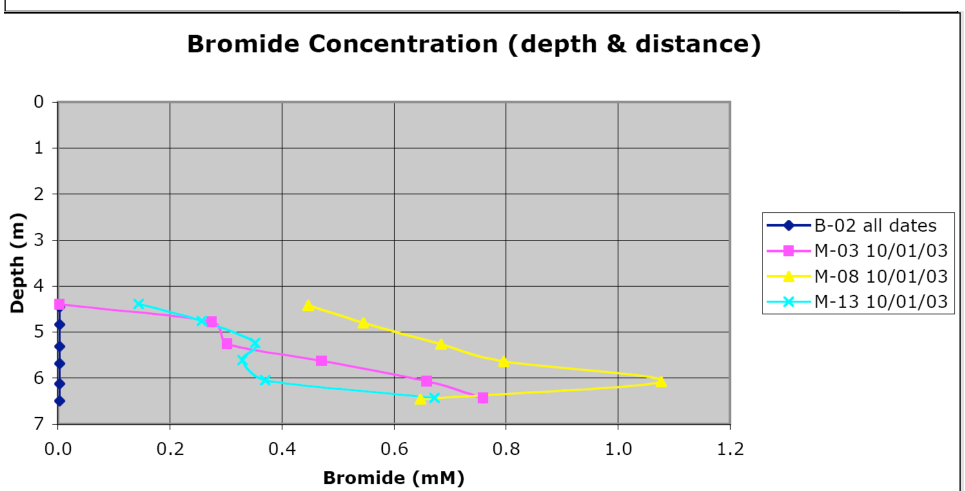


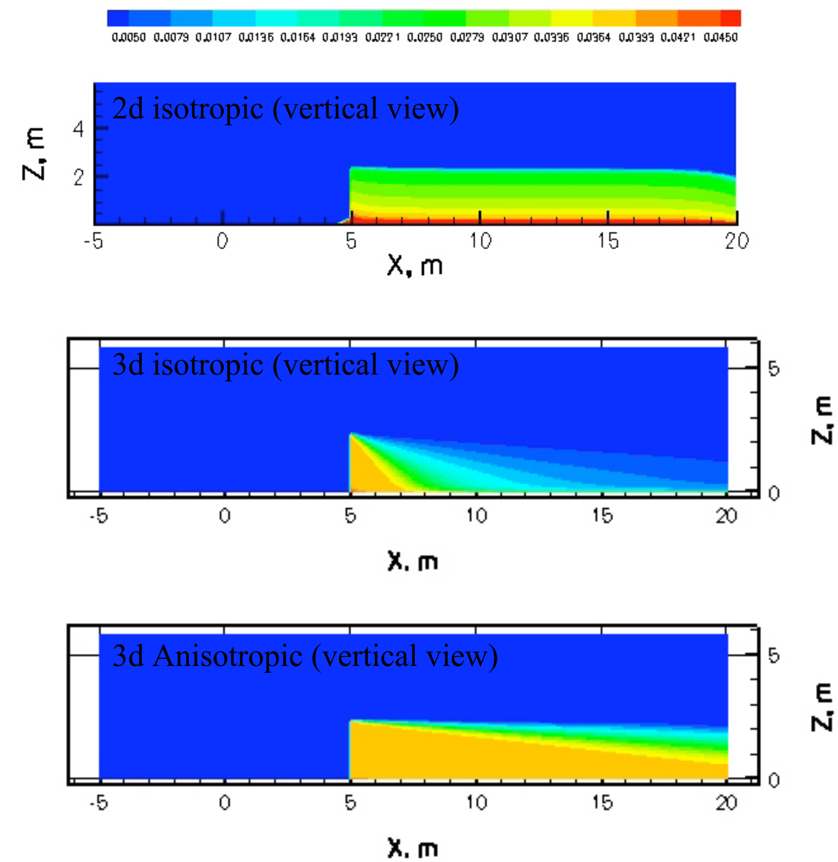


Density-Dependent Transport

- Acetate – bromide injectate is denser than GW
- Multilevel samplers show effect in 2003
- 3D modeling of individual gallery wells is necessary to accurately represent phenomenon
  - Modeling identifies sensitivity to anisotropy



