In Situ Immobilization of Uranium in Heterogeneous Porous Media via Biostimulation

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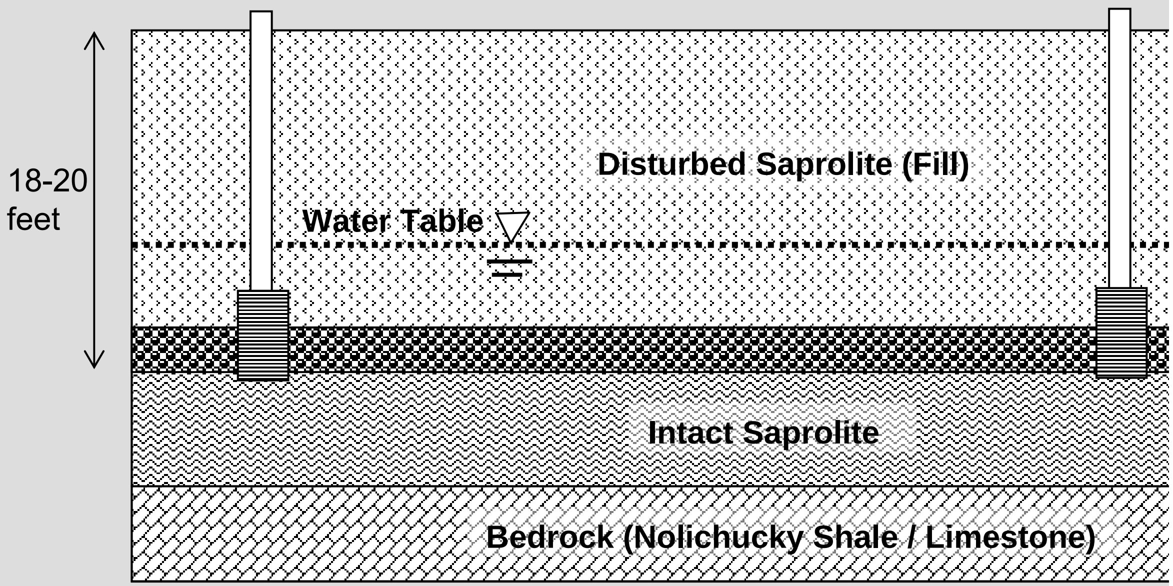
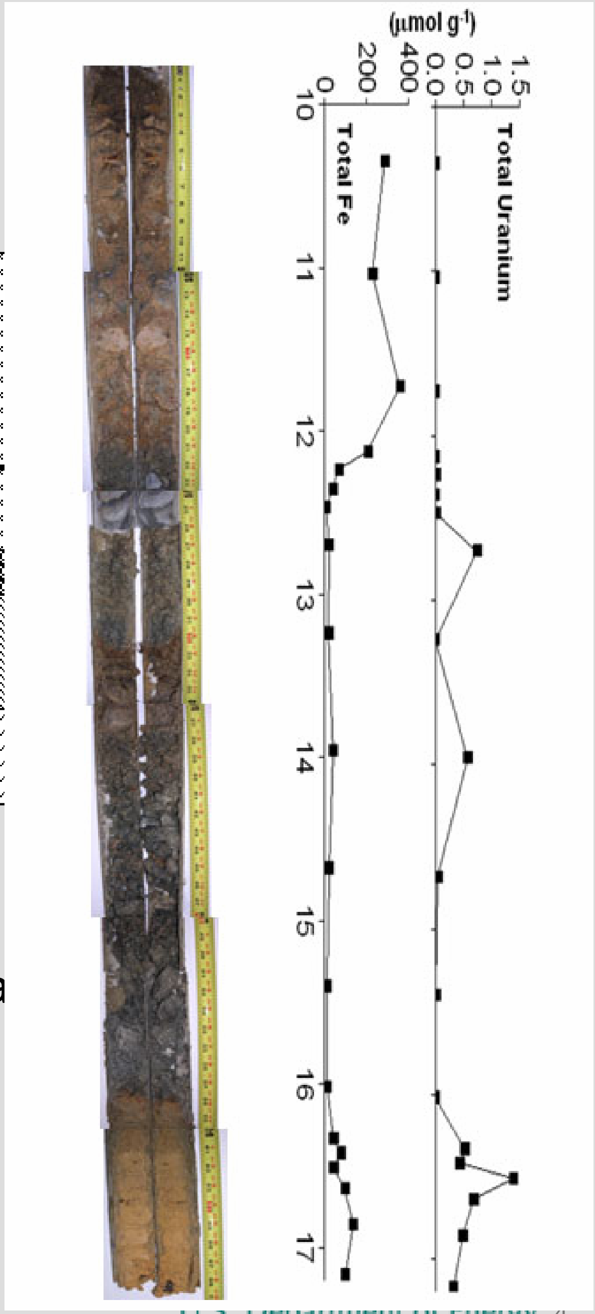
MLS
A B C D E

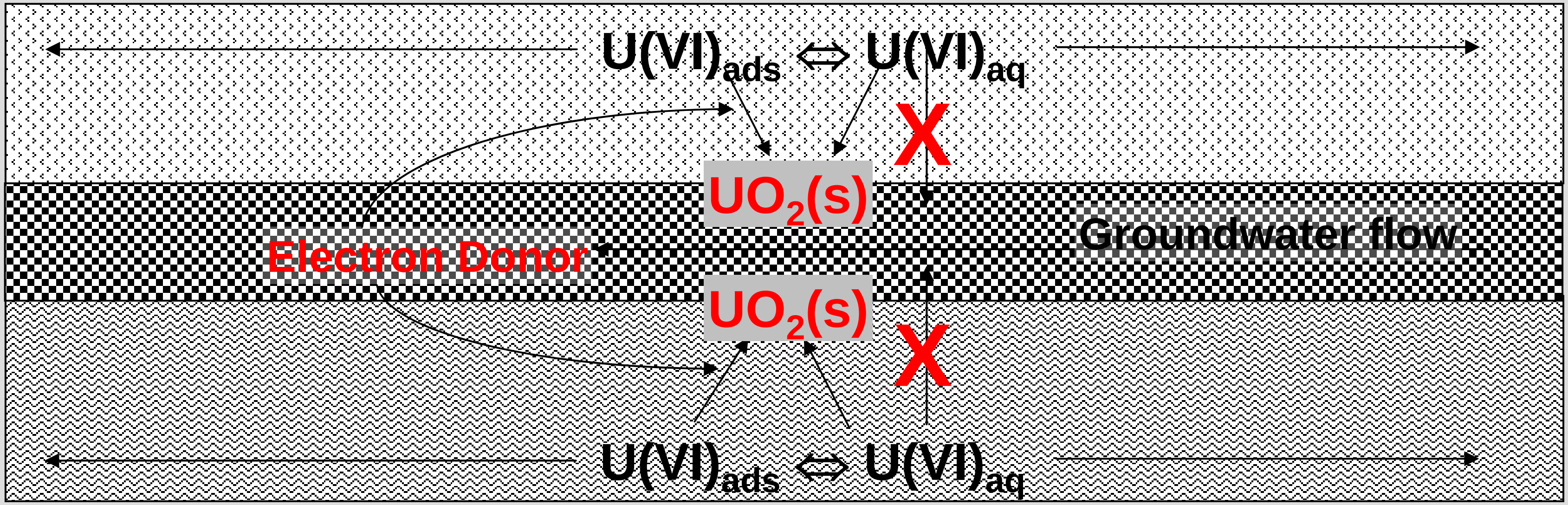
Introduction





- Three geologic materials
- Gravel layer at the bottom of the historically excava zone is dominant groundwater flow path
- High solid-associated uranium concentration at the gravel zone and saprolite zone

