



*Subsurface Flow and Transport  
Modeling Research: Incorporating  
Biologically Mediated Processes*

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# Predicting Coupled Process Behavior in Field-Scale Systems

## Recent Workshops

- “Integrating Numerical Models of Reactive Flow and Transport into Fundamental Geoscience Research,” DOE-BES, June 2003
  - “A Science-Based Case for Large-Scale Simulation,” DOE-SC, June 2003
  - “Conceptual Model Development for Subsurface Reactive Transport Modeling,” Multiagency Working Group on Subsurface Reactive Solute Transport, April 2004
- ▶ Reliable prediction of field scale behavior is 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
  - ▶ Reactive transport models integrate fundamental earth science research and focus on complex natural environments where individual time and space-dependent processes are linked
  - ▶ Need for multidisciplinary research teams dedicated to developing a quantitatively mechanistic understanding of behaviors at a particular field site to address the range of scales and multiple interacting processes
  - ▶ Build field-scale process models on a framework of understanding from fundamental experiments and characterization studies at complementary length scales in the field

# Conceptual Model: Old Rifle Biostimulation Experiments

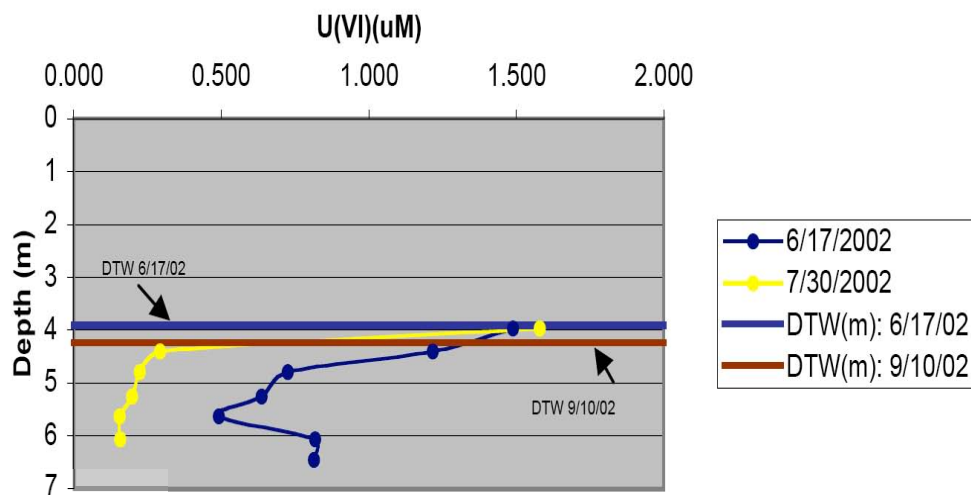
- ▶ Bulk of uranium and sulfate in the aquifer originated as leachate from mill tailings
- ▶ Uranium transported as U(VI) with the bulk adsorbed to the sediments under background geochemical conditions
- ▶ Acetate stimulates the growth of microbial populations that remove aqueous U(VI) from solution via homogeneous reduction reactions that form uraninite
- ▶ Initial bioreduction of aqueous U(VI) is 75 to 85 percent efficient and is attributed to iron reducing bacteria that use Fe(III) minerals as a terminal electron acceptor
- ▶ Once bioavailable iron is depleted, the iron reducing bacteria are succeeded by sulfate reducing bacteria, which are less efficient at U(VI) removal from groundwater



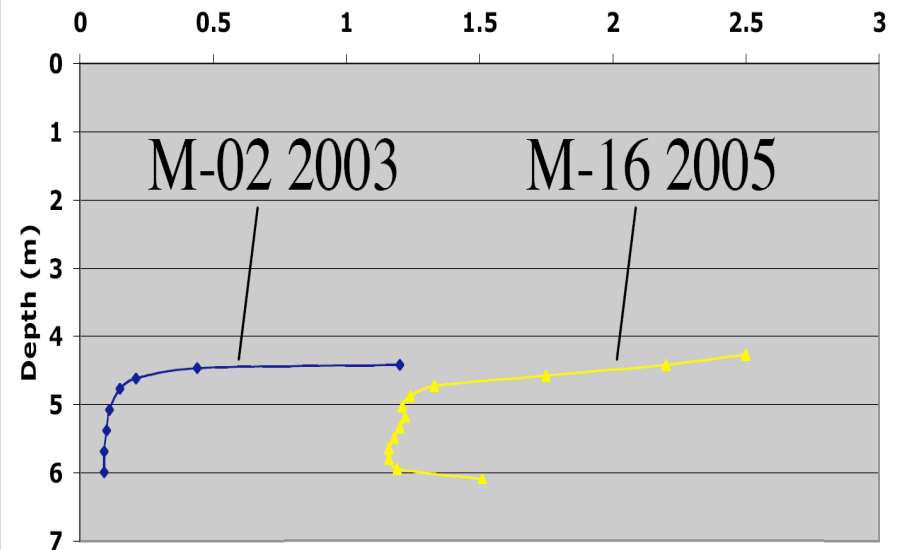
# How do spatial and temporal variations in hydrogeology and chemistry affect uranium behavior?

- ▶ Heterogeneous materials
  - Permeability
  - Iron and uranium
- ▶ 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

M-03 U(VI) vs. Depth (m) 6/17-9/19/02



DO (mg/l)



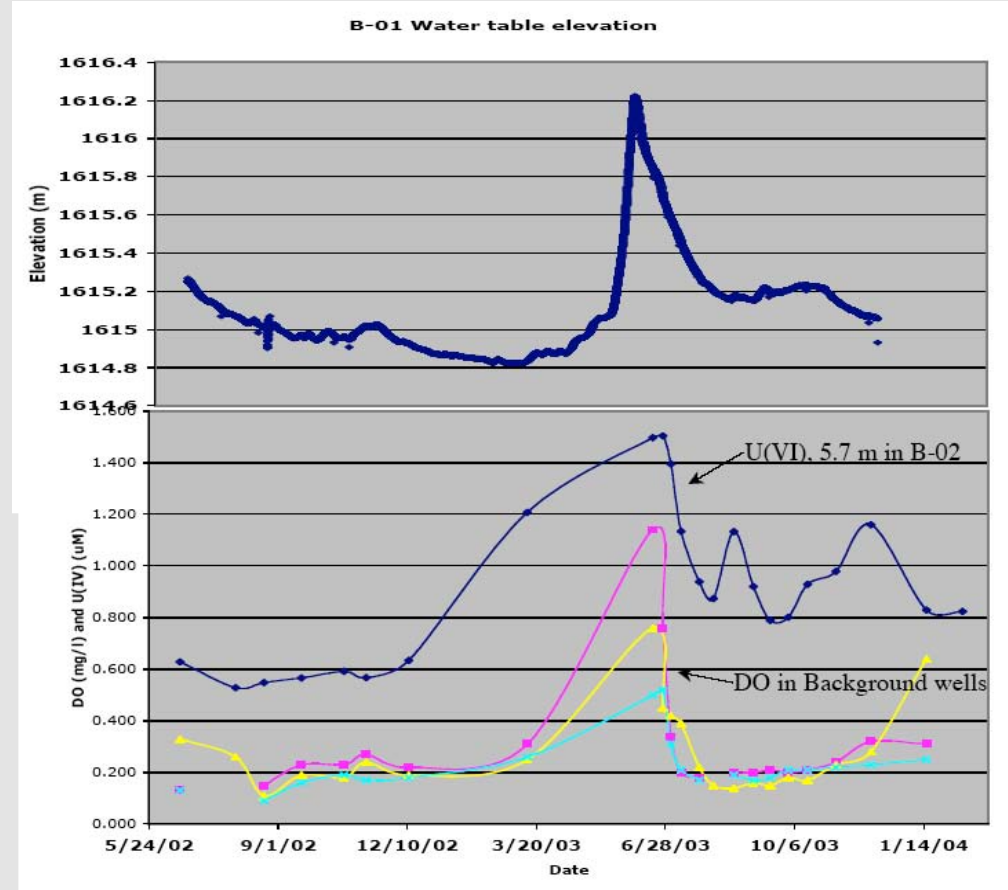
# How do seasonal and episodic hydrologic events affect uranium behavior?