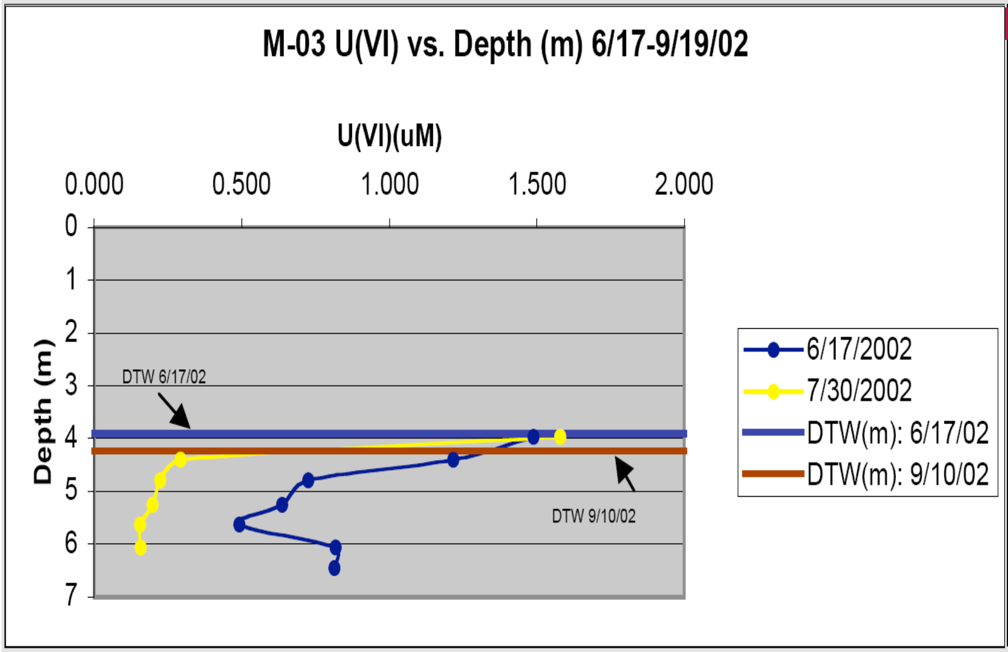


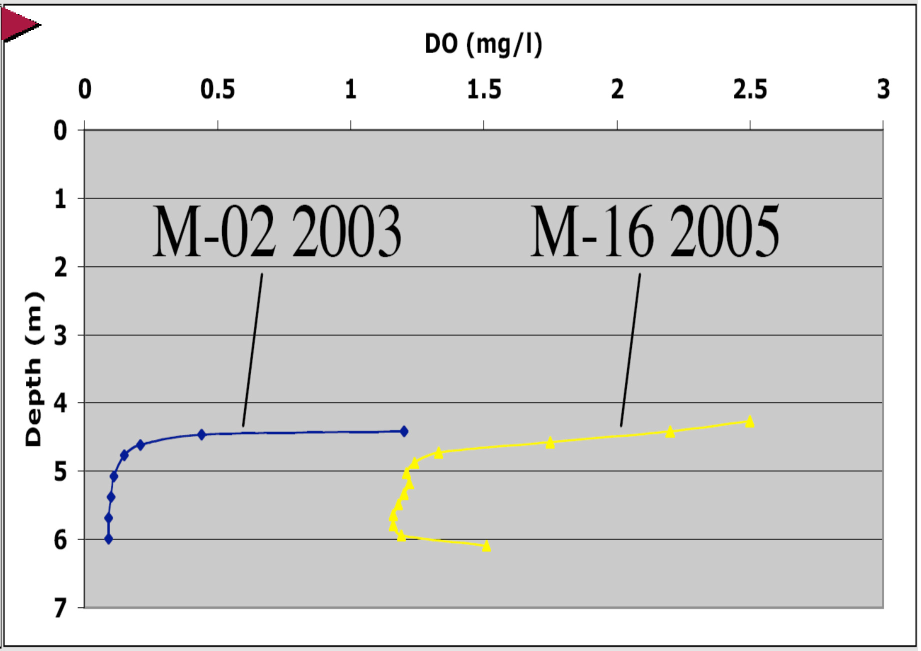


Stratified Water Chemistry

Depth-dependent U(VI) and DO

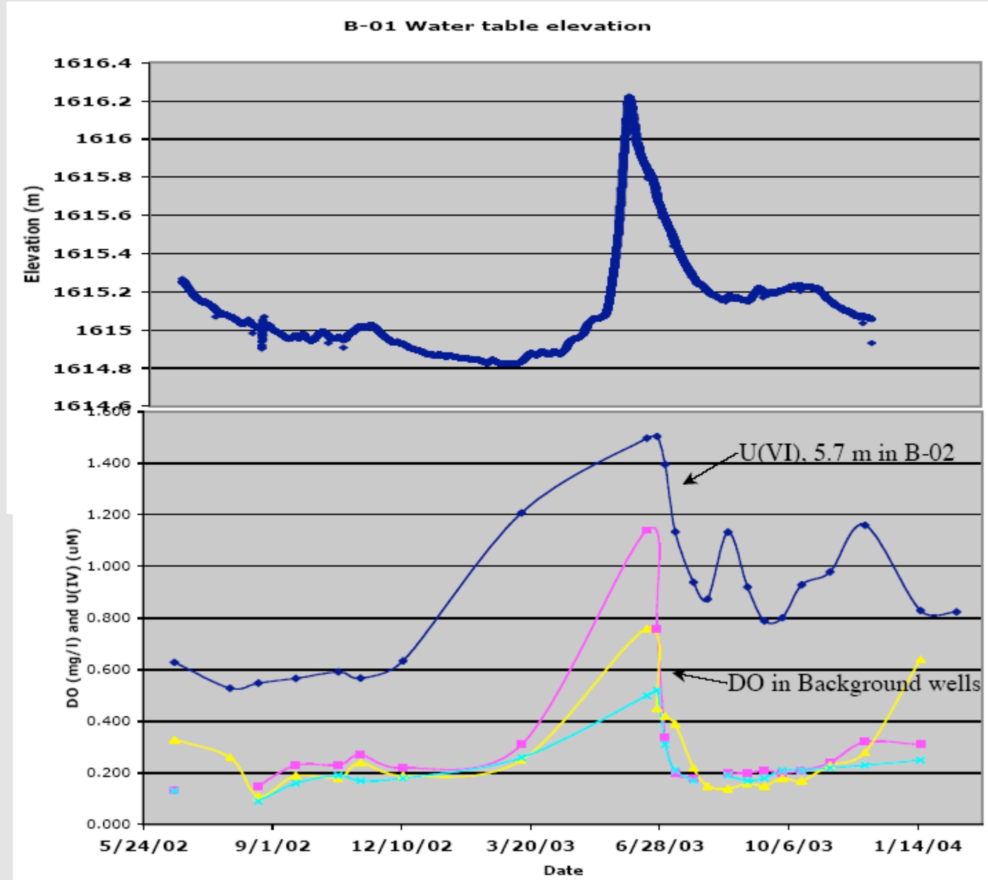
- Highest DO and U(VI) near the water table
- Issues
  - Oxygen diffusion through water table
  - Background utilization of DO
  - Screened interval of wells





