FIELD SCALE EVALUATION OF BIOSTIMULATION FOR REMEDIATION OF URANIUM-CONTAMINATED GROUNDWATER AT THE NABIR FIELD RESEARCH CENTER IN OAK RIDGE, TN

Stanford University

Craig Criddle
Scott Fendorf
Michael Fienen
Margy Gentile
Matt Ginder-Vogel
Peter Kitanidis
Jian Luo
Anna Michalak
Jennifer Nyman
Weimin Wu

Oak Ridge National Laboratories

Craig Brandt
Scott Brooks
Sue Caroll
Matthew Fields
Baohua Gu
Philip Jardine
Tonia Melhourne
Ye-Kyoung Ku
Ken Lowe
Stacy Rast
Jeff Riggs
Jizhong Zhou
Yul Roh

Universität Stuttgart

Olaf Cirpka
Frank-Andreas Weber

NABIR Field Research Center

David Watson

Retec

Robert Hickey
Raj Rajan
Dan Wagner

LBNL

Susan Hubbard
Ken Williams

Argonne

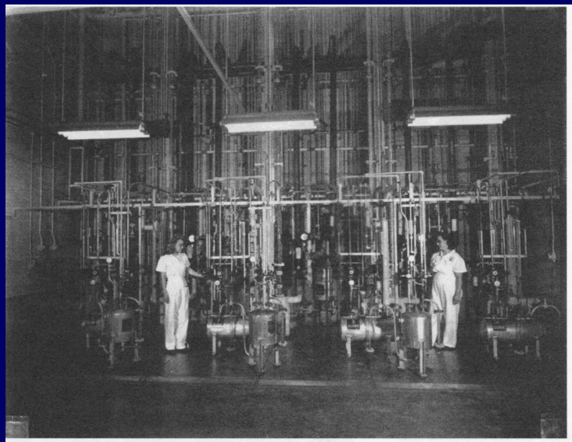
Ken Kemner

INEEL

Gill Geesey
David Cummings

Michigan State University

Terry Marsh

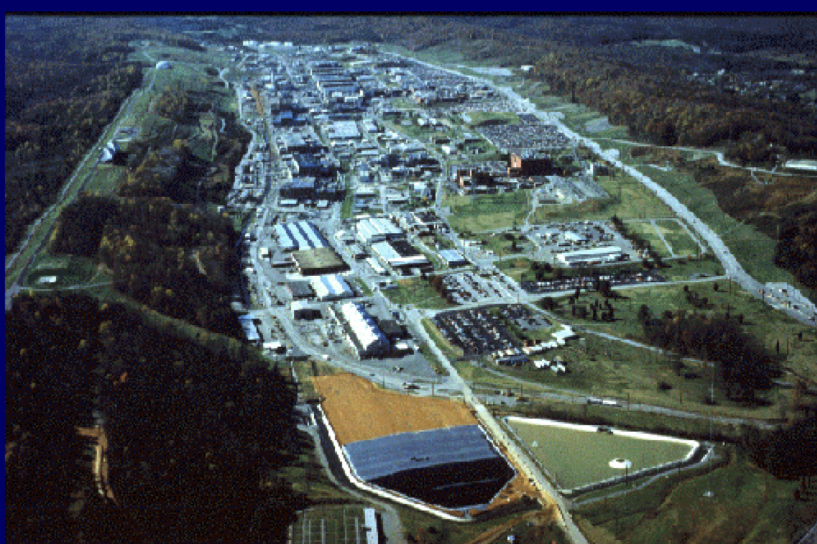


The Oak Ridge S3 ponds

"Gunk" extraction towers at Y-12

A legacy of the Cold War:
- Uranium
- Strong acids
- Chlorinated solvents
- Heavy metals

Waste was stored in unlined ponds (31 years)



Near source zone research station

A large parking lot now covers ponds (the "source")

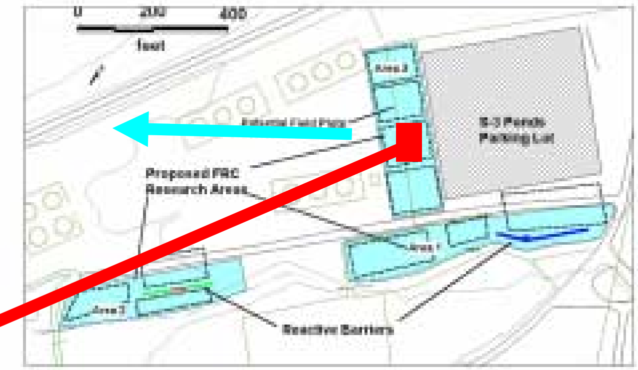
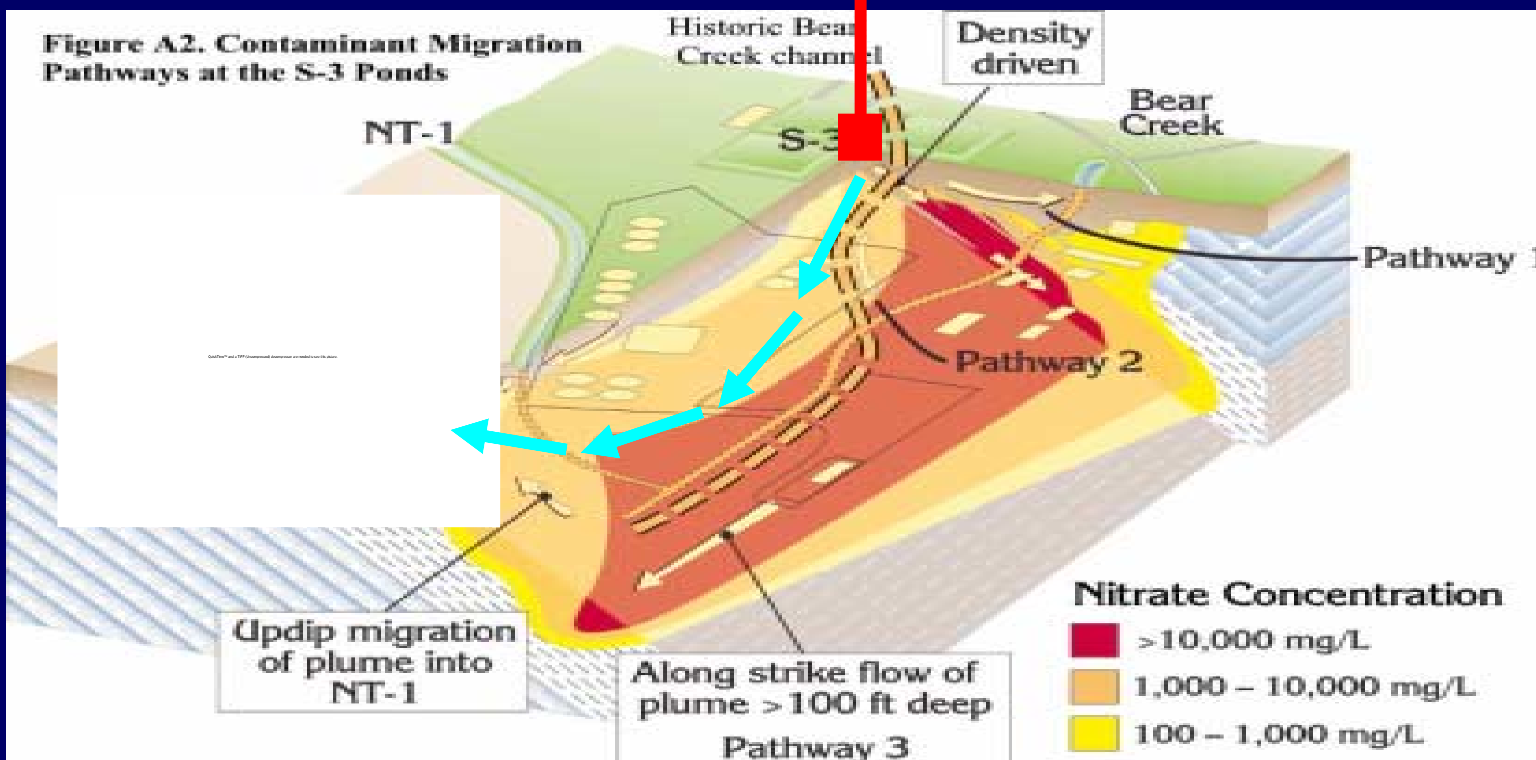


Figure A1. Location of potential field plots within Areas 1, 2, and 3

Where we are

Figure A2. Contaminant Migration Pathways at the S-3 Ponds



Rationale for work near the source zo

The source zone is a reservoir of U(VI) supporting long-term groundwater contamination.