## Seasonal and event-driven changes

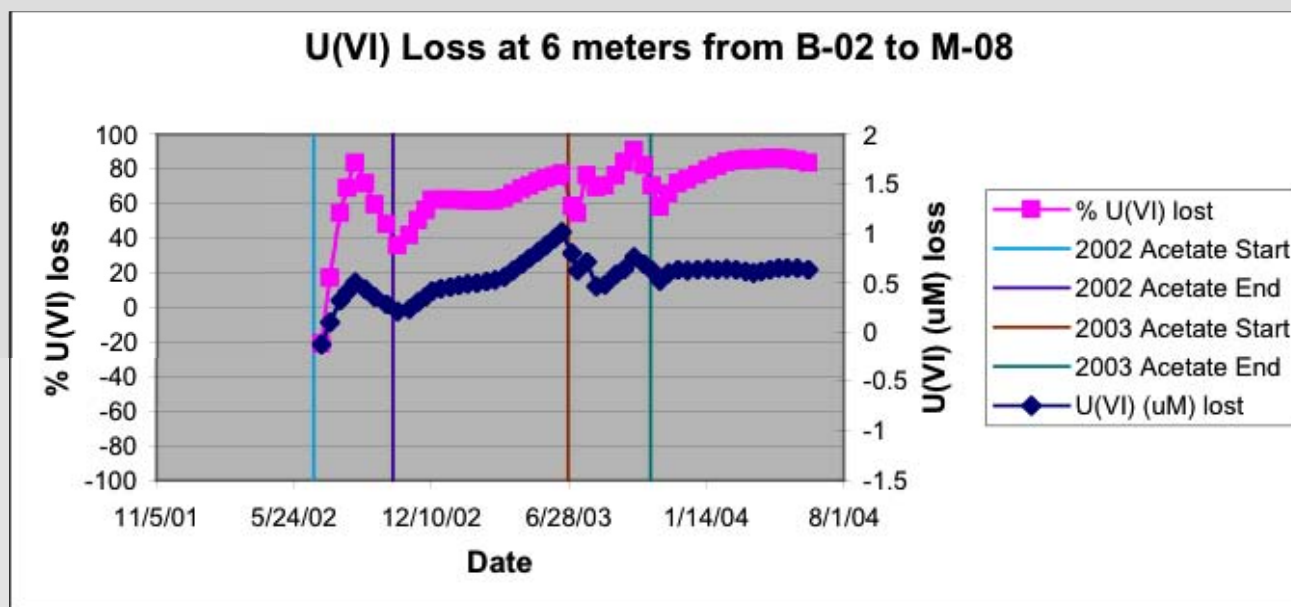
- Velocity field
- Oxidation of zones affected by water table fluctuations

## Issues

- Rapid oxidation of zones affected by water table fluctuations
- Highest U concentrations bypassing treatment zones



# What controls the post-amendment uranium behavior?



- ▶ Residual enzymatic reductive capacity of biomass
- ▶ Uranium surface complexation
- ▶ Fe(II) adsorption / desorption
- ▶ Mineral precipitation and dissolution [Fe(III) oxides/hydroxides, uraninite, FeS(am), siderite, calcite]
  - Coprecipitation
  - Alteration in surface reactivity
  - Alteration of access to reactive surfaces

# Goal and Objectives

## Goal

**Systematic and quantitatively predictive understanding of the mechanistic contribution by individual subsurface processes to the observed uranium behavior at the Old Rifle UMTRA field site.**

## ► Objectives

- *Determine the interplay between microbial and abiotic reactions governing field-scale bioremediation in the context of site-specific hydrologic and geochemical conditions*
- *Determine the impact of biostimulation on the geochemical controls (Eh, carbonate speciation and complexation, pCO<sub>2</sub>, mineral solubility, adsorption, pH) governing the mobility and long-term fate of uranium*

# Approach

- ▶ Build field-scale conceptual process models
  - Flow and transport
  - Biogeochemistry of biostimulation
  - Uranium surface complexation
- ▶ Systematically integrate process models into a comprehensive field-scale flow and biogeochemical reactive transport simulation capability
  - TEAPs and abiotic consequences of biostimulation affecting uranium mobility
  - Reoxidation and uranium mobility
    - Latent capacity for removal of aqueous U(VI)
    - Evolving surface chemistry (mineral precipitation/dissolution, adsorption/desorption)
- ▶ Philosophy
  - Start simple to isolate major behaviors
  - Systematically add process complexity and detail
  - Use modeling to gain insight and target knowledge gaps



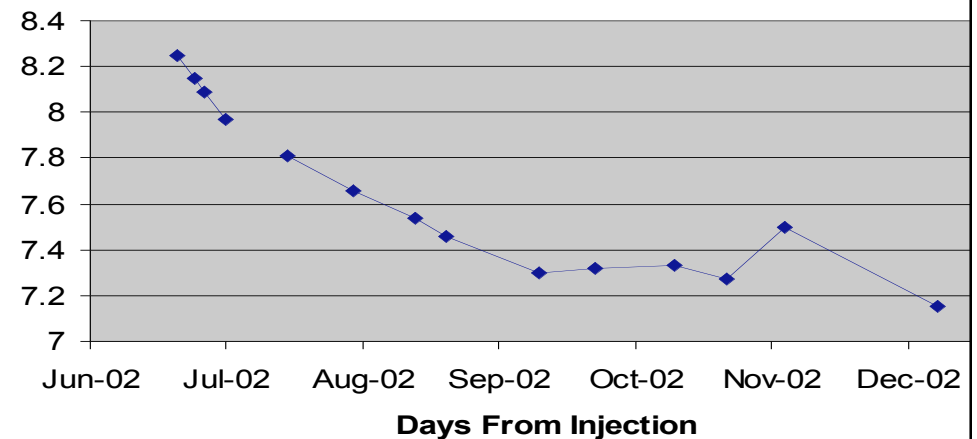
# 2002 Flow Field

- ▶ 2002 field experiment
  - No prior augmentation
  - Steady flow field
  - Injection June 22 – Oct 23
- ▶ Modeling assumptions
  - 1-D domain
  - Constant velocity and dispersivity based on bromide transport
  - Bulk tank release rate distributed uniformly over injection gallery
  - Injection averaged over saturated thickness