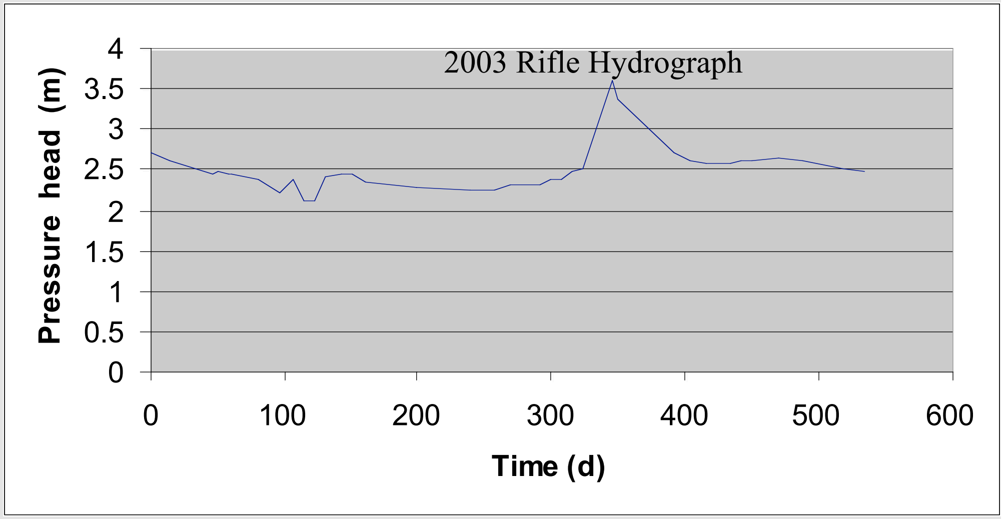
How do seasonal and episodic hydrologic events affect uranium behavior?

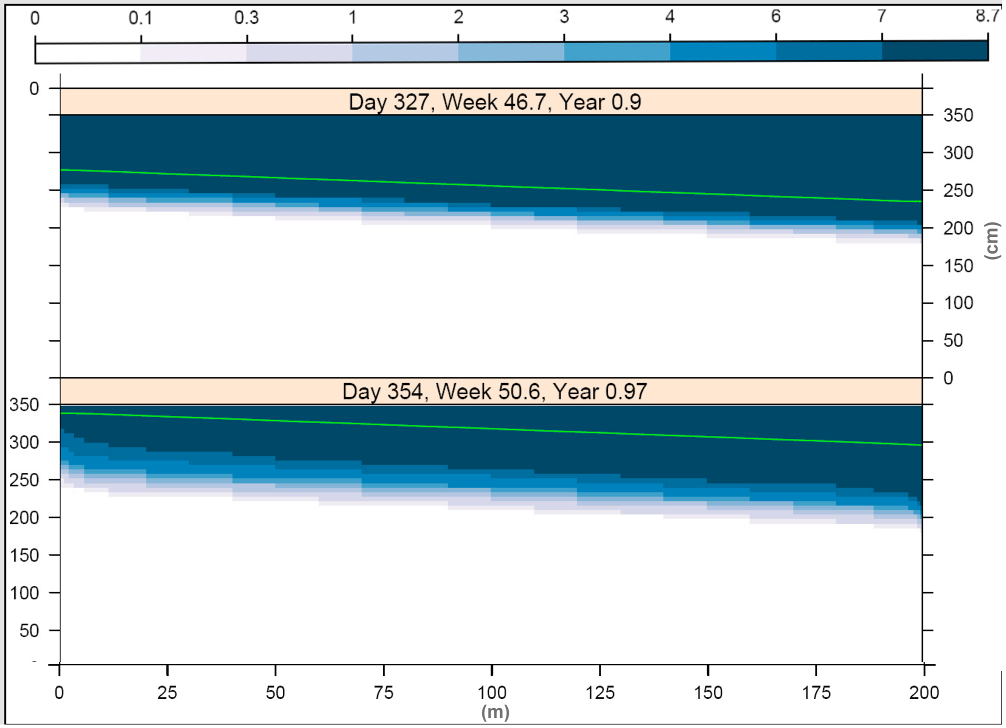
- Seasonal and event-driven changes
  - Velocity field
  - Oxidation of zones affected by water table fluctuations
- Issues
  - Rapid oxidation of zones affected by water table fluctuations
  - Highest U concentrations bypassing treatment zones