Introduction



Hypothesis - The injection of electron donor into the gravel layer will result in:

- ►Dispersive mass transfer into the adjacent fill/saprolite zones
- ►Formation of a microbarrier at the interface
- ►Immobilization of uranium

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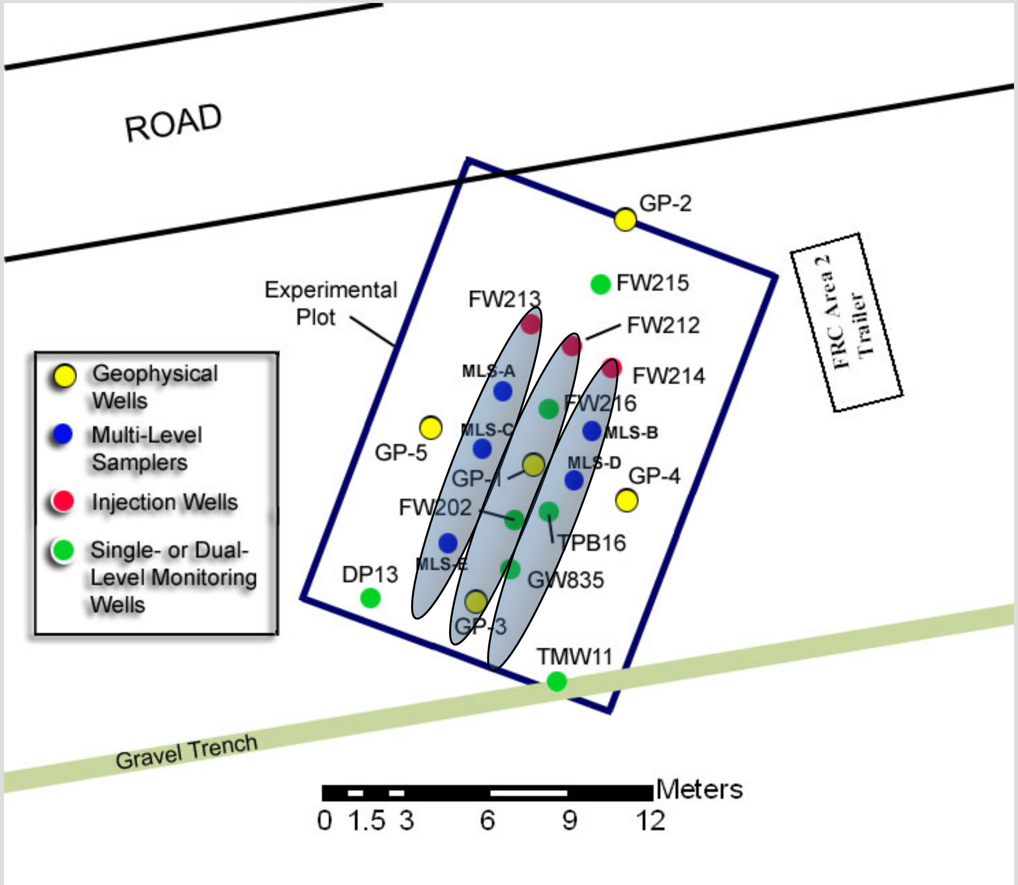
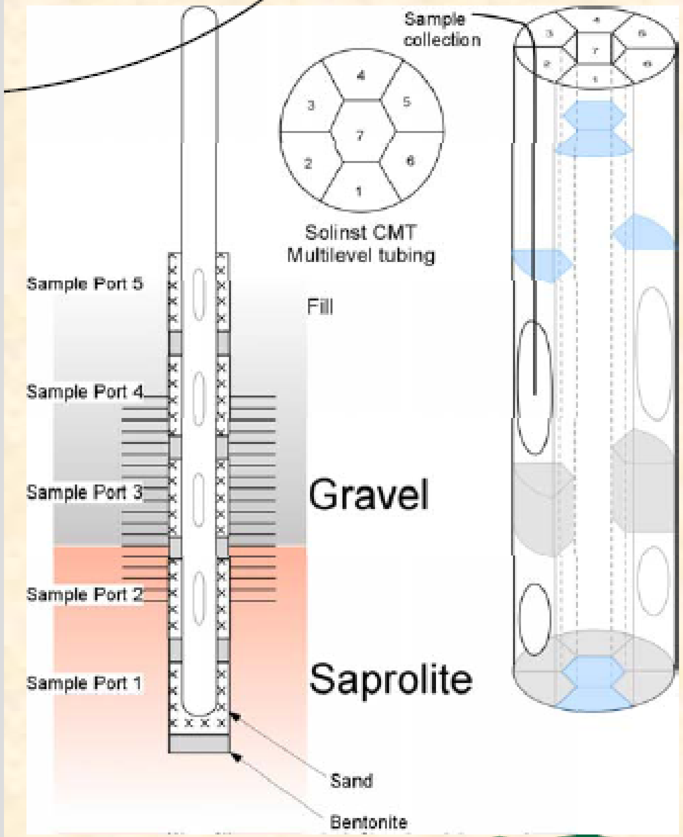
Biostimulation Experiment

- 10 mM ethanol, 5 mM bromide solution
- Three injection wells, 3 L/min each well
- 24-hour initial injection pulse followed by daily one-hour pulses
- Inflow of 0.5 mM NO_3, 0.885 mM SO_4 and 0.5 μM U from up-gradient
- Started late September 2005

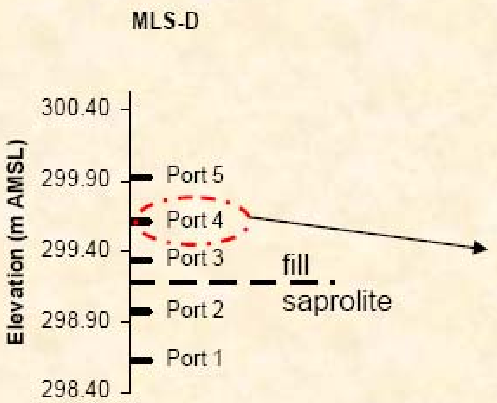


Multi-level Sampling (MLS) Wells – vertical resolution and across fill/ saprolite interface