## Gradient Direction and Relative Magnitude

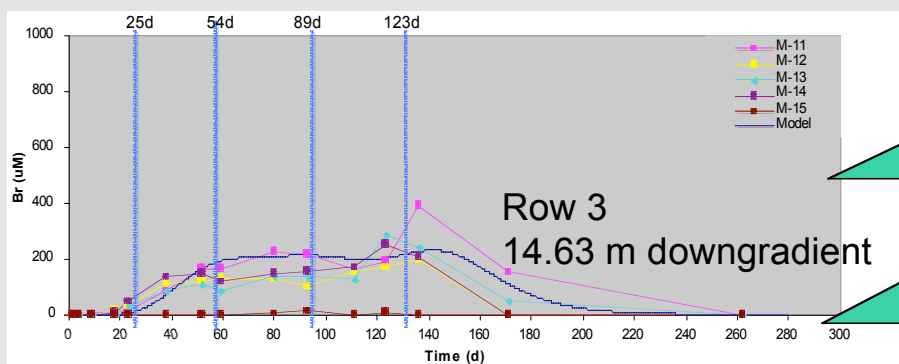
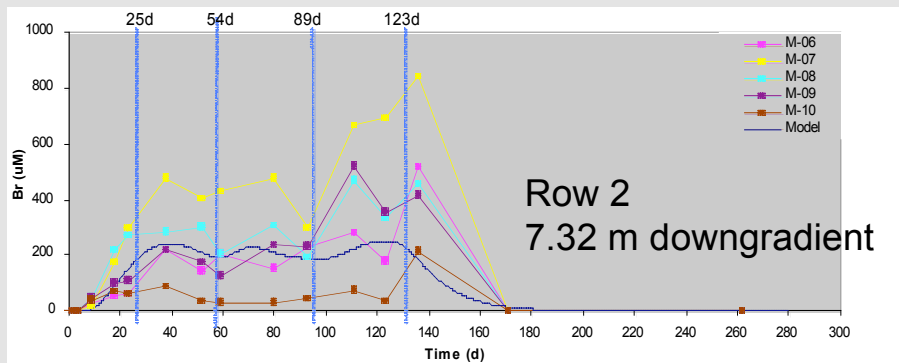
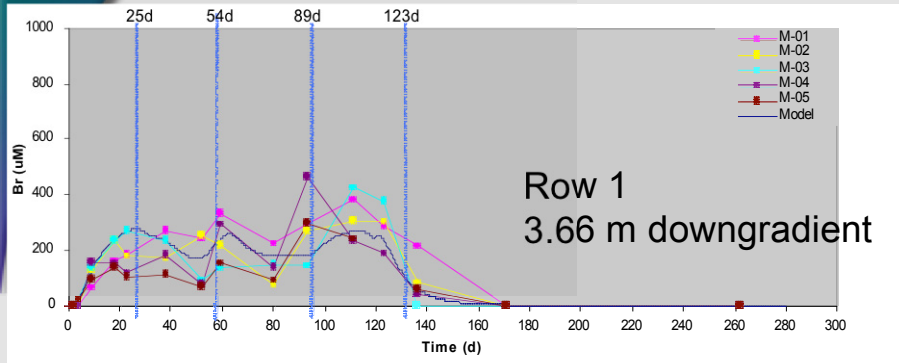


2002 M-07 Water Level

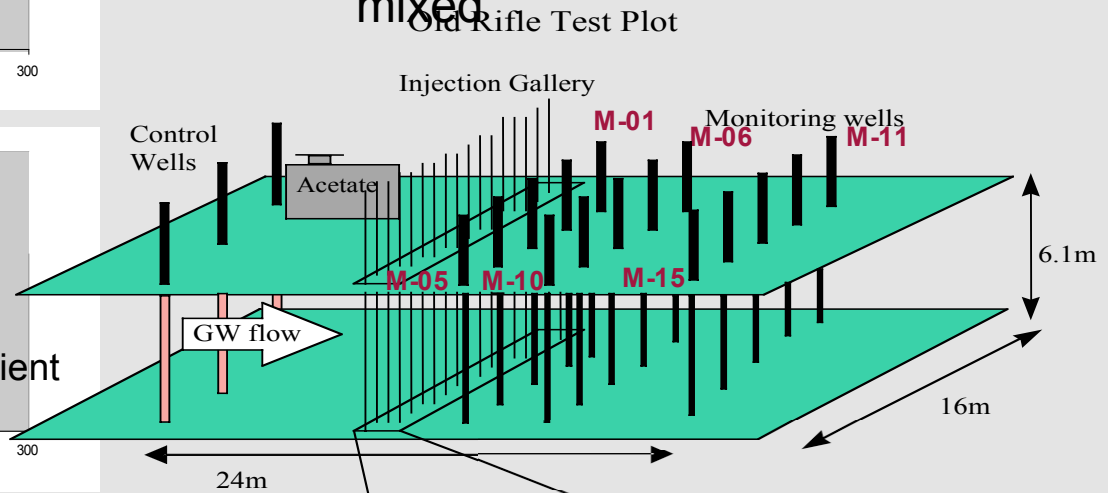


# Initial Flow and Transport Modeling

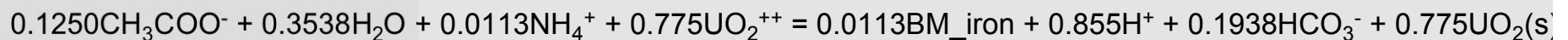
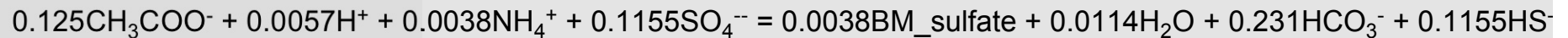
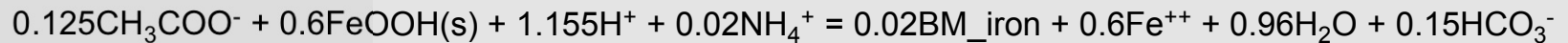
- ▶ 10 mM Bromide injected
- ▶ Breakthrough at monitoring wells



- General trends reproduced with constant velocity and dispersivity
- Row 2 has highest concentrations and maximum variability missed by average injection
  - Preferential flow paths
  - Release not uniform or fully mixed



# Biologically Mediated Reactions



## ▶ 3 energetics-based TEAP reactions

- Stoichiometry from Rittman/McCarty 2001
- Includes biomass yield
- Uranium reduction only active during iron reduction

## ▶ Dual Monod Rate Law

- Half-saturation constants from Wang/Jaffe et al. 2003
- Calibrate rate and threshold concentration for utilization

$$R_C^{bio} = - \sum_{eA}^{N_{eA}} \chi_{eA} \mu_{m,eA} \left( \frac{C_C}{K_{s,C} + C_C} \right) \left( \frac{C_{eA}}{K_{s,eA} + C_{eA}} \right)$$

(Fe(III) TEAP replaces last term with free sorption sites)

where

$N_{eA}$  = number of terminal electron acceptors

$C_C$  = dissolved organic substrate concentration (i.e., acetate)