About 98% of the U(VI) in the near source zone is sorbed to solids or part of a solid phase.

The remaining 2% of U(VI) is dissolved in the groundwater at highly toxic levels (20-50 mg/L).

Conversion of solid-associated U(VI) into highly insoluble U(IV) will prevent

PRIMARY OBJECTIVE

Evaluate the rates and mechanisms of U(VI) reduction by microbial populations

Hypotheses

- **Biological reduction of U(VI) is a multistep process involving desorption/dissolution of U(VI), followed by uptake/reductive mineralization.**

- **Desorption/dissolution will limit reduction rate, with highest rates observed under conditions that favor partitioning of U(VI) into the aqueous phase (i.e., elevated pH and TIC levels).**

- **Both metal- and sulfate-reducing bacteria will play a role in U reduction, with iron-reducing bacteria acting first followed by sulfate-**

Chemistry

Low pH (about 3.5):
- buffered by Al^{3+} (~20 mM)

High U(VI):
~98% on the soil (~400 mg/kg)
~2% in groundwater(~ 40 mg/L)

High NO_3^-:
130-480 mM in groundwater - NO_3^- and denitrification intermediates inhibit U(VI) reduction (Senko et al., 2001)

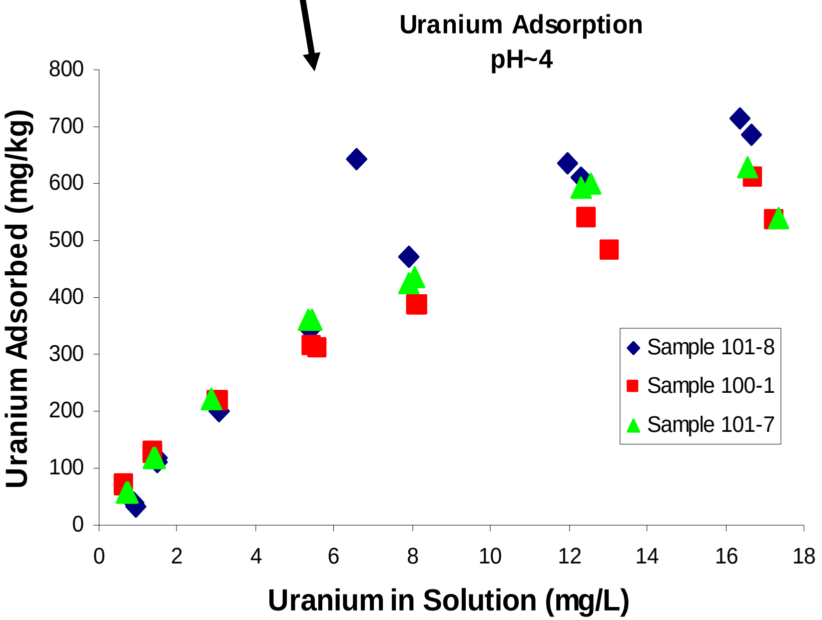
High Ca^{2+}:
~20 mM in groundwater - Ca^{2+} inhibits U(VI) reduction at 5 mM (Brooks et al., 2003)

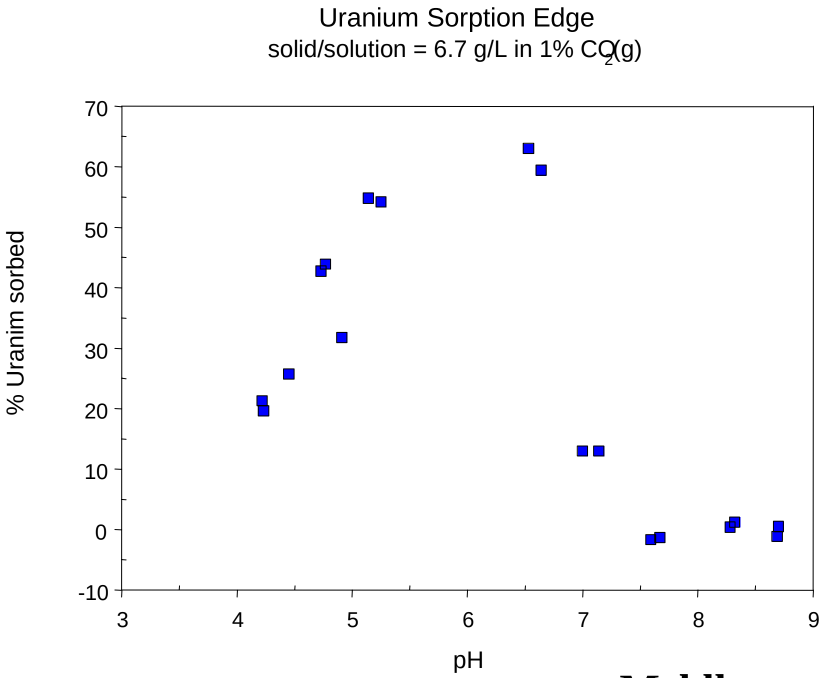
$UO_2(CO_3) + H^+ + 2e^- = UO_2 + HCO_3^-$ $E°' = +0.105$ V

$Ca_2UO_2(CO_3)_3 + 2e^- = 2Ca^{2+} + UO_2 + 3CO_3^{2-}$ $E°' = -0.046$ V

Uranium adsorption

U sorption is concentration dependent and it is strongly pH dependent.





Mehlhorn, 2003

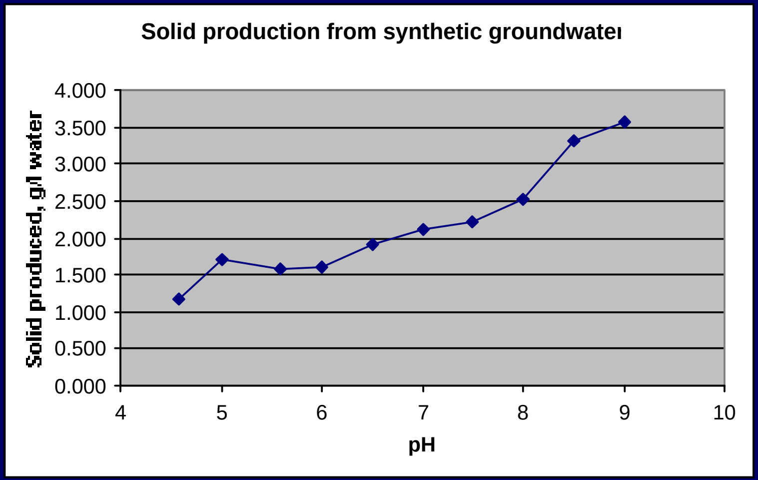
Potential clogging agents

- Aluminum hydroxide form at pH 5.
- Calcium and magnesium carbonates form at pH 7-9.
- N_2 gas forms during denitrification.
- High levels of biomass are produced during denitrification.

pH adjusted to 7 with 50% liquid from denitrifying batch cultures

pH adjusted to 7 with Na_2CO_3

pH adjusted to 7 with KOH



2 g/L solids produced

Geology

• Saprolite contains a highly interconnected fracture network with densities of 100-200 fractures/m. Fractures are < 5-10% of the total porosity, but carry >95% of the groundwater flow.

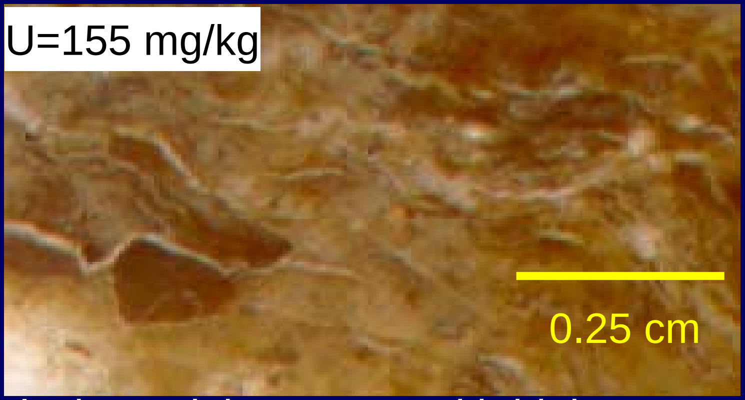
• The fractures surround a high porosity, low permeability matrix that is a source and sink for contaminants.