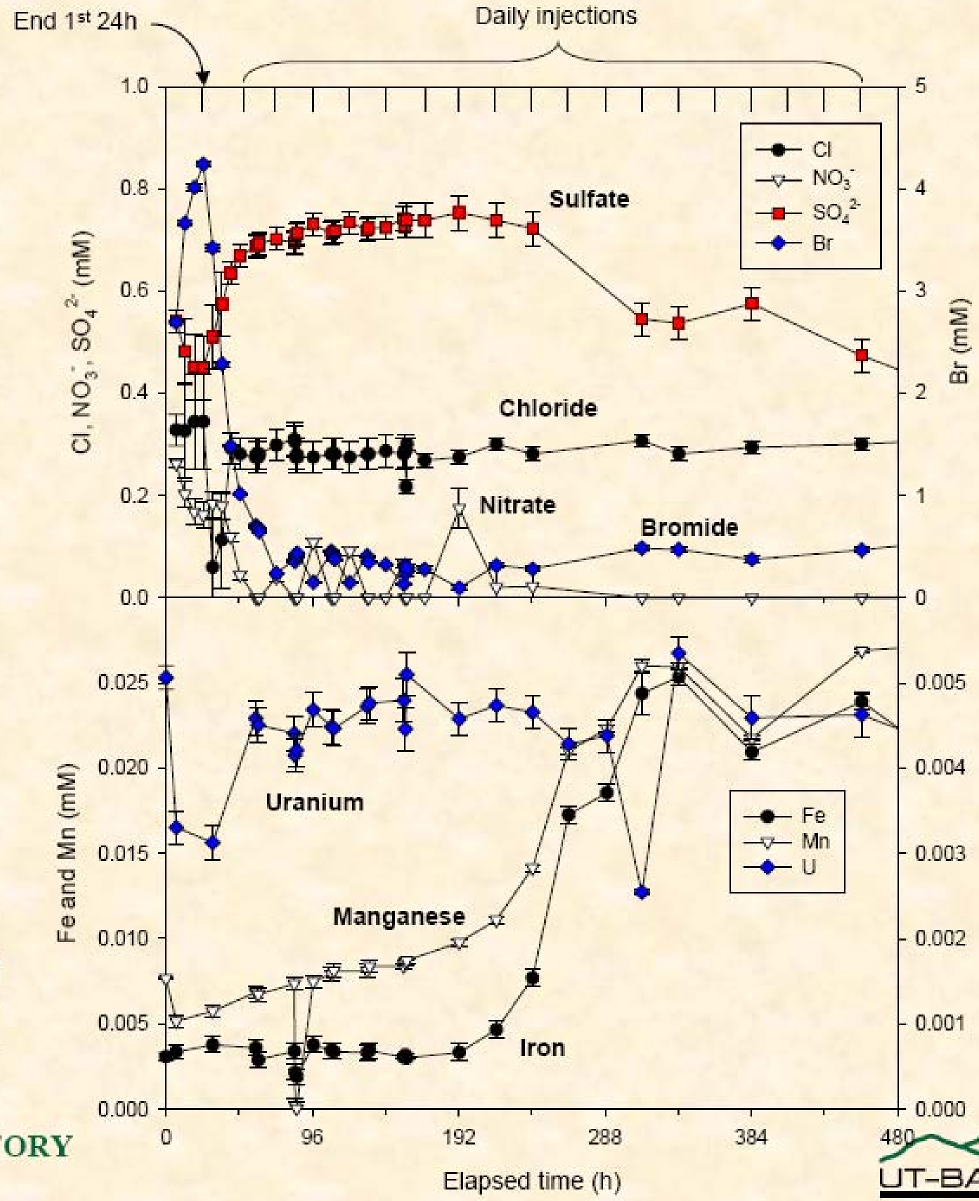
UT-BATTELLE

Short-Term Response

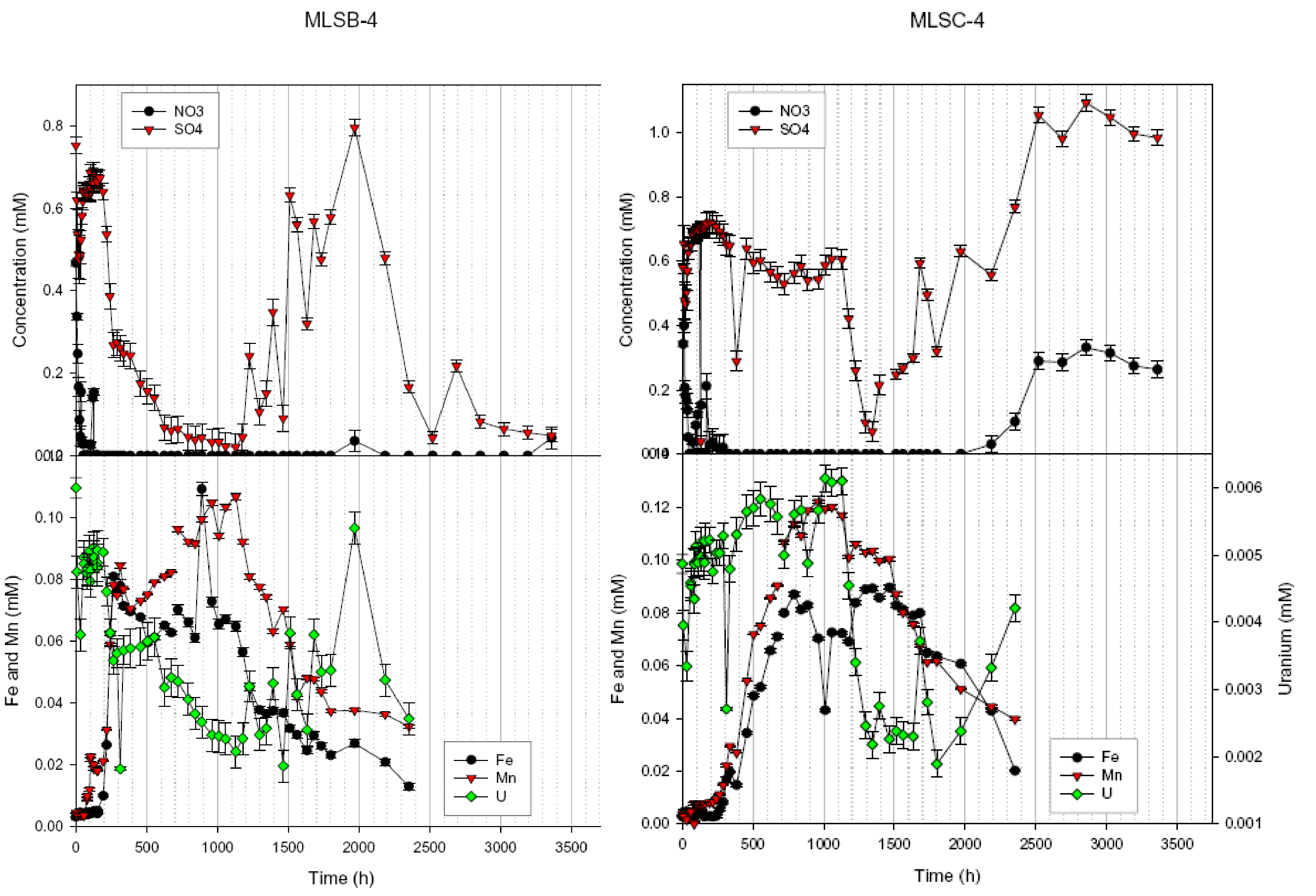


MLSD-4

- In the first 20 days
  - NO_3^- reduction
  - Mn reduction
  - Fe reduction
  - SO_4^{2-} reduction
    - Sulfide generation
- Coupling of [Br] (surrogate for EtOH delivery) and $[NO_3^-] + [SO_4^{2-}]$