$C_{eA}$  = terminal electron acceptor concentration

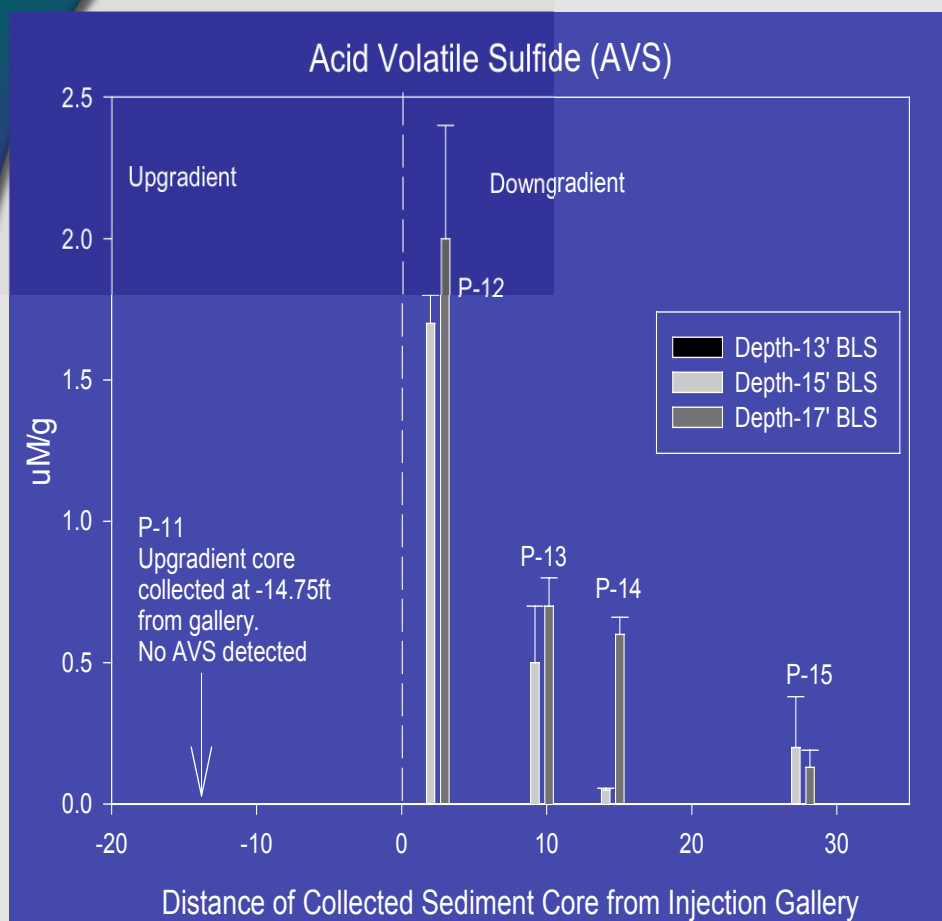
$\chi_{eA}$  = indicator coefficient for terminal electron acceptor utilization

$\mu_{m,eA}$  = organic substrate oxidation rate for terminal electron acceptor

$K_{s,C}$  = half – saturation coefficient for organic substrate

$K_{s,eA}$  = half – saturation coefficient for terminal electron acceptor

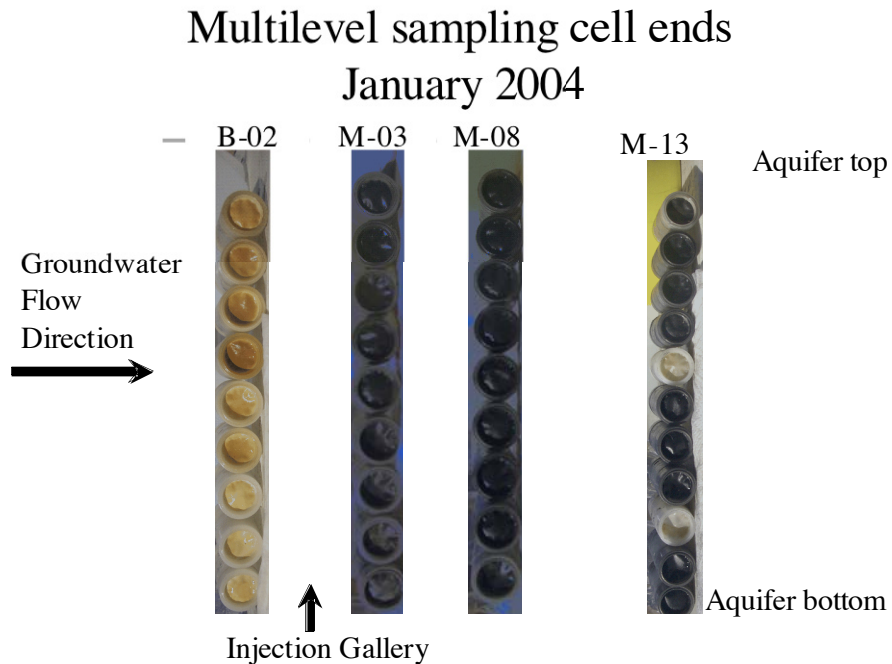
# Sulfate / Sulfide Behavior



- ▶ 3-4 mM/L sulfide generation
- ▶ Typical field aqueous sulfide measurement 3 uM/L
- ▶ Implies sulfide associated with sediment
- ▶ 2003 AVS: equivalent to ~15 mM/L, 5 mM/L, 4 mM/L, 1.5 mM/L



# Insights: Need for additional Fe<sup>++</sup>



- ▶ FeS formation on surface inferred
- ▶ Need 3-4 mM/L Fe<sup>++</sup> to react sulfide
- ▶ Maximum aqueous Fe<sup>++</sup> measurement is 196  $\mu$ M/L
- ▶ Additional Fe<sup>++</sup> would have to be associated with solid phases
- ▶ Fe<sup>++</sup> adsorption
  - Consistent with other investigators

## PNC-CAT x-ray microprobe

- Blackened sediment
- Fe and Sulfur
- No XRD for sulfide minerals
- evidence for FeS(am)

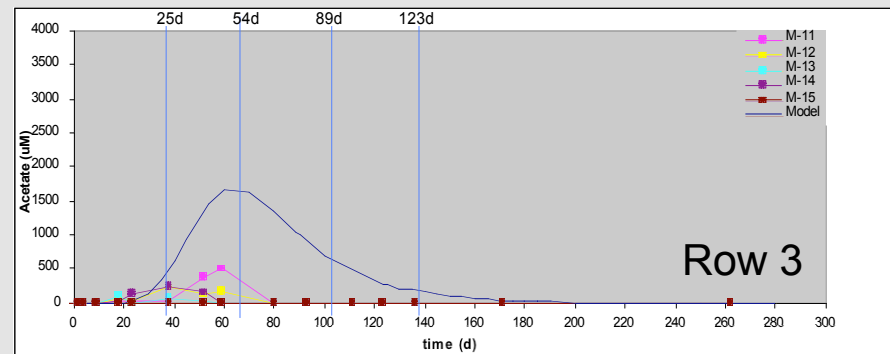
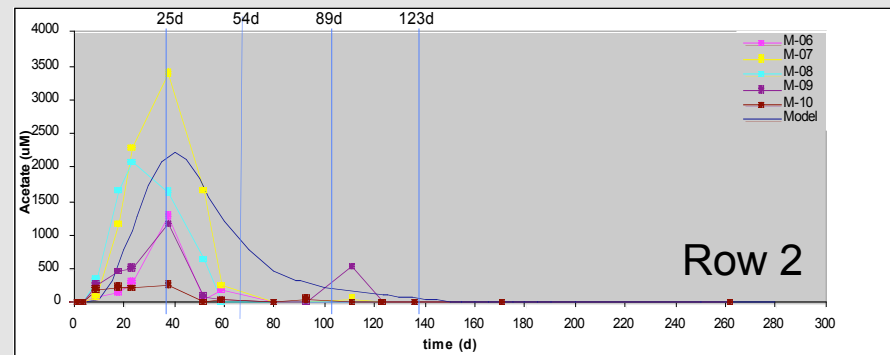
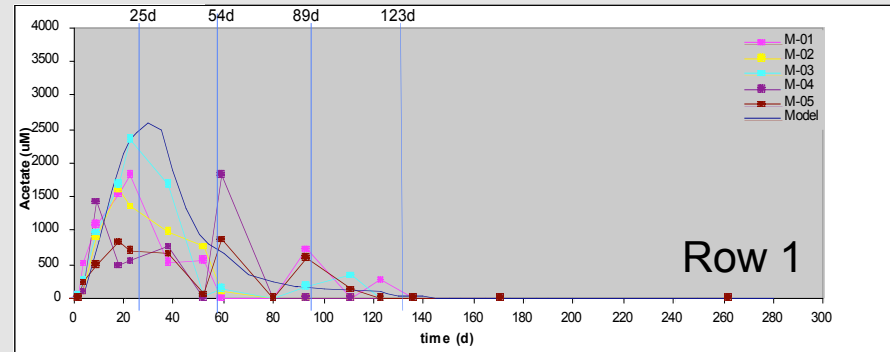
# Expansion of the Biogeochemical Reaction Network