Overlying Saprolites

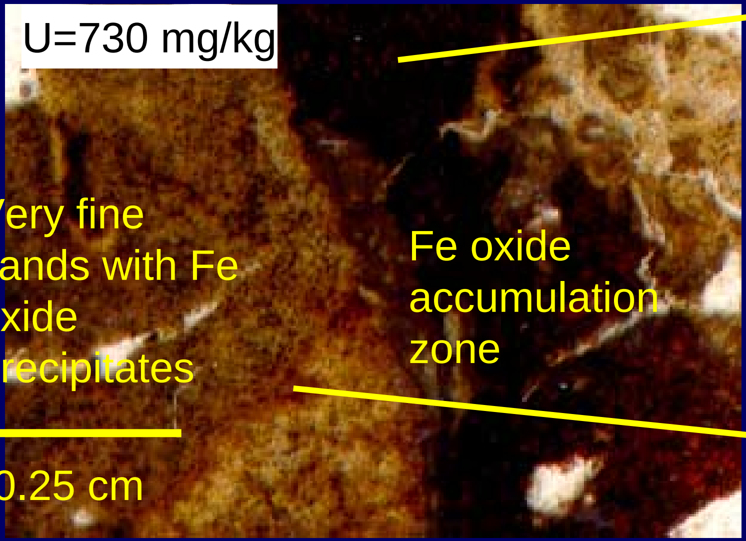
Underlying Bedrock

Core Mineralogical Evaluations

Overlying Gleyed leached flow zone with high U, low pH groundwater



Black precipitate Zone with higher pH and lower U in groundwater

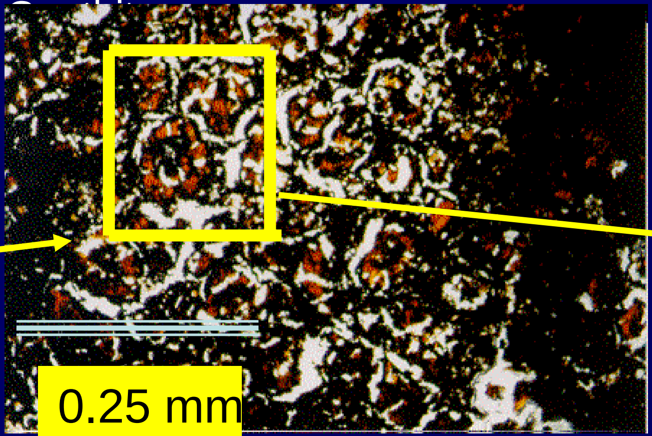


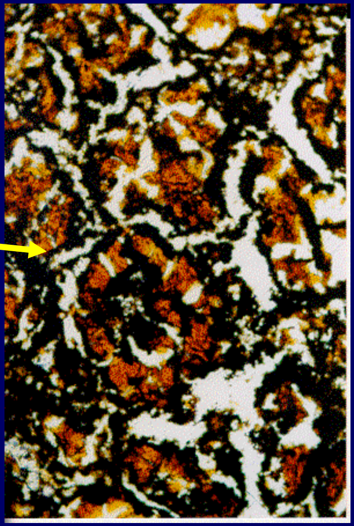
A high U zone was detected in the center of the test cell at a depth of 46'.

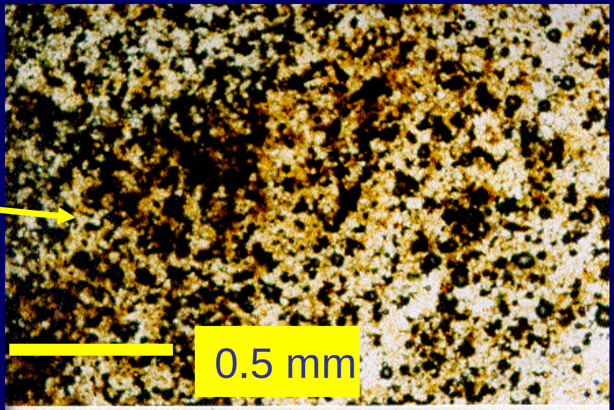
XRD results:

Gleyed Zone - Quartz, Vermiculite, Mica, HIV, Ca-feldspar

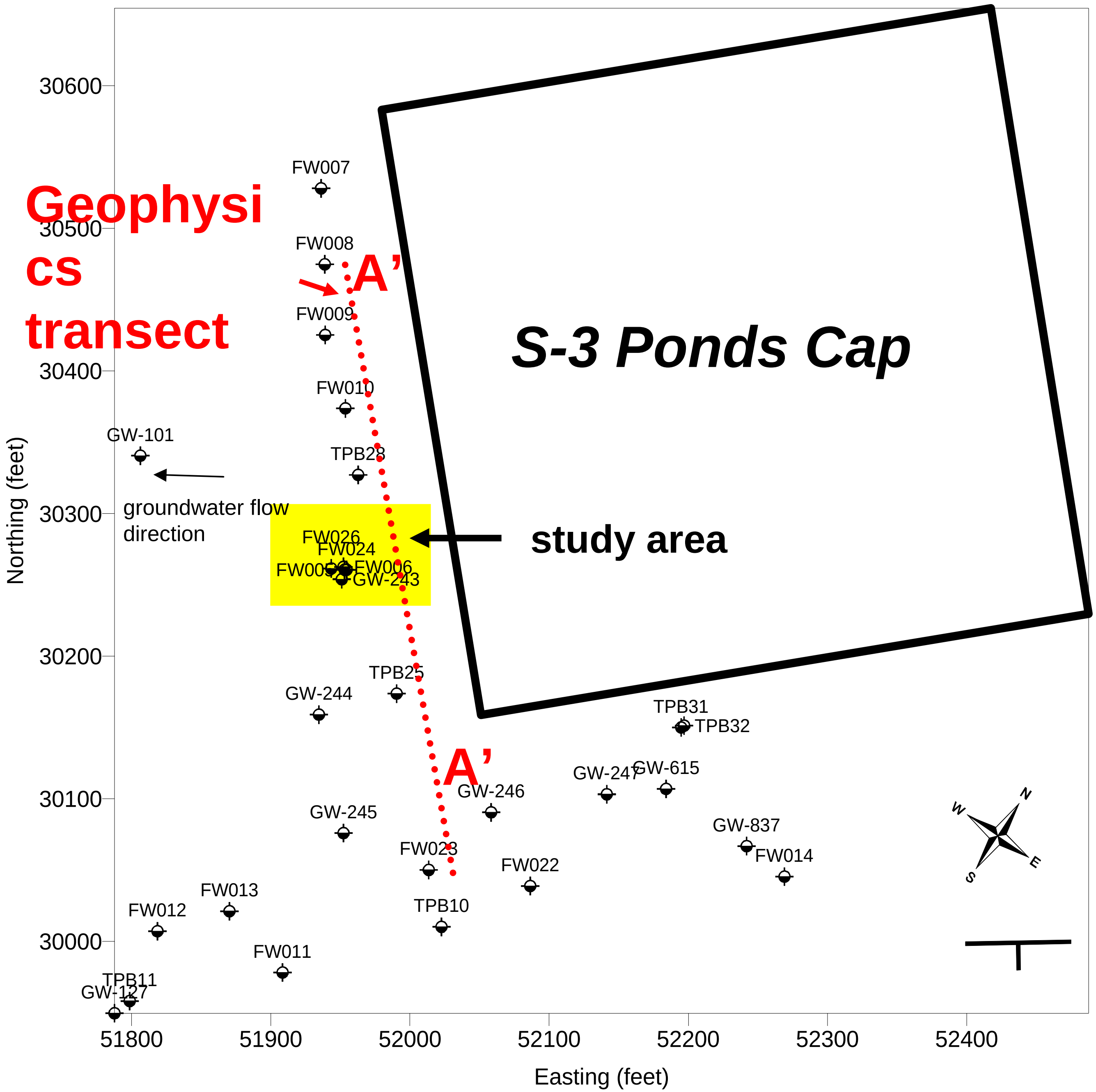
Black Zone - Quartz, Ca-feldspar, Vermiculite, Mica,