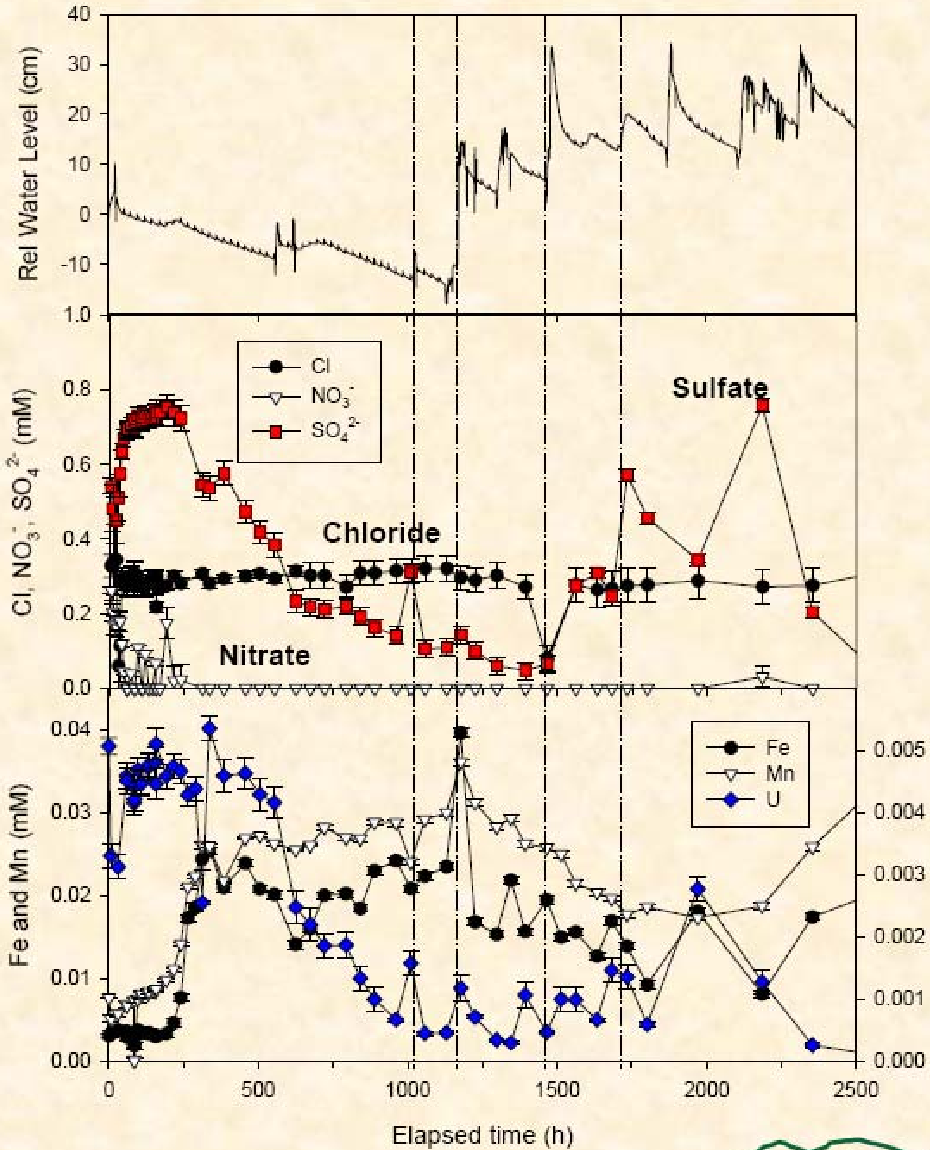


Mid-Term Response

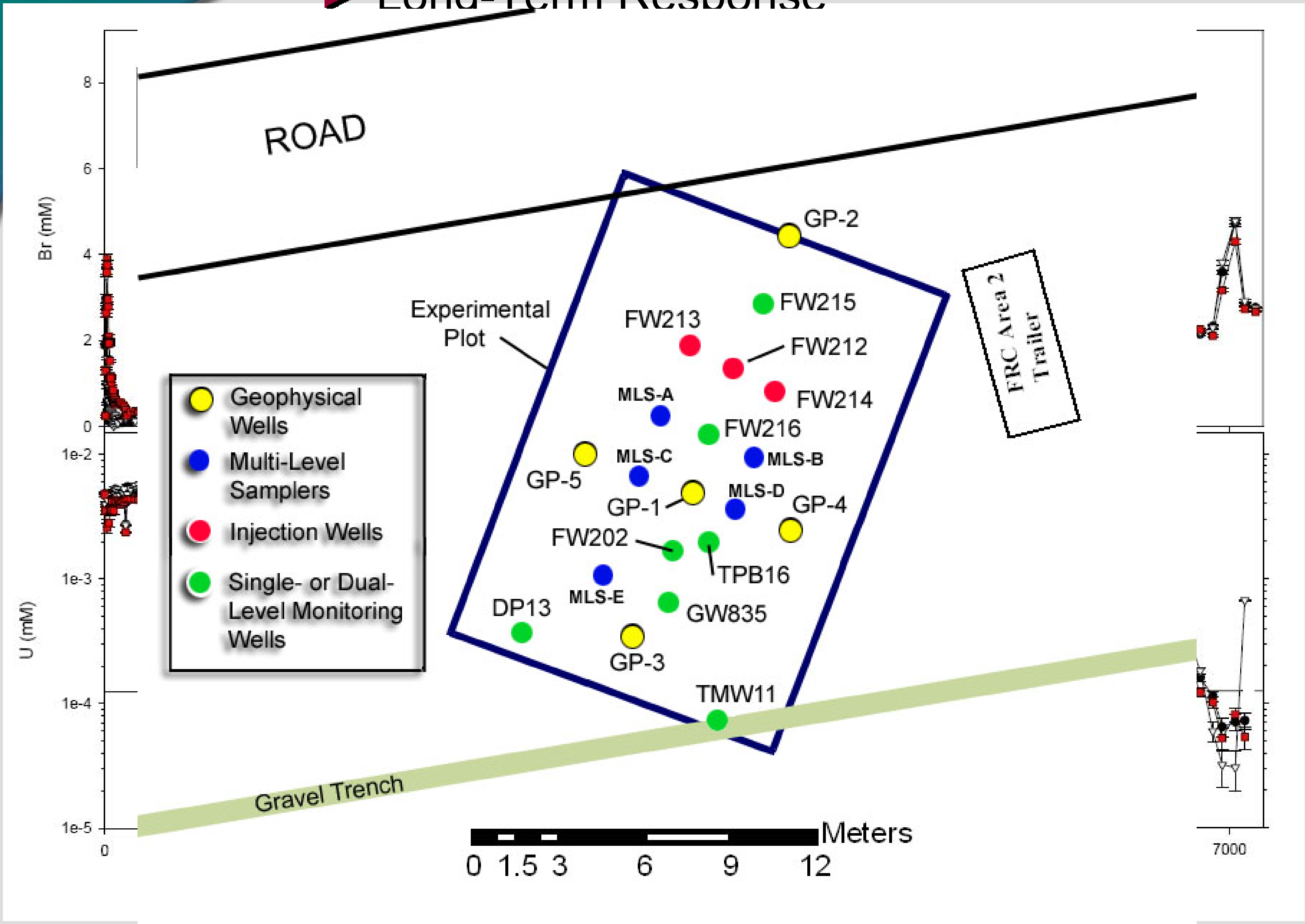


Regional recharge events drive biogeochemical dynamics in shallow aquifer

- Ethanol delivery promoted reducing conditions
  - $NO_3^- \rightarrow Mn \rightarrow Fe \rightarrow SO_4^{2-} \rightarrow U(VI)$
- Recharge water introduced dissolved O_2
  - Nitrate reduction continues but other terminal electron accepting processes are disrupted
- System restabilizes with continued EtOH delivery.