Oxygen Entrapment during Water Table Fluctuation

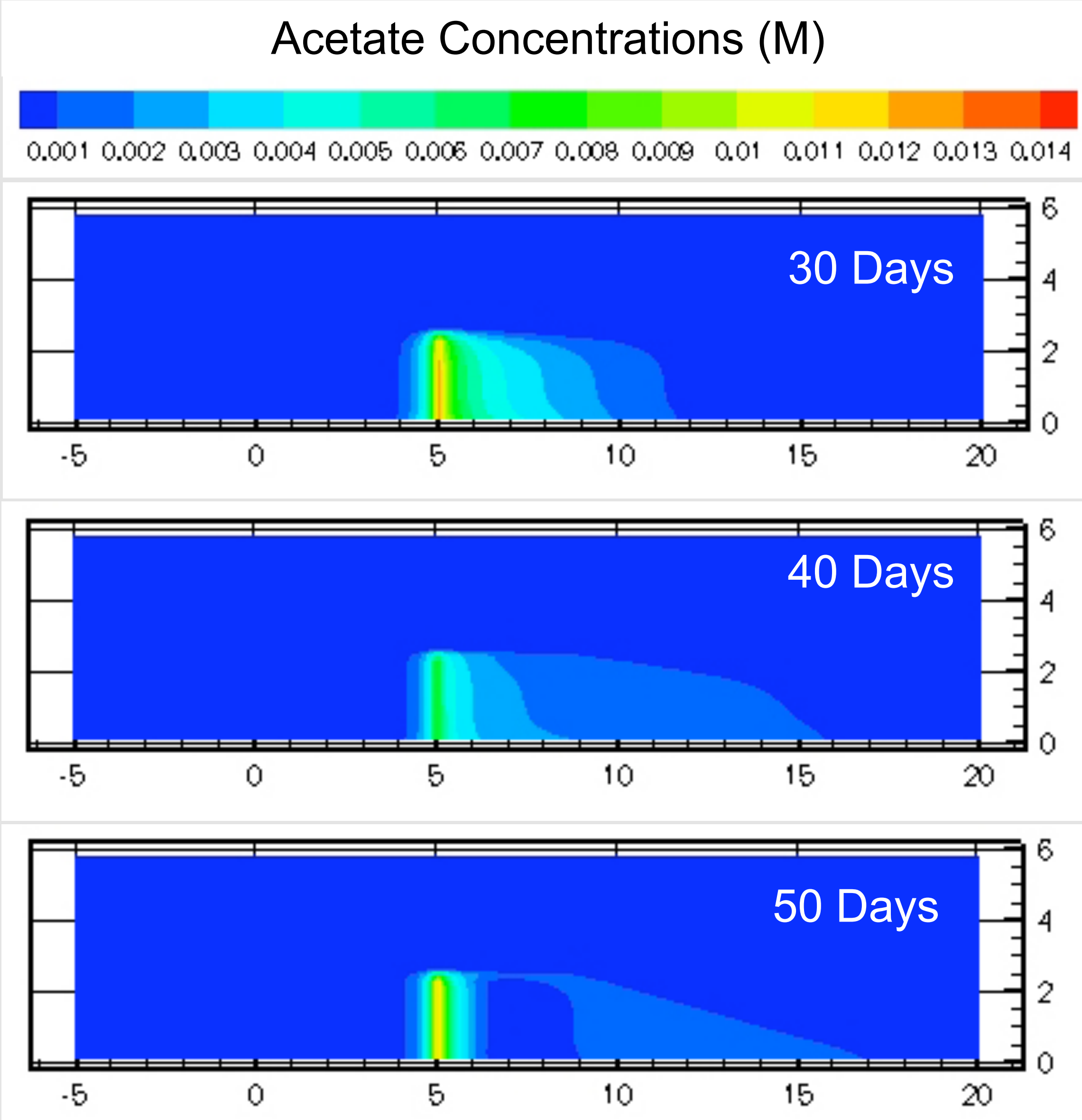
- 2-phase flow model of aquifer-vadose zone system
- Hysteretic saturation function calculates entrapped gas during 2003 transient
- Oxygen entrapped during water table rise dissolves into GW
- Water table recession moves enhanced DO deeper in the aquifer