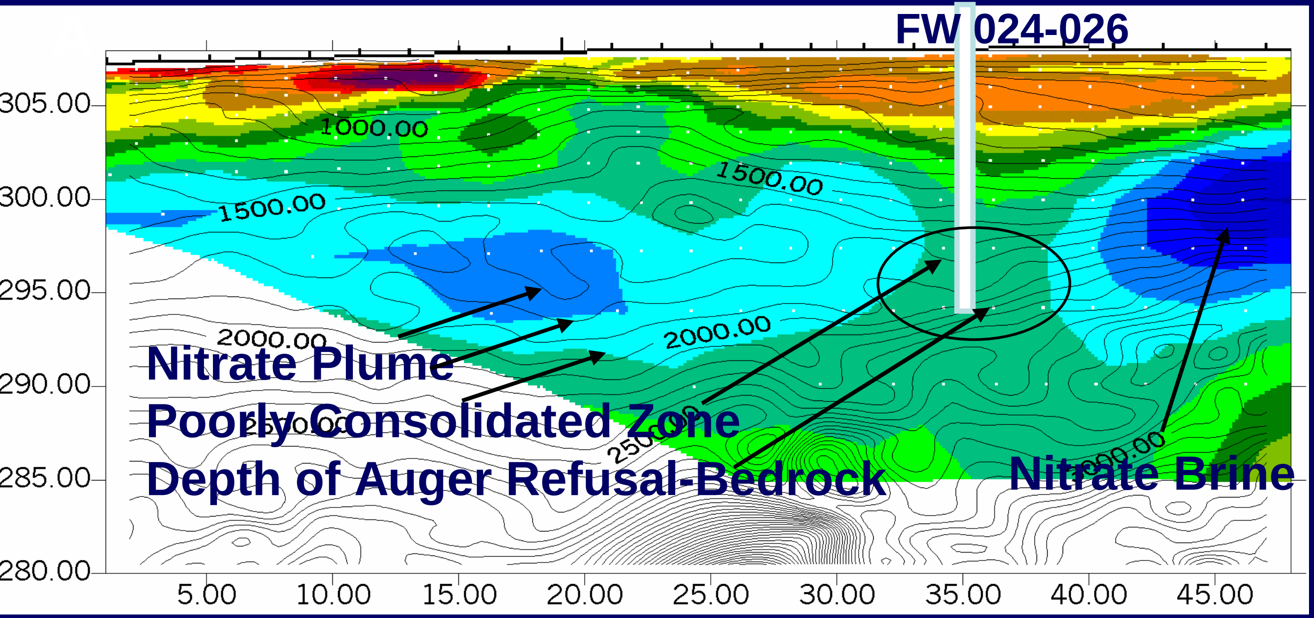
Phillips/Watson, 2003



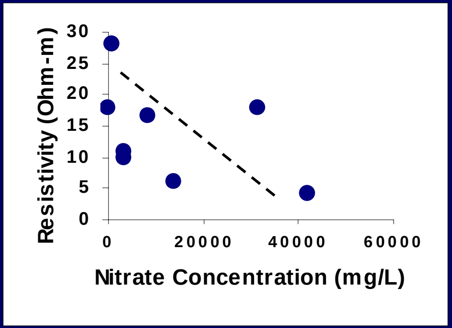
Geophysics transect
A'
A'
S-3 Ponds Cap
study area
groundwater flow direction
FW007
FW008
FW009
FW010
GW-101
TPB28
FW026
FW024
FW005
FW006
GW-243
TPB25
GW-244
TPB31
TPB32
GW-247
GW-615
GW-246
GW-245
GW-837
FW014
FW023
FW022
FW013
FW012
TPB10
FW011
TPB11
GW-127
30600
30500
30400
30300
30200
30100
30000
Northing (feet)
51800
51900
52000
52100
52200
52300
52400
Easting (feet)
N
E
S
W

Geophysics was used to identify areas of contaminant transpo

***S*-3 Ponds Cap**
Surface Seismic/Electrical Resistivity
(Doll et al., *SAGEEP*, 2002).

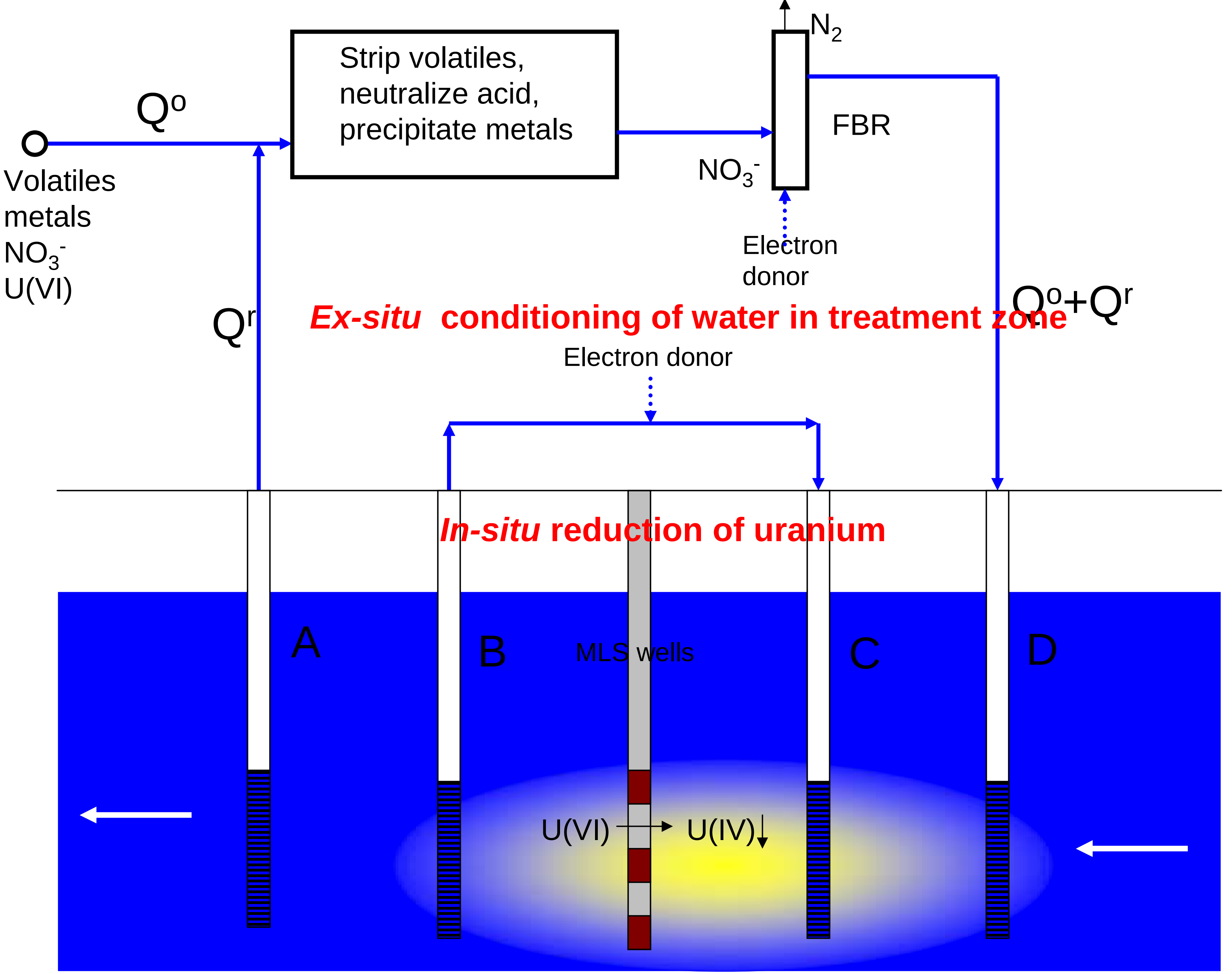


Electrical Resistivity
Low (~4 Ohm-m)
High (~150 Ohm-m)