▶ Long-Term Response



Sediment Sampling

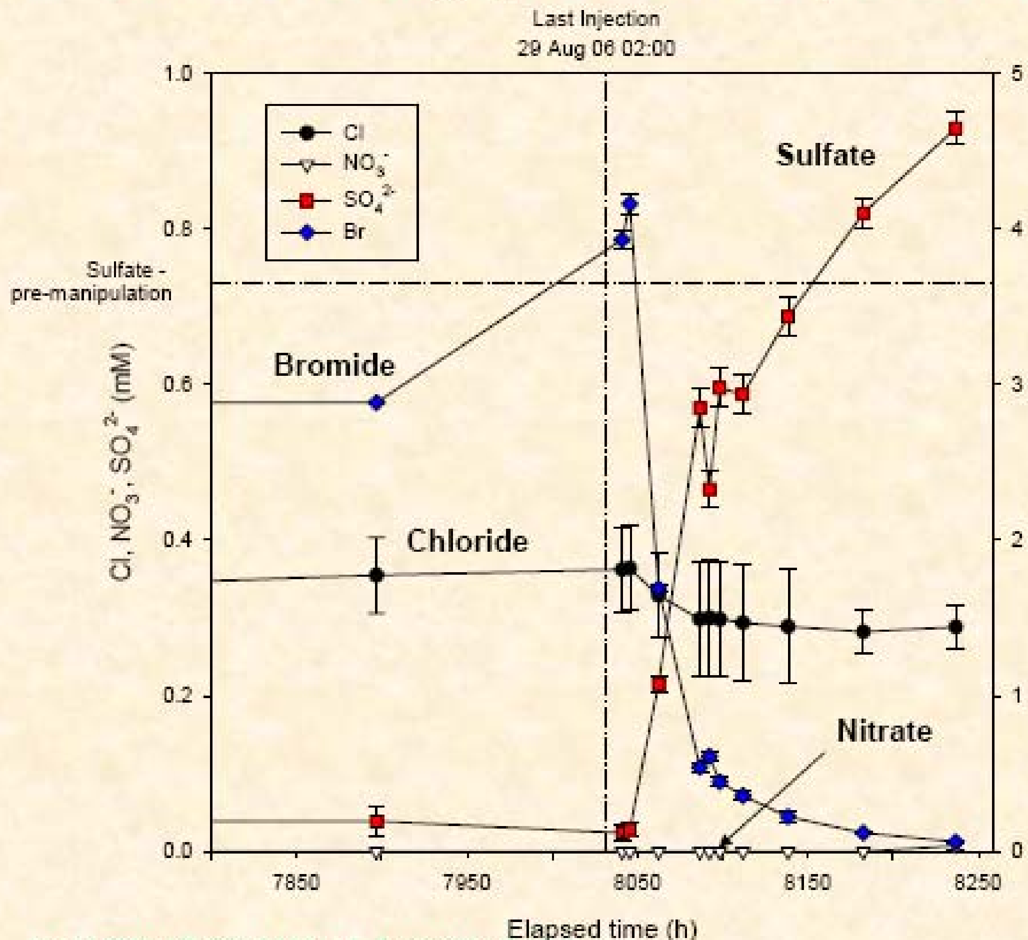
Prebiostimulation
(Saprolite, 0-2 cm below gravel)

Postbiostimulation
(Saprolite, 0-2 cm below gravel)

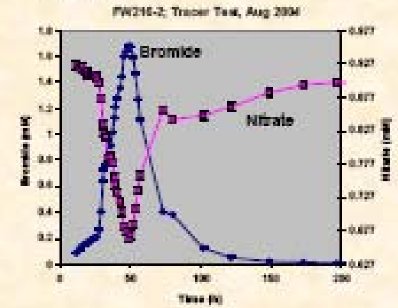
INSIDE BIOSTIMULATION ZONE

OUTSIDE BIOSTIMULATION ZONE

Monitoring post-manipulation dynamics



- Bromide is flushed out of system
- Nonreactive system: NO_3^- ***should*** increase to pre-manipulation levels (~0.9 mM) at the same rate Br decreases – it does not.



- Excess sulfate indicative of (ferrous) sulfide precipitate oxidation – redox barrier to U remobilization ?

Conceptual Model

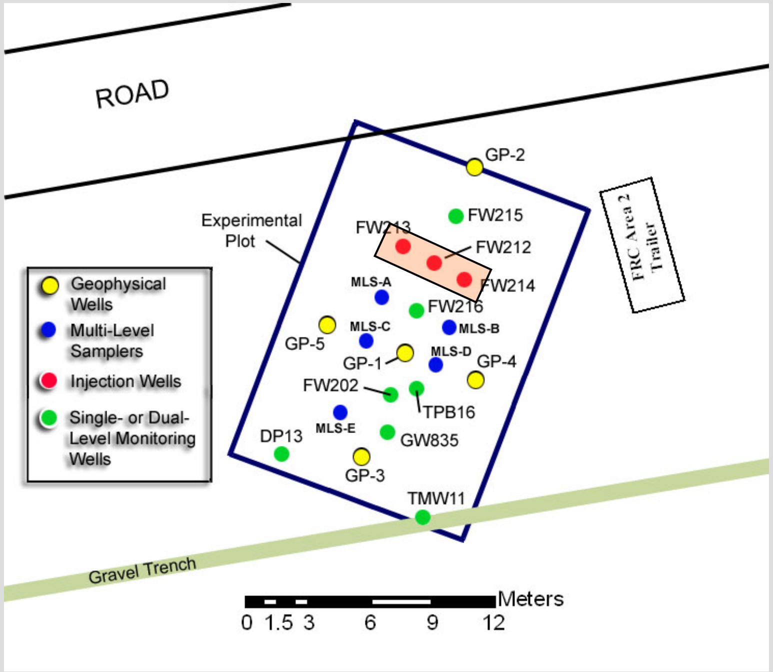
- Water table 4 meters below ground surface
- Model Domain:

  Lx = 20 m, Ly = 10 m, Lz = 4 m
- Hydraulic Gradient 0.03, specified head in the x direction
- Well screen depth: 4.5m-6m

	Thickness (m)	Porosity	K (cm/s)
Disturbed Saprolite Fill	1.5	0.3	1.3e-2
Gravelly Fill	0.5	0.3	3.8e-2
Intact Saprolite	2	0.1	4.1e-5

Multicomponent Reactive Transport

- Conceptual model and hydrologic parameters from tracer test analysis
- 3 Injection Wells
  FW213, FW212, FW214
- 92 Species
- 127 Reactions(50 fast, 77 slow)
- 29 Terminal Electron Accepting Processes (TEAPs)