Battelle

Coupling the Processes

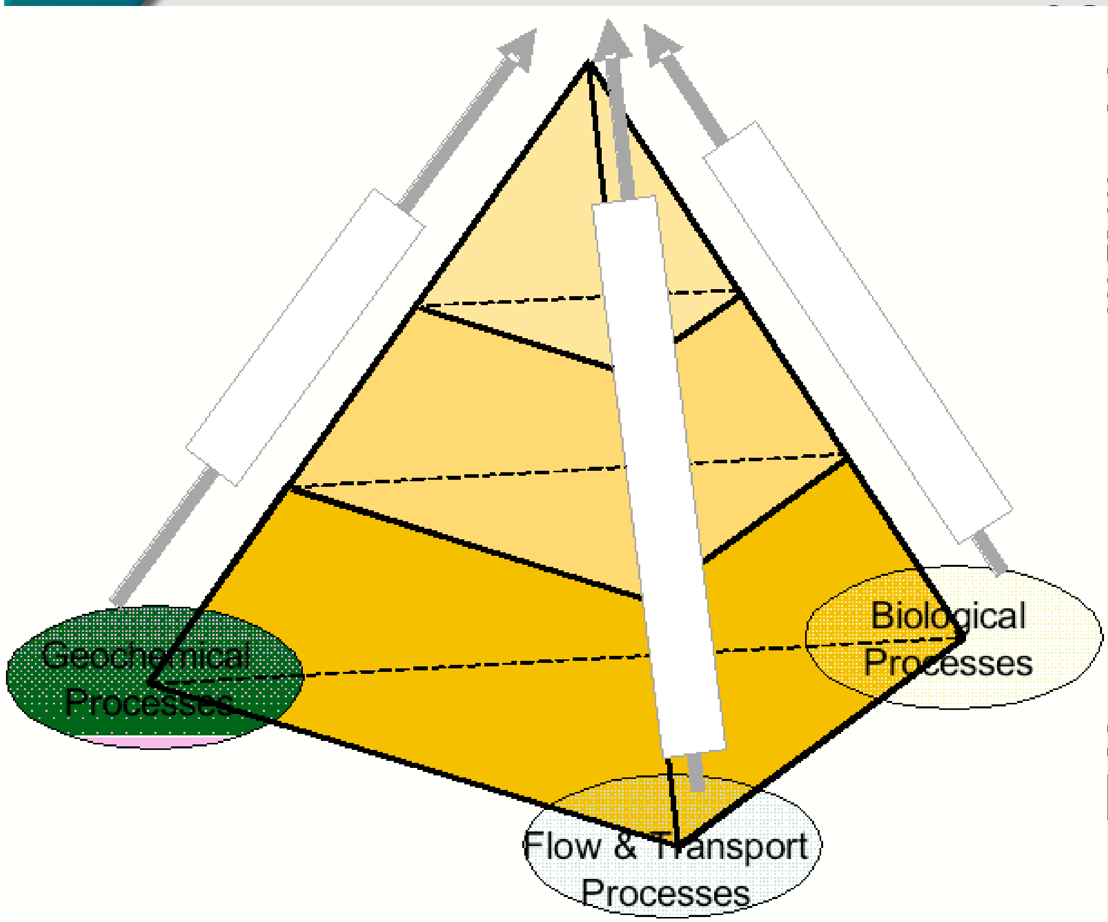


2002 Field Experiment

- 2-phase 3D flow simulation
- Oxygen entrapment during water table transients
- Transient influent water chemistry
- Transient acetate injection
- Density effects
- Biogeochemical reactions

Battelle

Path Forward



- Plenty of issues identified by
  rlier work
- C providing opportunity to
  gin to holistically address
  e goal of a quantitative field
  ale understanding of
  anium bioremediation
  - Paradigm shift from extension of laboratory studies to field-scale context of site-specific conditions
  - Address “THE GAP” between fundamental research and field-scale reactive transport modeling
- llaborative modeling
  pertise
  - Carl Steefel, biogeochemical reactive transport from Hubbard et al. EMSP project
  - Mahadevan/Scheibe, in silico modeling from Lovley et al. ERSP project