42 total reactions

- Aqueous
  - $\text{Ca}^{++}$ ,  $\text{Fe}^{++}$ ,  $\text{K}^+$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$ ,  $\text{H}^+$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^-$ ,  $\text{HS}^-$ ,  $\text{SO}_4^{--}$
- Mineral
  - $\text{CaCO}_3$ ,  $\text{FeOOH}$ ,  $\text{FeCO}_3$ ,  $\text{FeS}$ ,  $\text{UO}_2$
- Sorption
  - $\text{Fe}^{++}$
- Biologically-mediated (by acetate)
  - $\text{Fe(III)}$ ,  $\text{U(VI)}$ , sulfate TEAPs

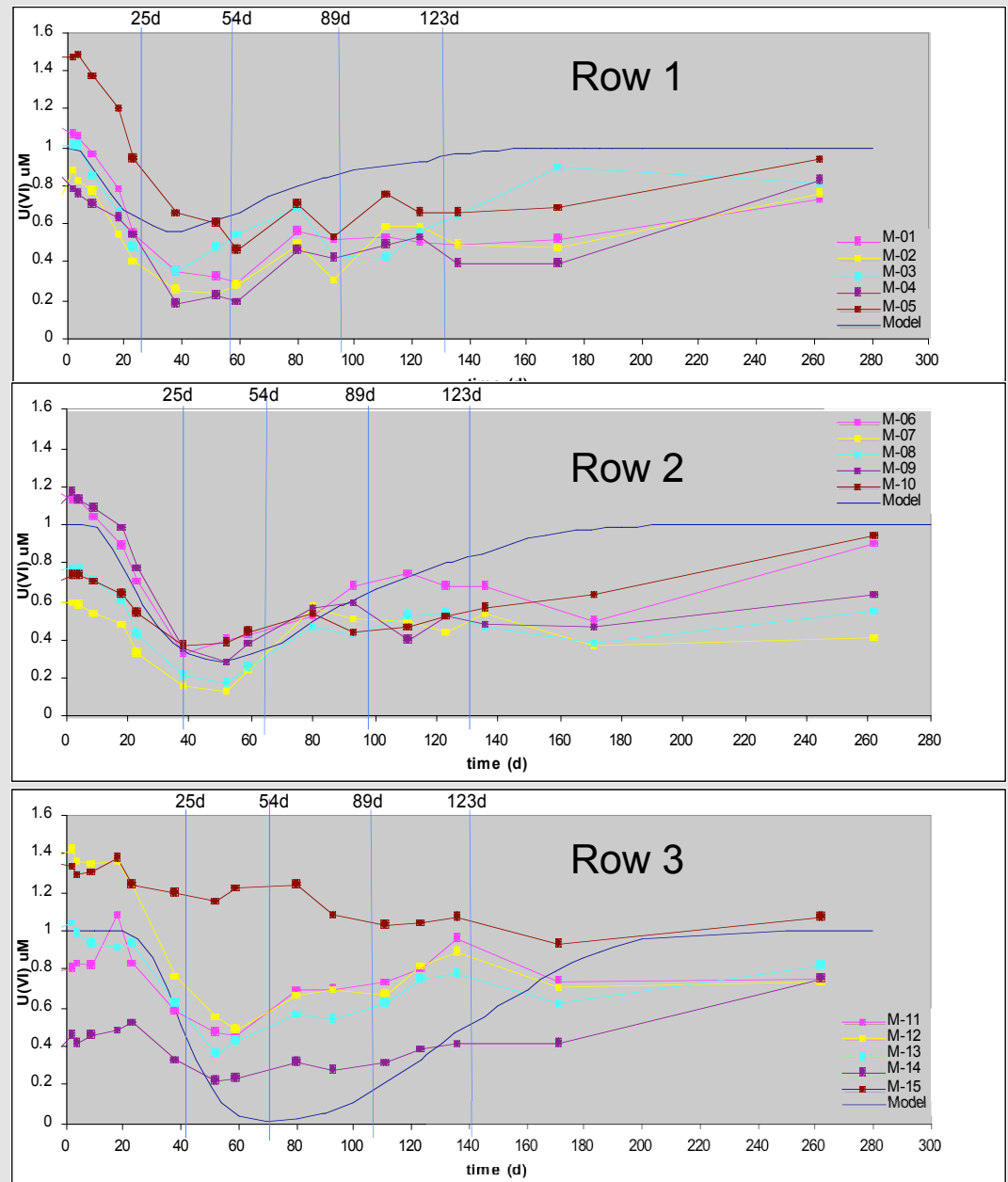
# Acetate

- ▶ Acetate injected for 123 days
- ▶ In Row 1, acetate concentrations diminish significantly after 40 days
  - Decrease in sulfate
  - Decrease in Fe<sup>++</sup>
- ▶ Model: acetate peak diminishes with travel distance
- ▶ Acetate concentrations are spatially and temporally variable
  - Multiple peaks with later arrivals in Row 1
  - Highest concentration in Row 2
  - Row 3 has much lower acetate than predicted