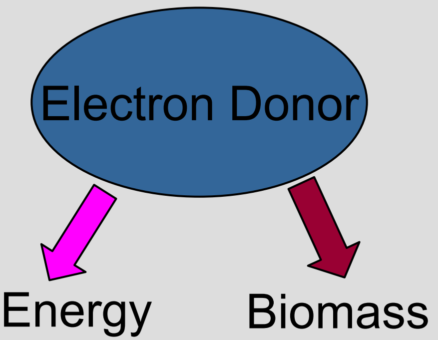
TEAP Reactions

Reaction	Catalyzed By
CH3CH2OH + 3O2 → 2HCO3- + H2O + 2H+	AM, DM
CH3CH2OH + 2.4NO3- + 0.4H+ → 2HCO3- + 1.2N2 + 2.2H2O	DM
CH3CH2OH + 0.5NO3- → CH3COO- + 0.5NH4+ + 0.5H2O	DRM1, DRM2, DRM3
CH3CH2OH + 2MnO2 + 3H+ → CH3COO- + 2Mn2+ + 3H2O	DRM2, DRM3
CH3CH2OH + 4FeOOH + 7H+ → CH3COO- + 4Fe2+ + 7H2O	DRM2, DRM3
CH3CH2OH + 0.5SO42- → CH3COO- + 0.5HS- + 0.5H+ + H2O	DRM3, SO4RM
CH3CH2OH + 2S0 + H2O → CH3COO- + 2HS- + 3H+	DMR3, S0RM
CH3CH2OH + 0.5HCO3- → CH3COO- + 0.5CH4 + 0.5H+ + 0.5H2O	MGM
CH3COO- + 2O2 → 2HCO3- + H+	AM, DM
CH3COO- + 1.6NO3- + 0.6H+ → 2HCO3- + 0.8N2 + 0.8H2O	DM
CH3COO- + NO3- + H2O + H+ → 2HCO3- + NH4+	DRM2, DRM3
CH3COO- + 4MnO2 + 7H+ → 2HCO3- + 4Mn2+ + 4H2O	DRM2, DRM3
CH3COO- + 8FeOOH + 15H+ → 2HCO3- + 8Fe2+ + 12H2O	DRM2, DRM3
CH3COO- + SO42- → 2HCO3- + HS-	DRM3, SO4RM
CH3COO- + 4S0 + 4H2O → 2HCO3- + 4HS- + 5H+	DRM3, S0RM
CH3COO- + H2O → HCO3- + CH4	MGM

Reactions in red: Complete oxidation Reactions in green: Incomplete oxidation
DRM – dissimilatory reducing microorganisms, AM – aerobic microorganisms
DM – denitrifying microorganisms, SO4RM – sulfate reducing microorganisms
S0RM – sulfur reducing microorganisms, MGM – methanogenic microorganisms

TEAP Reactions

- **Overall balanced reaction for biological growth derived from bioenergetics-based approach in which the partitioning of electron flow between energy generation and biomass production is dependent on the free energy of the corresponding TEAP** (Rittman and McCarty, 2001)



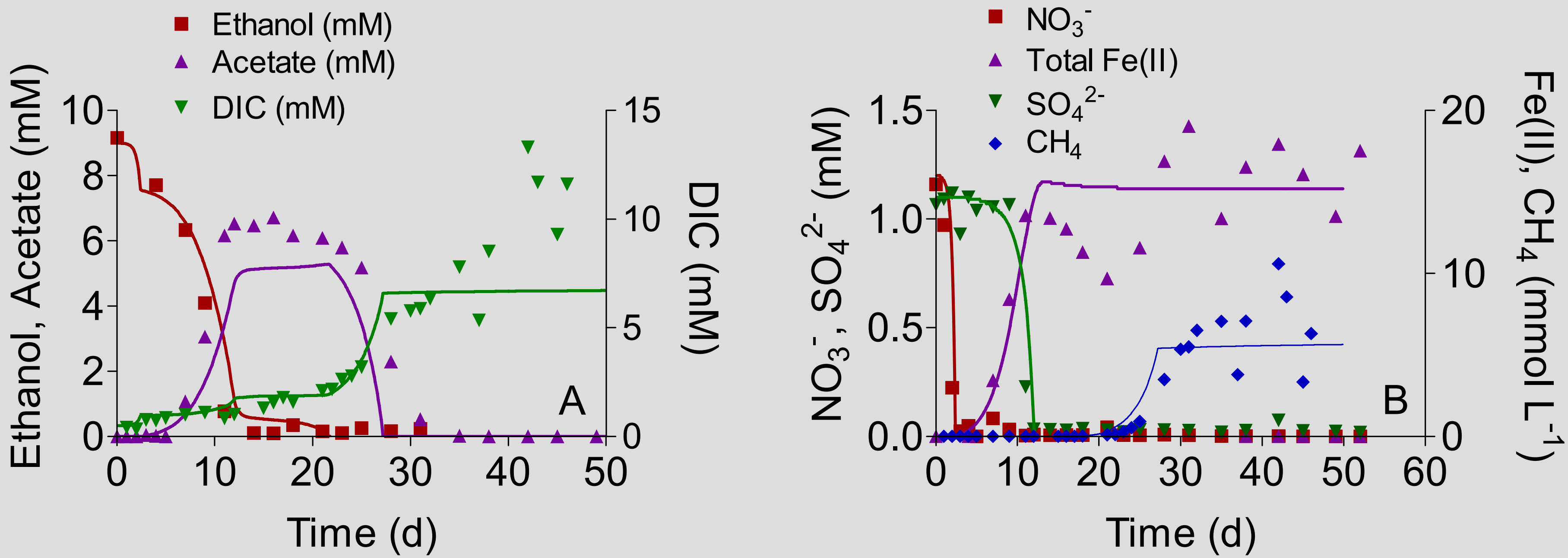
0.2500CH3CH2OH + 0.8256FeOOH(s) + 1.4391H+ + 0.0378HCO3- + 0.0038N2 = 0.2500CH3COO- + 0.0076DRM2_cell + 0.8256Fe++ + 1.4998H2O

- **Rate laws consider thermodynamic constraints**

$$R_{Fe(III)} = V\max_{Surf} \frac{[Cells]}{Km_{Cells} + [Cells]} [Fe(III)Surf_{Free}] f(\Delta G_{rxn})$$

$$f(\Delta G_{rxn}) = 1 - exp((\Delta G_{rxn} - \Delta G_{min}) / RT)$$

ΔG_{min} = minimum free energy change required to drive cellular energy metabolism (-20 kJ/mol) (Schink, 1997)