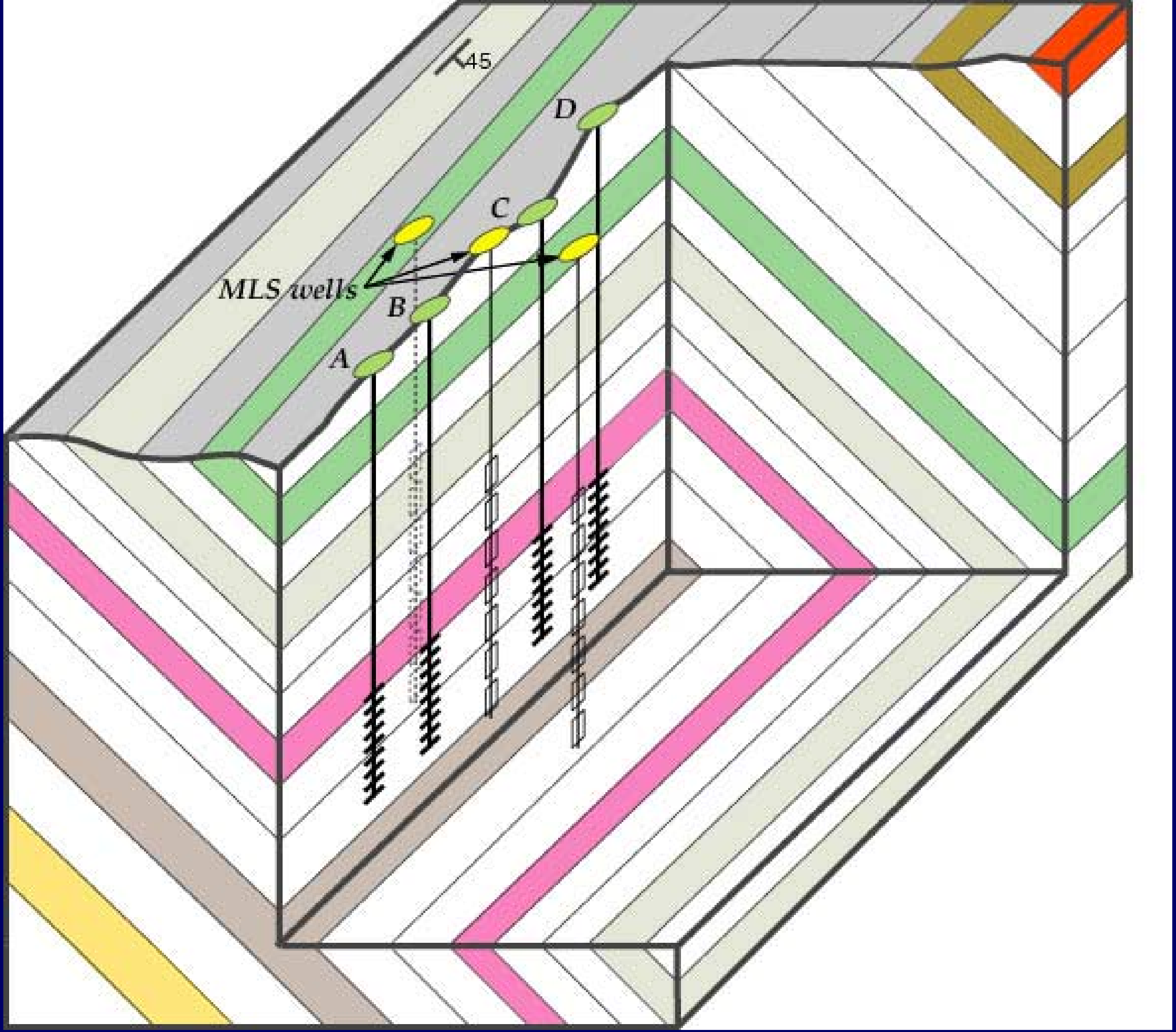


Low Resistivity ~ High Nitrate

Contour Lines: Seismic Velocity (m/s)



Strip volatiles, neutralize acid, precipitate metals
N_2
FBR
NO_3^-
Electron donor
Q^o
Volatiles
metals
NO_3^-
U(VI)
Q^r
Q^o+Q^r
Ex-situ conditioning of water in treatment zone
Electron donor
In-situ reduction of uranium
A
B
MLS wells
C
D
U(VI)
U(IV)



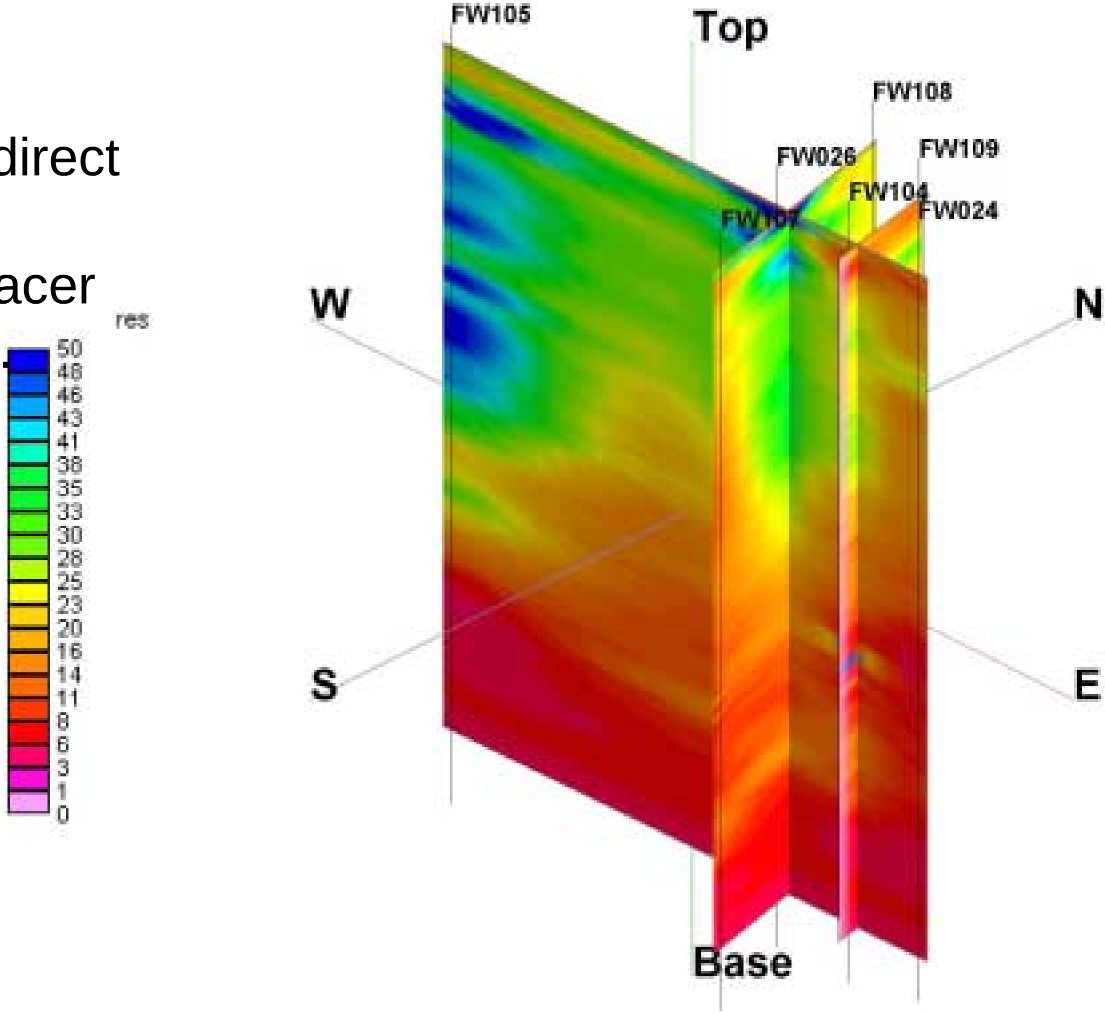
Screened Interval = 38-45’

Cross-sectional view of the injection/extraction wells and the MLS wells.

Electromagnetic Induction Logging

Spatial and temporal plume mapping during manipulation.