# Uranium Bioreduction

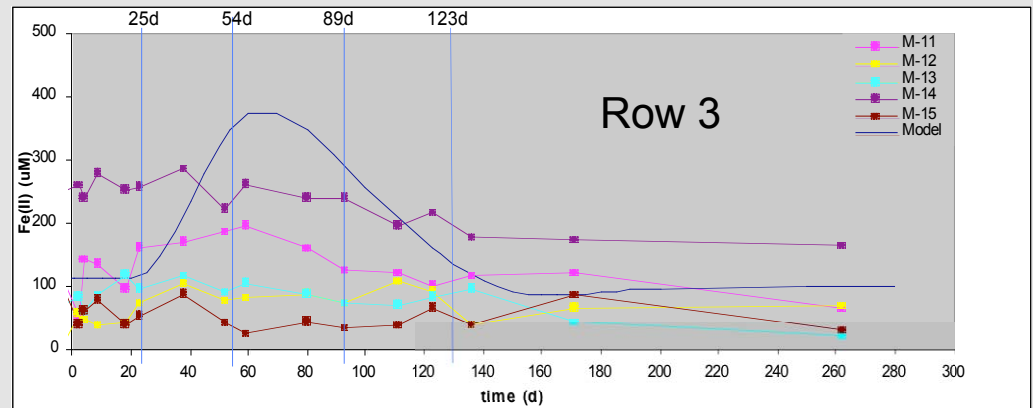
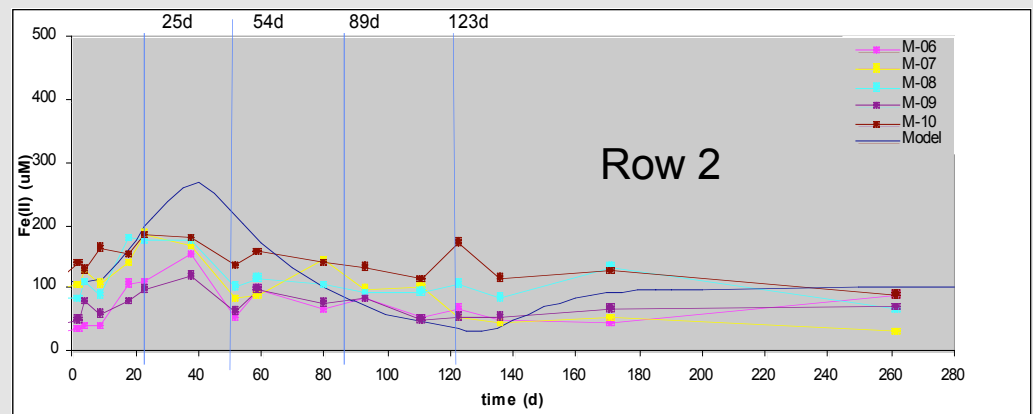
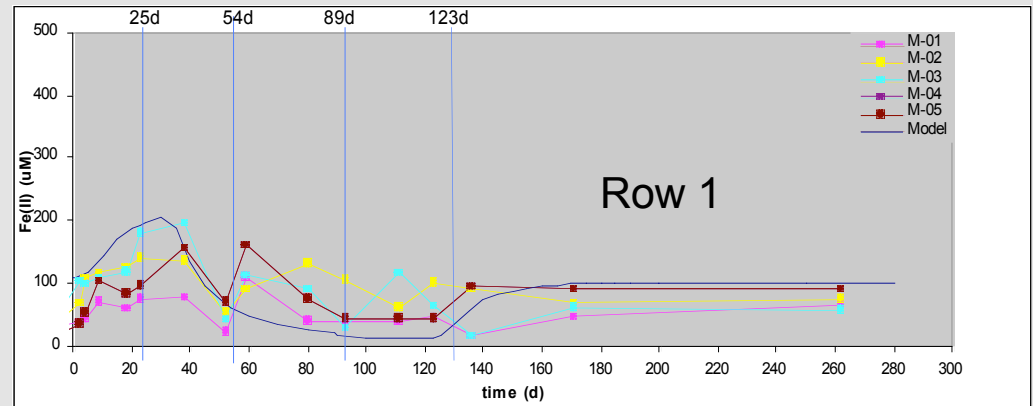
- ▶ Initial aqueous U(VI) spatially variable
- ▶ Initial timing of aqueous U(VI) removal reproduced by model





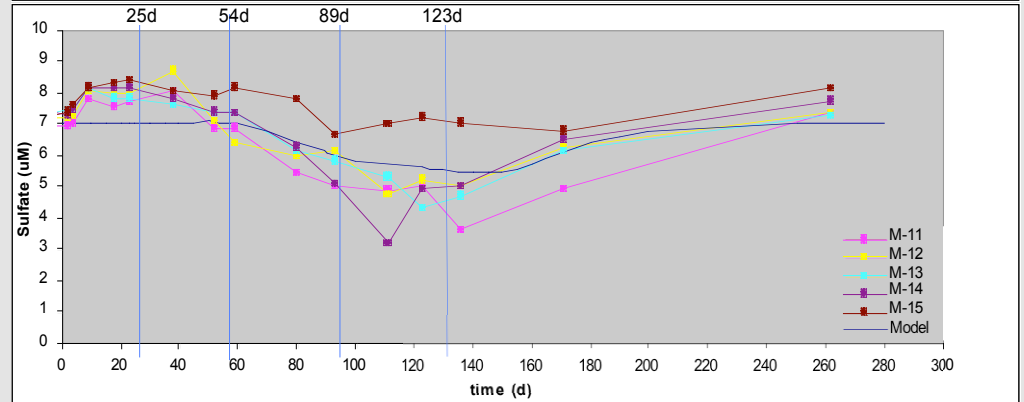
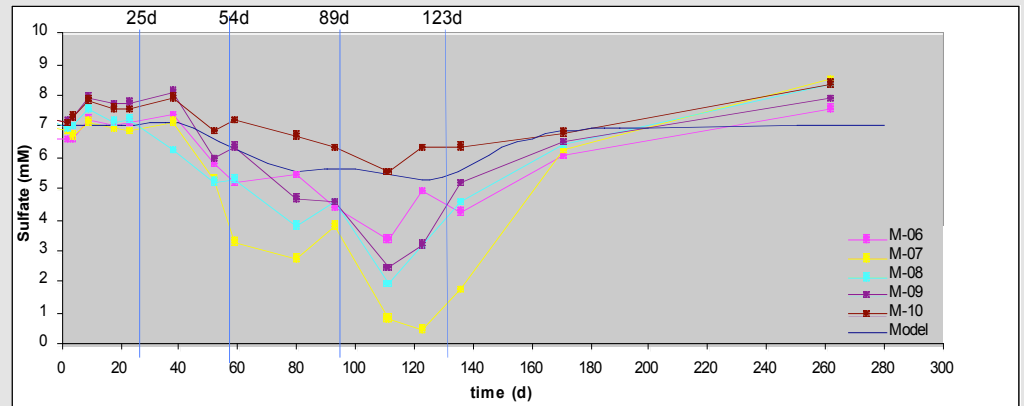
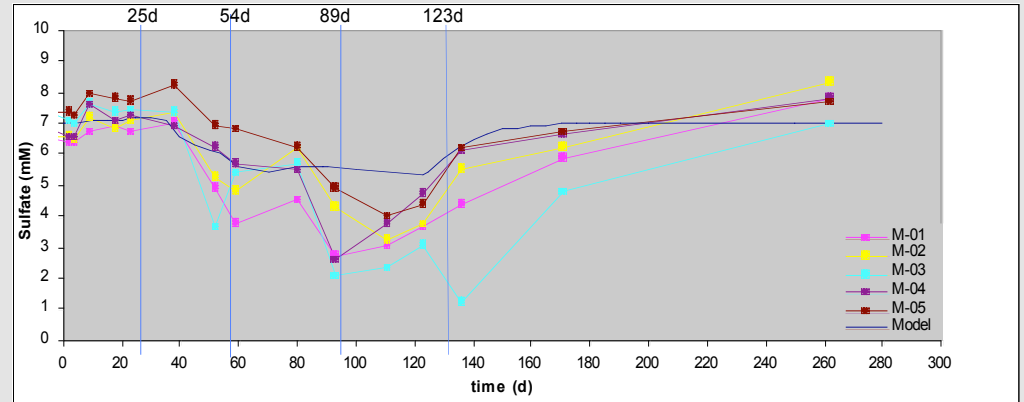
# Iron Bioreduction, Dissolution, and Sorption