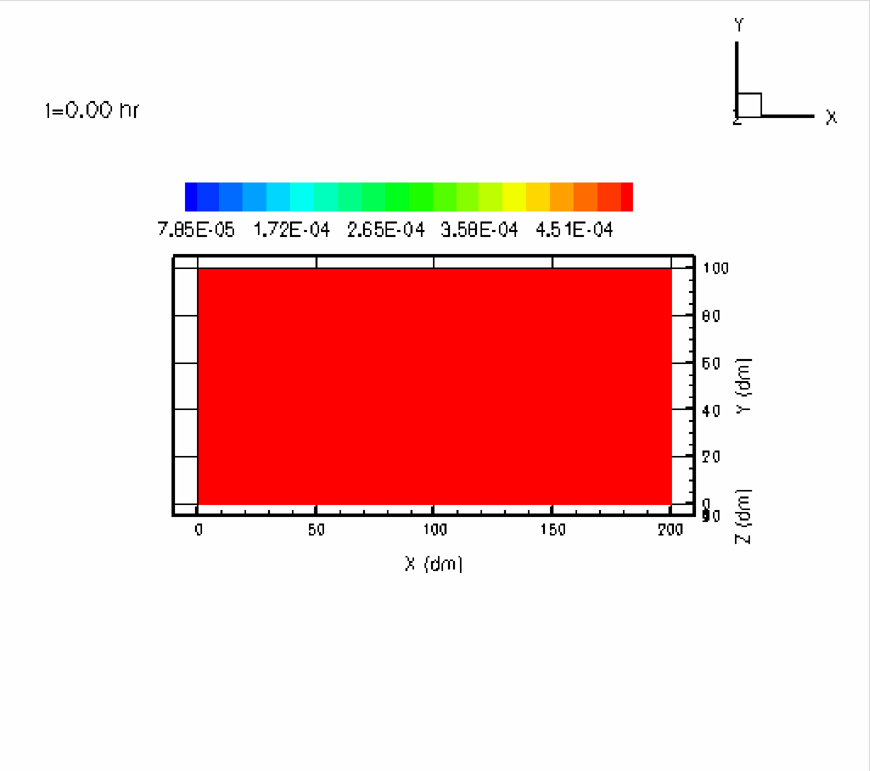


Only adjustable parameter values: 1. Fe(III) max. reduction rate V_{max}

2. Initial biomass values

Experimental Design

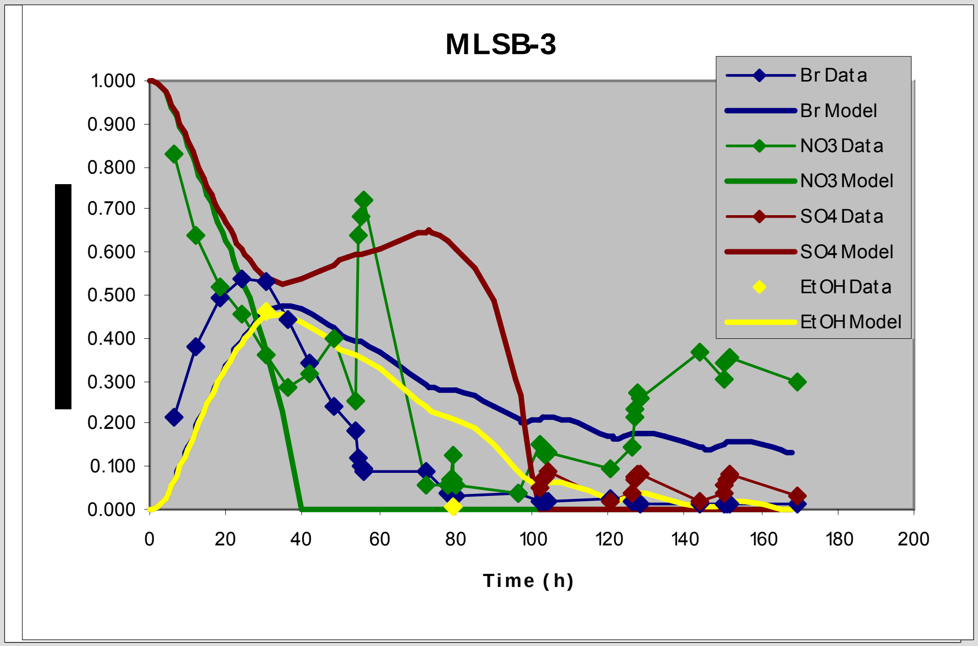
- Goal: Select injection strategy
  - Effectively remove nitrate from treatment zone
  - Create fairly uniform zone of ethanol delivery
  - Do not add too much electron donor
- Several alternatives simulated