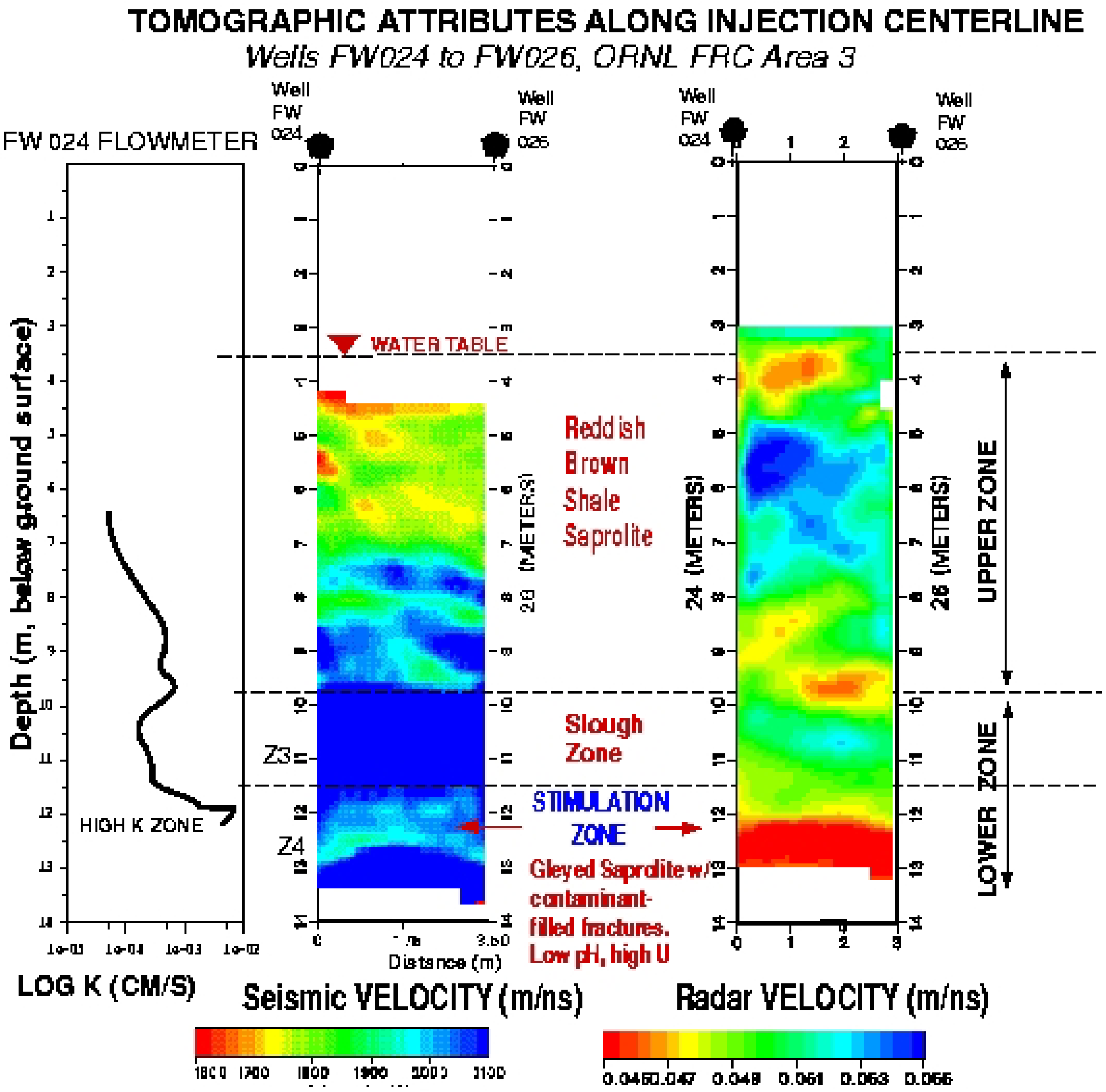
Complements direct groundwater geochemical tracer measurements.



Beard/Gamey/Doll, 2003

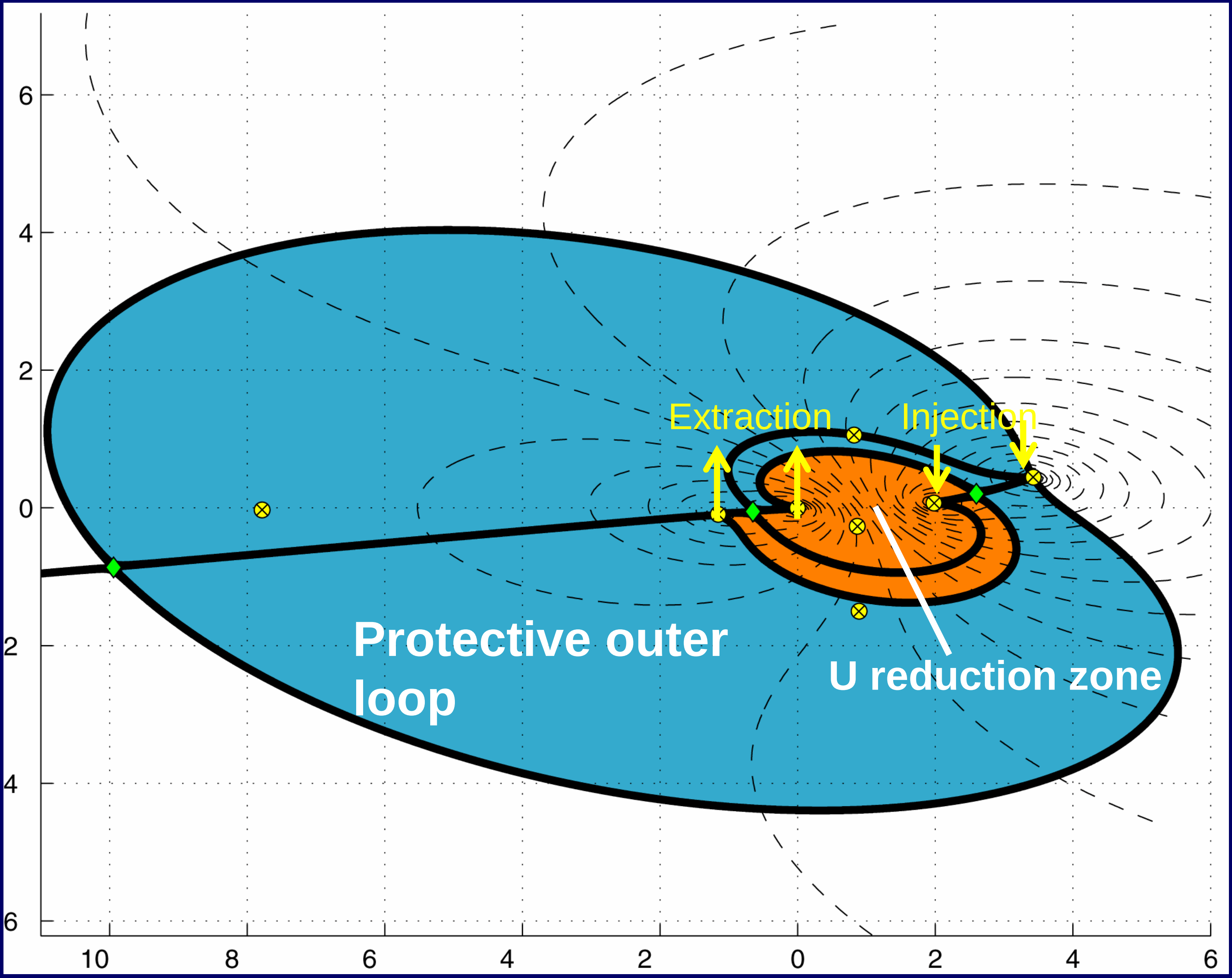
Seismic and Radar Tomography

Mapping subsurface material heterogeneities using cross-borehole techniques.