- ▶ Initial Fe<sup>++</sup> increase followed by decrease after onset of sulfate reduction
- ▶ Model predicts cumulative peak which is not obvious in well data
- ▶ Effect is observed in 2004 experiment
- ▶ Issues
  - Fe<sup>++</sup> adsorption
  - Fe<sup>++</sup> production may be much higher



# Sulfate Bioreduction

- ▶ Sulfate reduction begins after 40 days of iron reduction
- ▶ Rapid and complete utilization of acetate
- ▶ Sulfate reduction limited by acetate supply
- ▶ 3 - 4 mM sulfate removed underestimated by model



# Uranium Experiments on Rifle Sediments

- ▶ Rifle Aquifer Background Sample (RABS)
- ▶ Sediment sample collected December 2004
  - 10 gallons of < 2 mm prepared
  - Experiments
    - Grand Junction
    - Princeton (Jaffe)

## ▶ Issues

- High background U
- Break off point between labile and nonlabile
- Kinetics

	NABS	RABS
Particle size, mm	< 3	< 2
Surface area, m <sup>2</sup> /g	5.15	4.256
Labile U(VI), ug/g	0.208	<b>1.12</b>
Elapsed time, h	504	530

- ▶ Set of batch equilibrium adsorption experiments
  - RABS+AGW-3
  - 10<sup>-8</sup> to 10<sup>-5</sup> M/L U(VI)

	Solid to Solution	TIC	pCO <sub>2</sub>	pH
ADS-1	25 g/L	8.25 mg/L	0.10%	7.62
ADS-2	820	108.35	2.39	7.33
ADS-3	125	92.7	2.23	7.28
ADS-4	125	100.2	3.62	7.06
ADS-5	250	238.4	22.8	6.52
ADS-6	125	100.8	5.23	6.90
ADS-7	250	213.6	20.8	6.52

- ▶ Comparison of experimental results with Naturita surface complexation model
  - RABS appears to be more sorptive
  - Adsorption of lower U(VI) concentrations sensitive to labile U(VI)

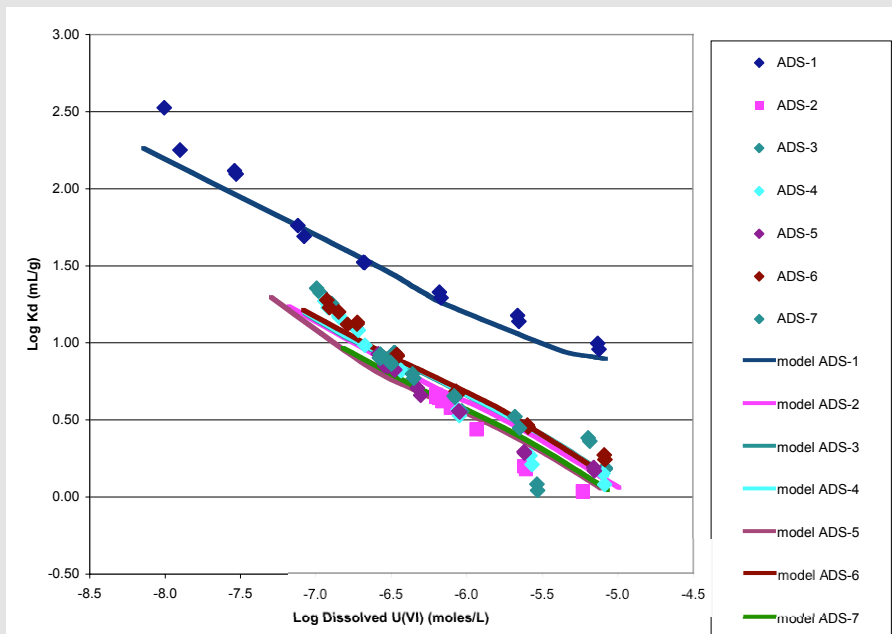
# Uranium Surface Complexation Modeling

## Generalized composite surface complexation model

- Preliminary fit of formation constants for 2 surface reactions, 3 site types
- 1.92  $\mu\text{M}/\text{m}^2$  site density (bidentate)
- 23 aqueous uranium complexation reactions
  - Includes Ca- $\text{UO}_2$ - $\text{CO}_3$  ternary complexes

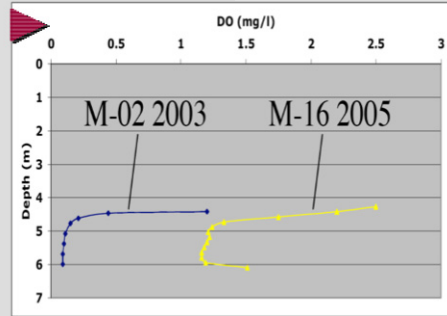
U(VI) Surface Reaction	Log $K_f$
$\text{SSOH} + \text{UO}_2^{2+} = \text{SSOUO}_2^+ + \text{H}^+$	12.28
$\text{SOH} + \text{UO}_2^{2+} = \text{SOUO}_2^+ + \text{H}^+$	6.95
$\text{WOH} + \text{UO}_2^{2+} = \text{WOUO}_2^+ + \text{H}^+$	2.74
$\text{SSOH} + \text{UO}_2^{2+} + \text{H}_2\text{O} = \text{SSOUOOH} + 2 \text{H}^+$	0.033
$\text{SOH} + \text{UO}_2^{2+} + \text{H}_2\text{O} = \text{SOUOOH} + 2 \text{H}^+$	-2.12
$\text{SOH} + \text{UO}_2^{2+} + \text{H}_2\text{O} = \text{SOUOOH} + 2 \text{H}^+$	-5.01

Total site concentration of 1.92  $\mu\text{moles}/\text{m}^2$   
 SSOH denoting very strong binding sites: 0.01% of total sites  
 SOH denoting strong binding sites: 0.1% of total sites  
 WOH denoting weak binding sites: 99.89% of total sites



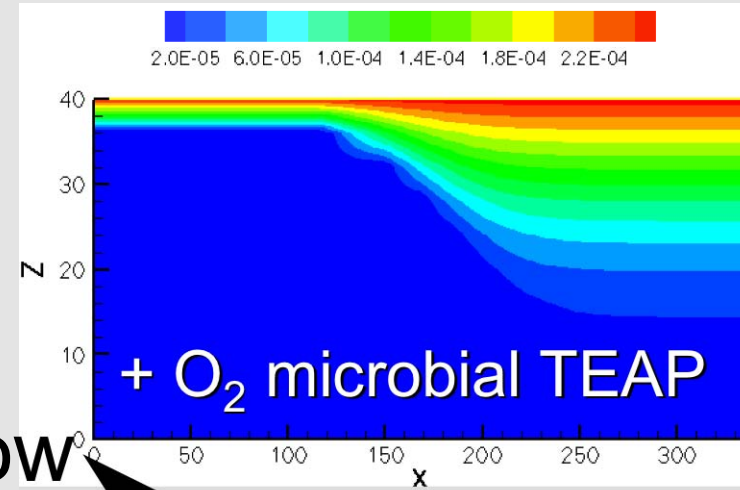
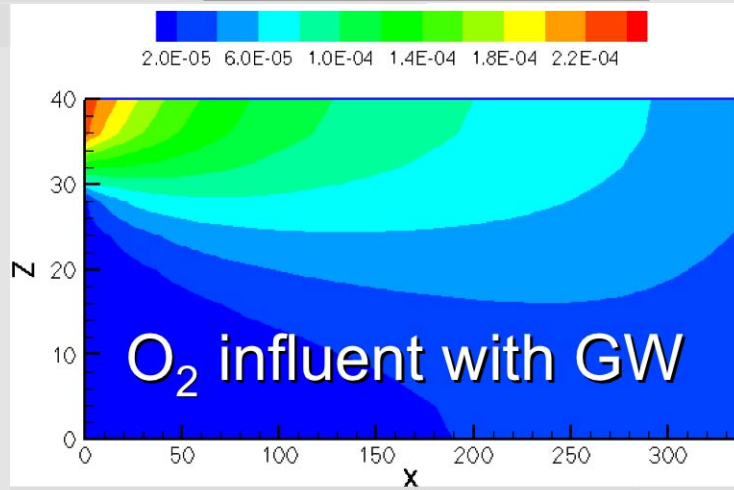