Nitrate in gravel layer

Short-Term TEAP Observations/Model

- MLS-B



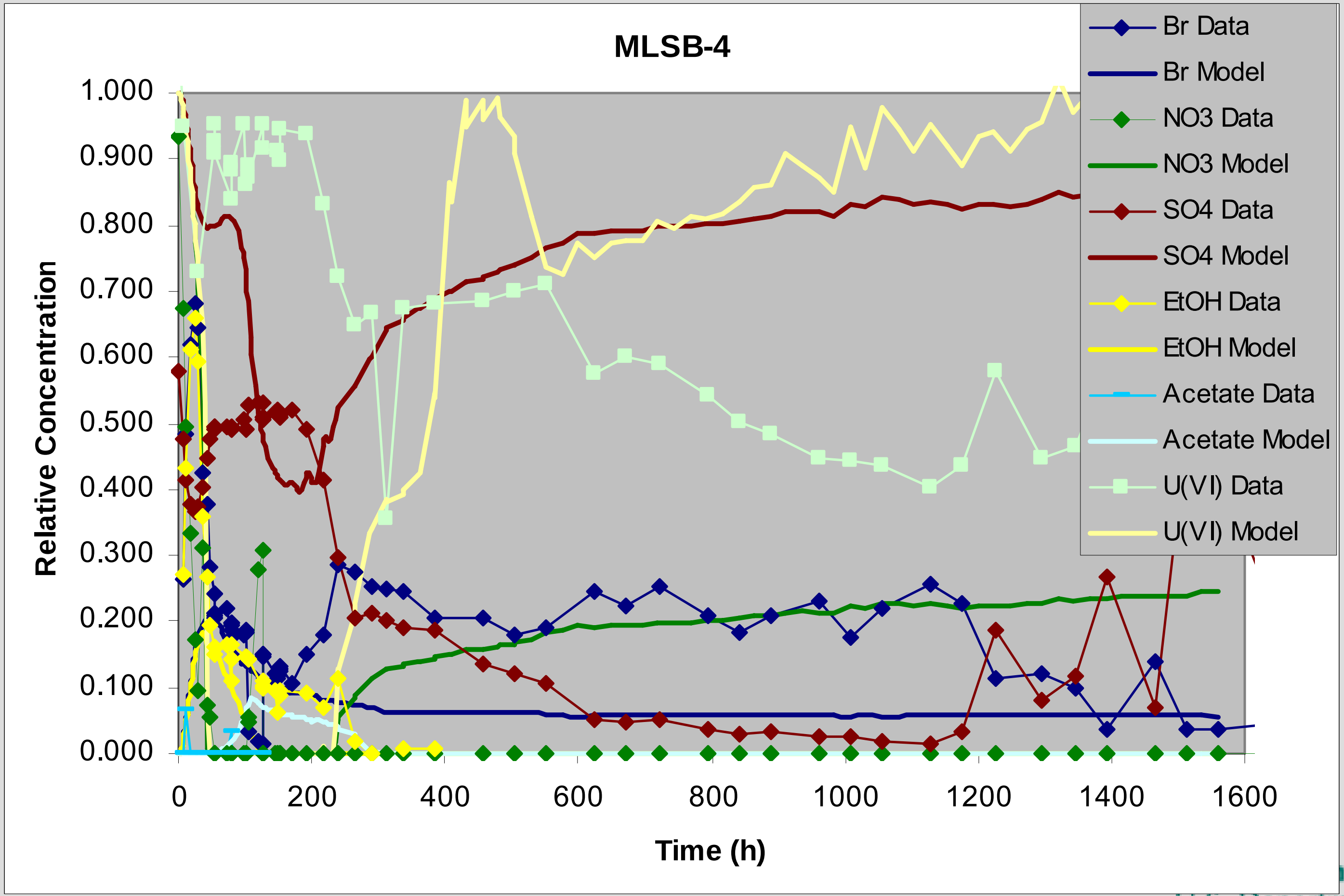
MLSB-5
100 cm above gravel

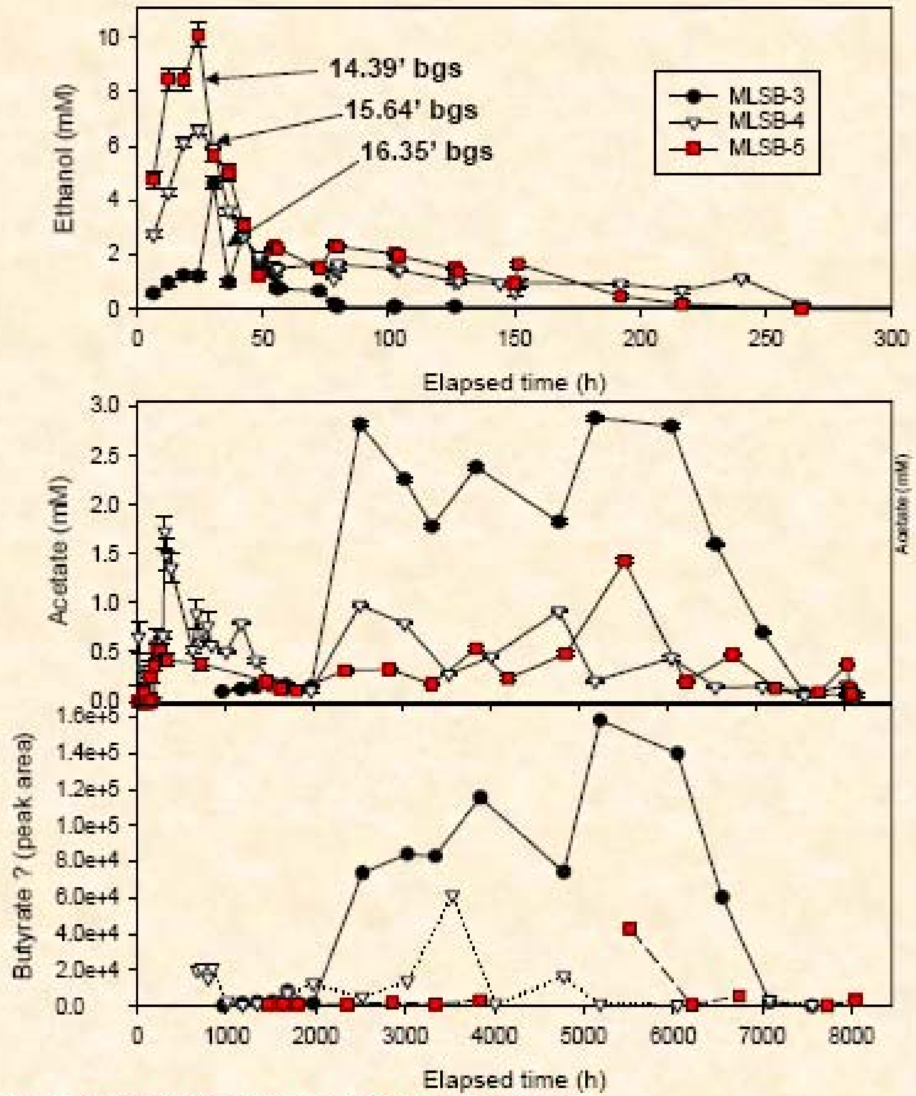
MLSB-4
50 cm above gravel

MLSB-3
Mid-Gravel

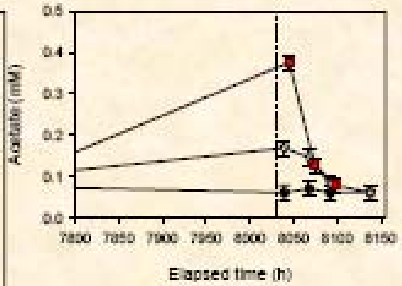
Mid-Term TEAP Observations/Model

- MLSB-4



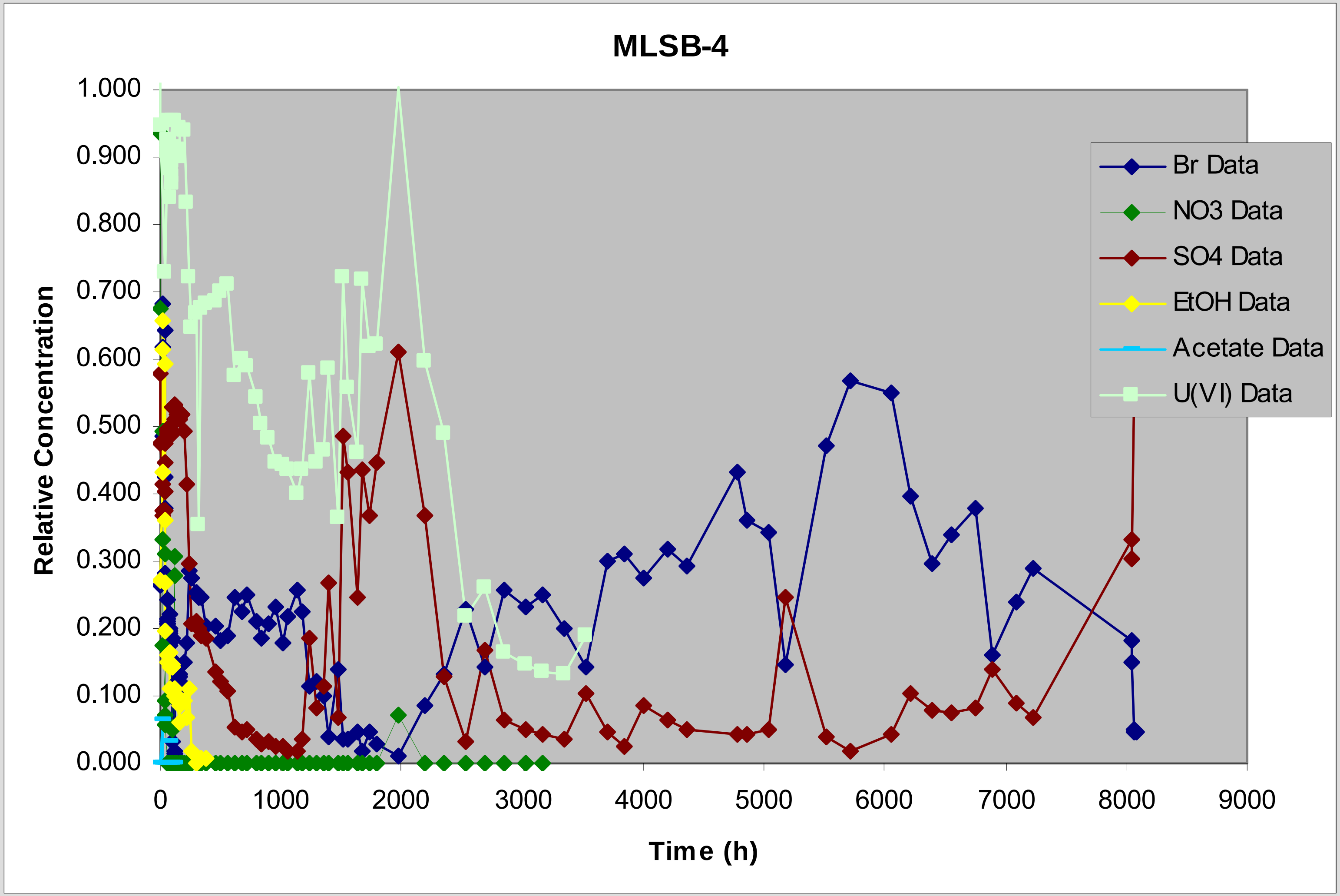


MLSB – inorganic, organic, and microbial analyses complete the picture



- *Clostridia* (anaerobic soil bacteria) ferment EtOH + Acetate to butyrate, H_2, and other fatty acids
- Butyrate yield increases as Acetate:EtOH ratio increases
- Phylogenetic analysis 16S rDNA fragments from DGGE gels of field samples from the same wells indicate *Clostridia*

Long-Term Shift in Flow Pattern?



Acknowledgments

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