Hubbard et al., 2003

Regions of the subsurface

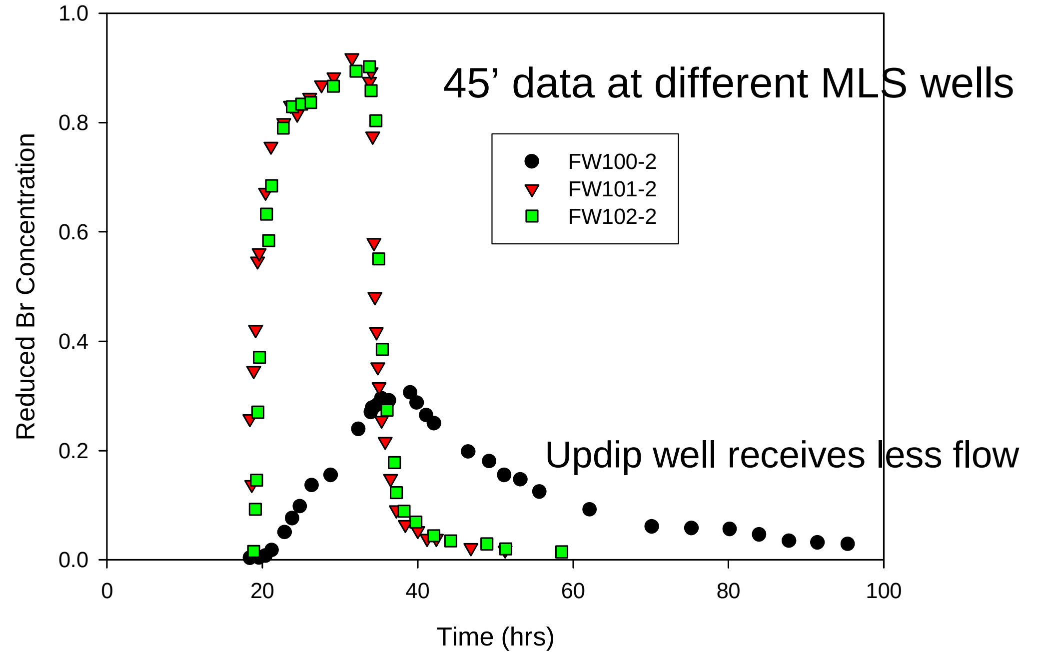


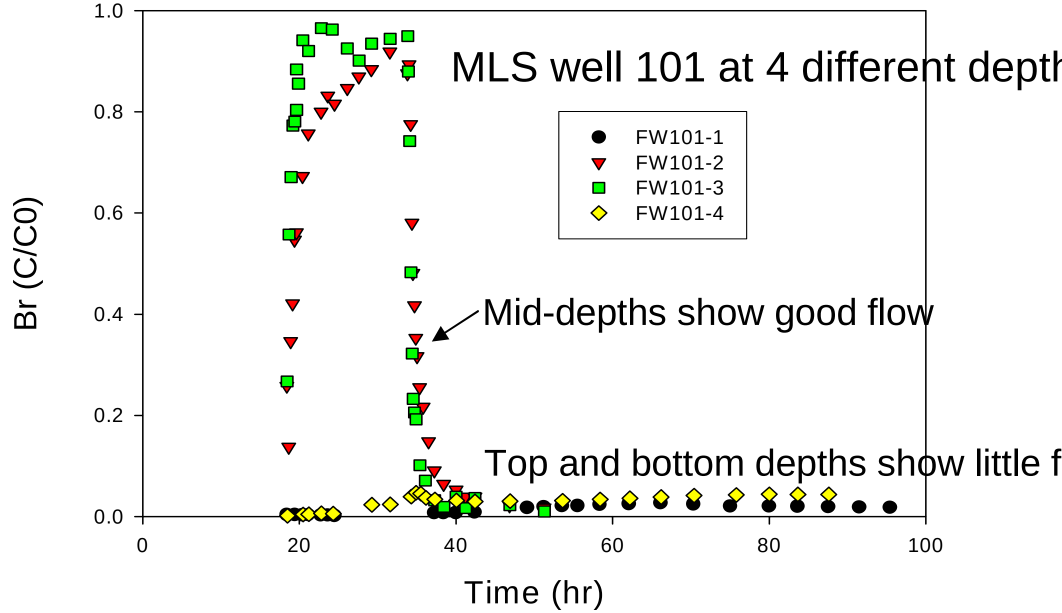
Tracer studies

A dual dipole tracer injection-withdraw test was conducted using $CaBr_2$ and $CaCl_2$ in an effort to create an inner and outer hydraulic cell.

Results confirmed location and transport features of preferential flow regimes and slow flowing matrix regimes.

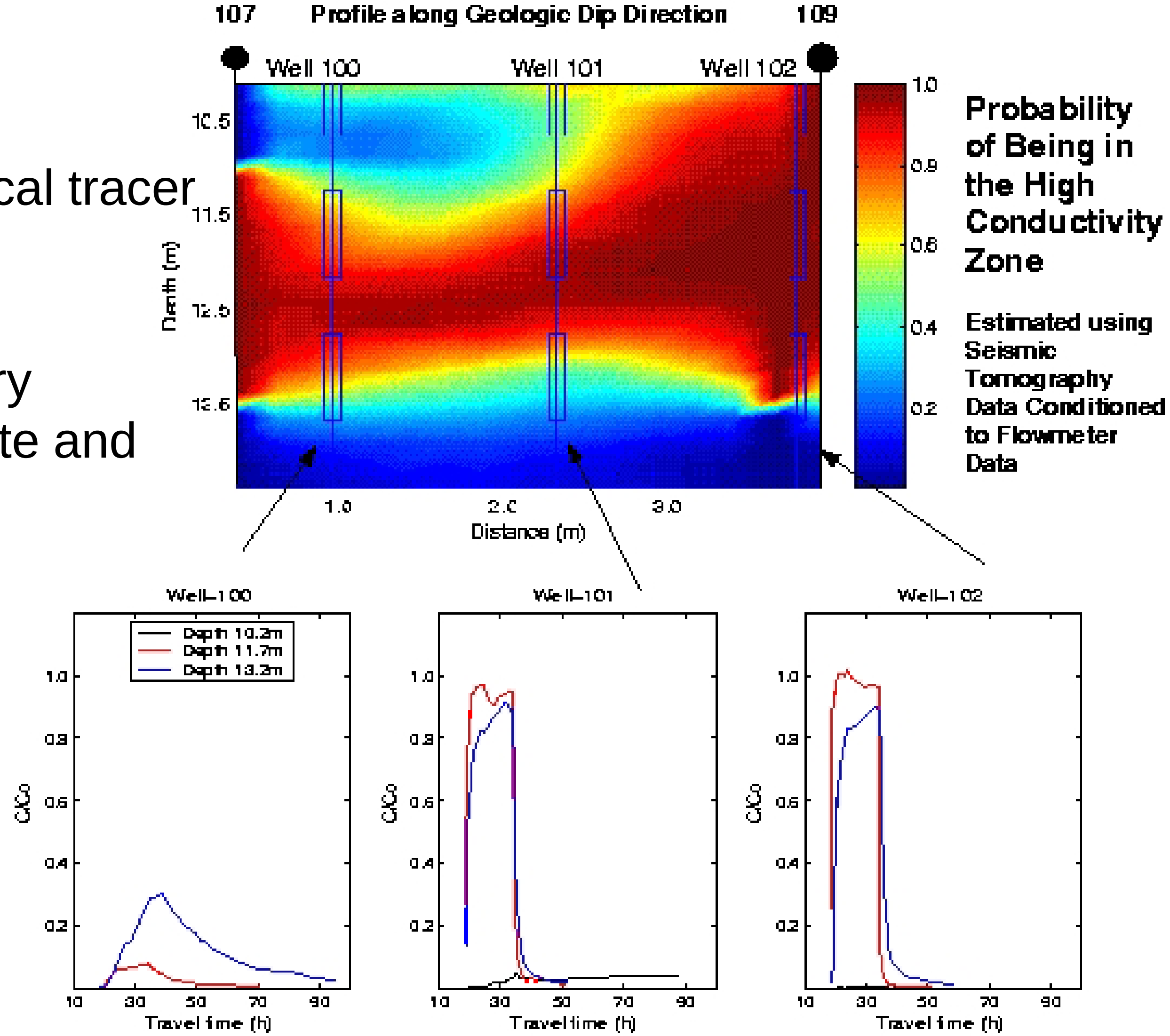
Experimental data was numerically simulated and the model used to design the *in situ* U bioreduction system.





Complements direct groundwater geochemical tracer measurements.

Provides complementary information on in situ fate and transport processes.