# Dissolved Oxygen Stratification: Framework for 2-D Reactive Transport

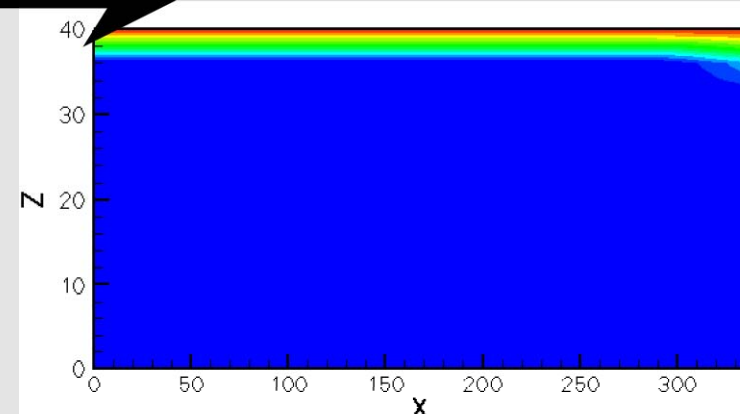
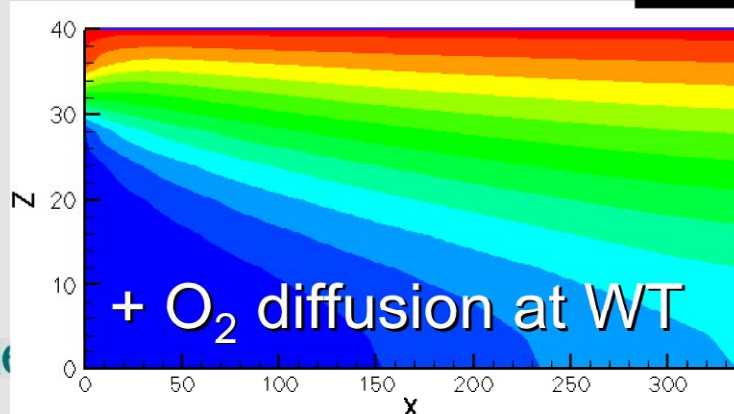


~20 cm layer of higher DO near water table

- Transported in from upgradient conditions
- Diffusion through water table



Flow →



# Next Steps

- ▶ 2-D simulations to investigate depth-dependent issues
  - Incorporate new information on permeability distribution in the vertical
  - Incorporate new information from geophysics
- ▶ Refine uranium surface complexation model
  - Assess labile uranium and adsorption kinetics
  - Consider other combinations of uranium surface complexation reactions and site types in calibration
  - Identify additional experiments for model refinement
- ▶ Incorporate new process models into comprehensive reactive transport simulator
  - Datasets
    - 2003 and 2004 field experiments
    - Laboratory experiments
  - Impacts of biostimulation on iron chemistry
    - dissolution of uranium-bearing Fe(III) minerals
    - generation of Fe(II) and effect of adsorbed Fe(II) on bioavailability of Fe(III) minerals
    - effect of precipitation and dissolution on the accessibility of Fe(III) and U(IV) mineral surfaces to aqueous components
  - Post-amendment uranium mobility
    - conditions for residual capacity to remove U(VI) from groundwater
    - conditions where ambient geochemistry is being re-established

# Acknowledgments

- ▶ University of Massachusetts
- ▶ University of Tennessee
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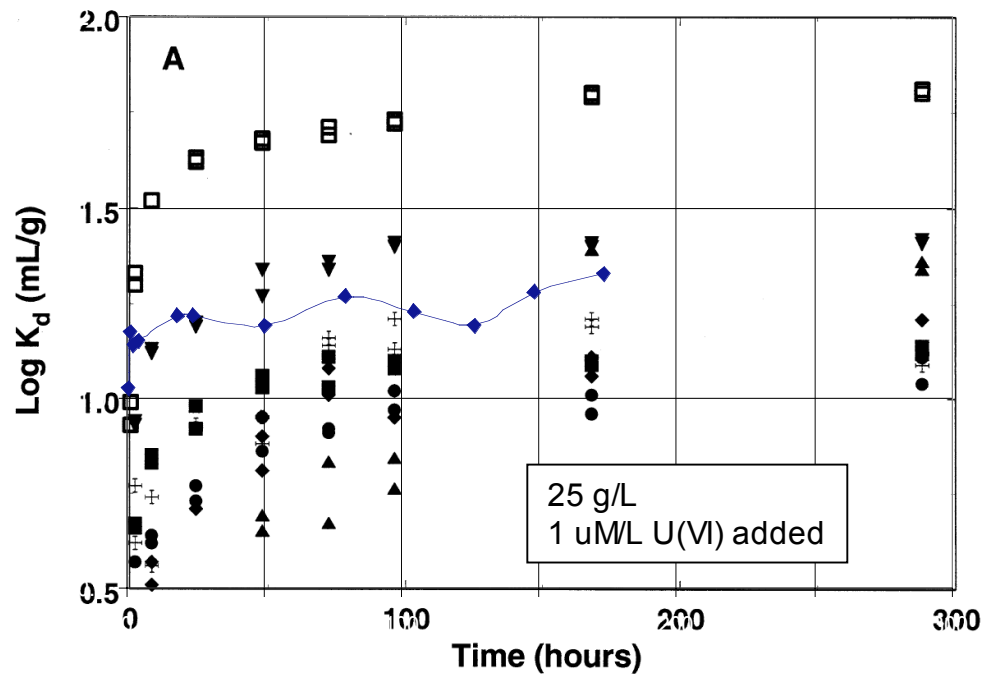
# Backup Slides

# Adsorption Experiments

## Experiments with AGW-3

- Approach based on Davis et al 2004
- Assess applicability of GC-SCM approach
- Compare with Naturita results

### Adsorption Kinetics



### AGW-3

in air at 0.8547 atm

pH 7.79

pCO<sub>2</sub> 0.06%

CaSO <sub>4</sub>	$2.33 \cdot 10^{-3}$
MgSO <sub>4</sub>	$1.52 \cdot 10^{-3}$
Na <sub>2</sub> SO <sub>4</sub>	$9.38 \cdot 10^{-4}$
CaCl <sub>2</sub>	$2.38 \cdot 10^{-3}$
KCl	$6.40 \cdot 10^{-5}$
NaHCO <sub>3</sub>	$5.38 \cdot 10^{-4}$



# Depth-Dependent Transport