Tracer Breakthrough at 3 Multi-Level Samplers along Geologic Dip Direction

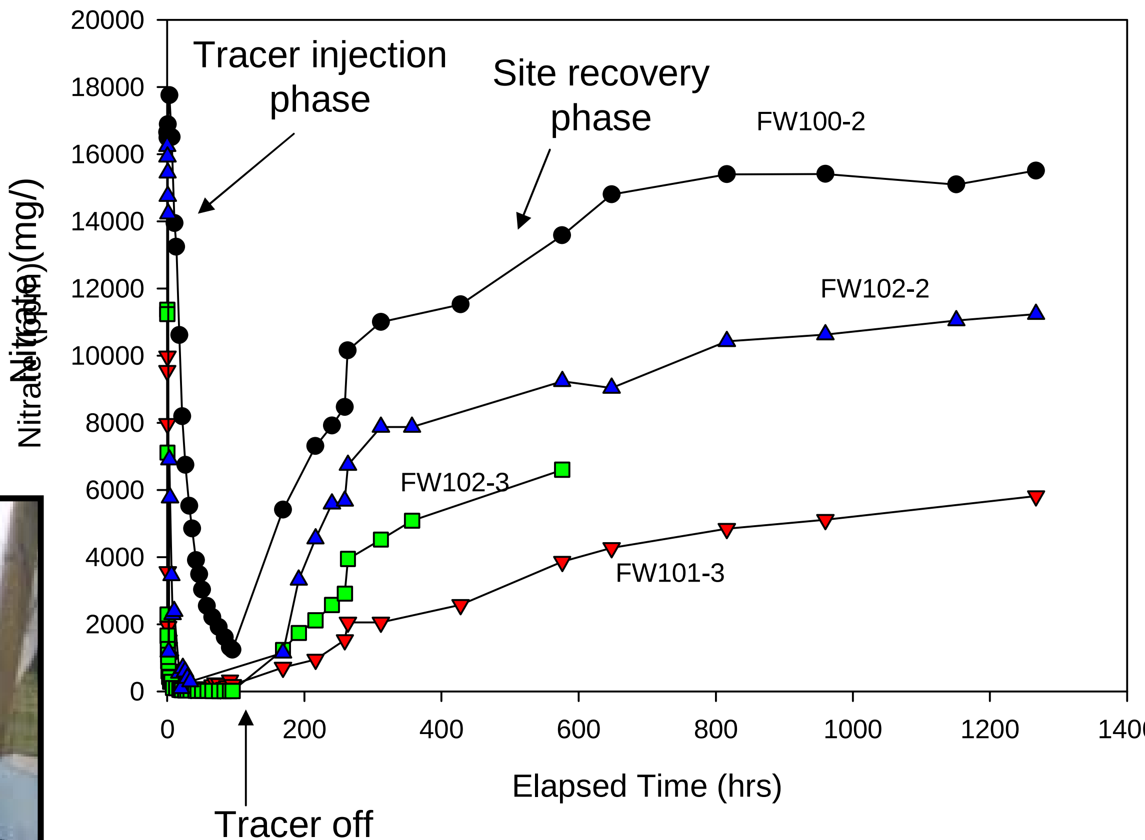
Hubbard et al., 2003

Mehlhorn et al., 2003

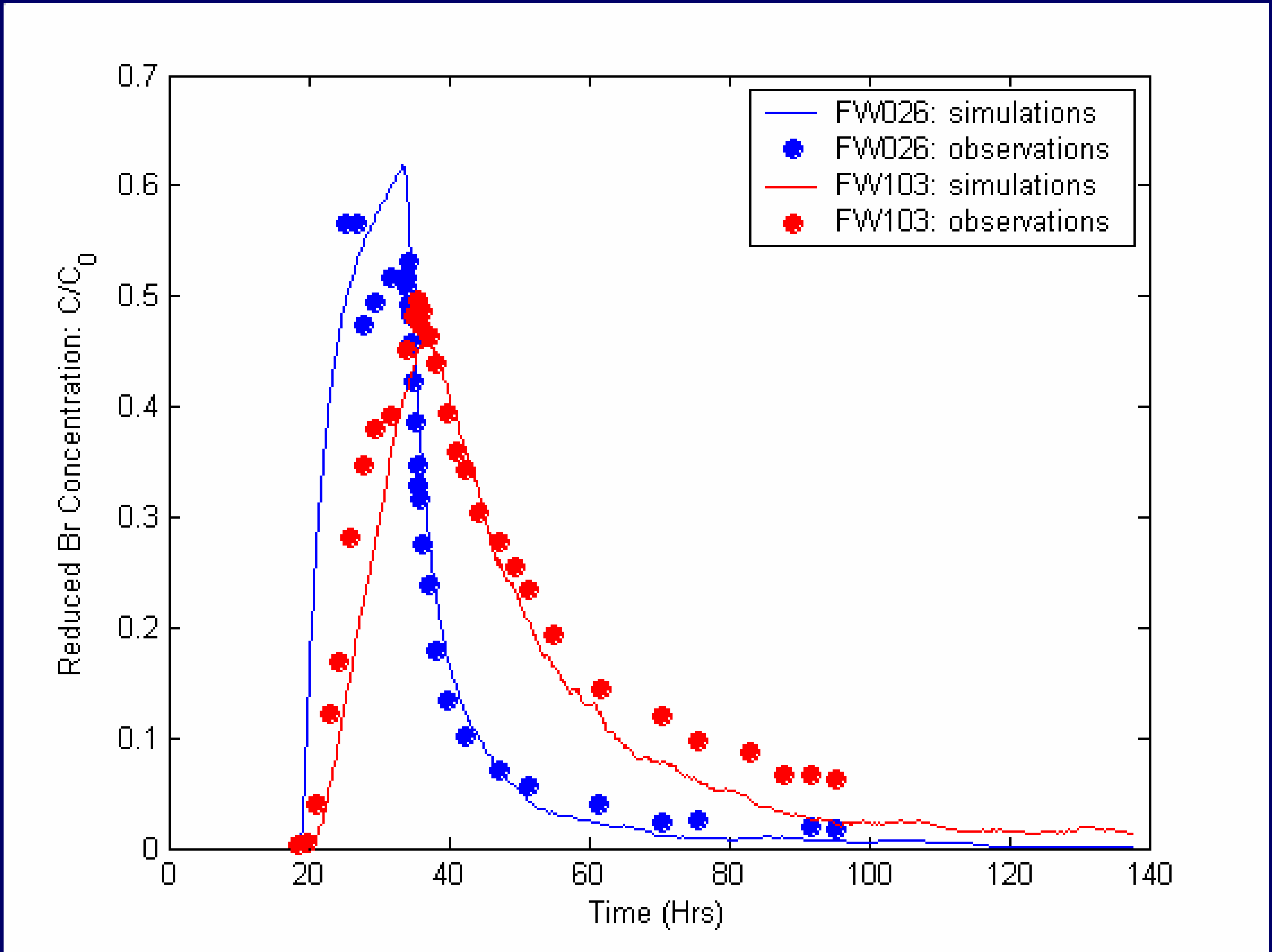
Natural gradient site recovery solute breakthrough

Natural gradient contaminant transport monitored during site recovery.

Quantification of solute residence times, direction of groundwater flow, and strike vs. dip interactions.



Tracer study simulations



Two-Part Strategy

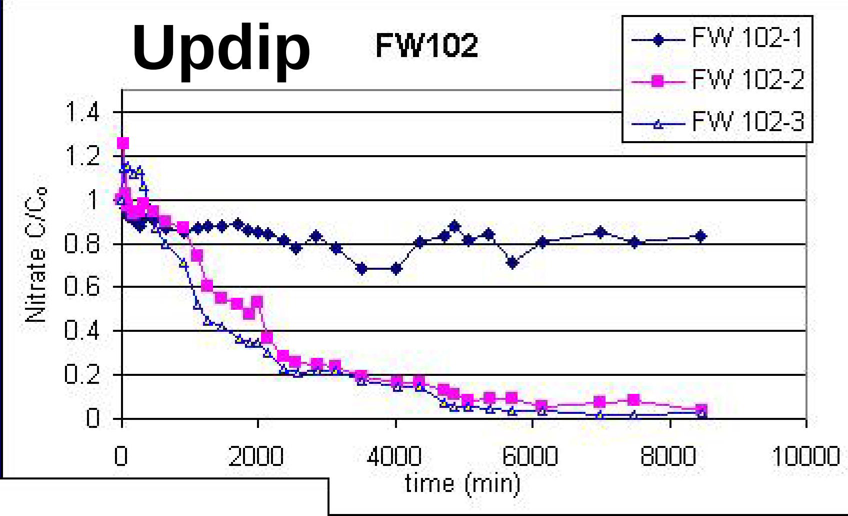
***Ex-situ* conditioning of water in treatment zone**

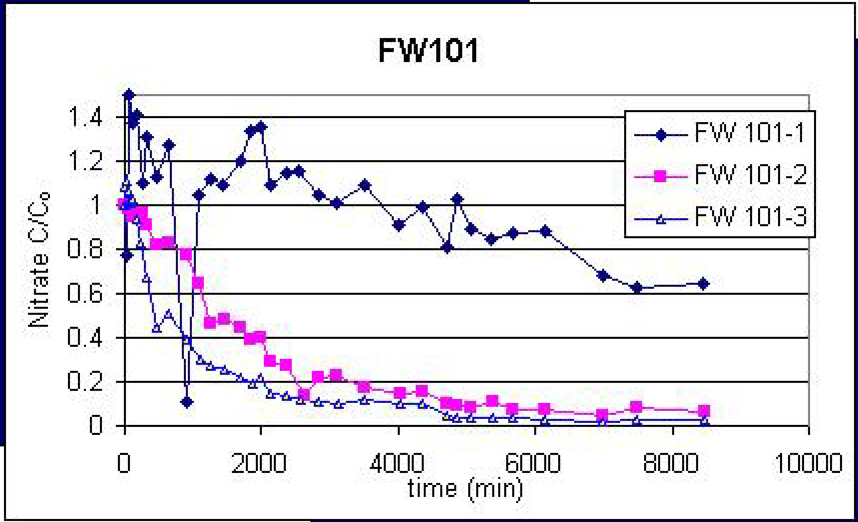
1. Precipitate Al and Ca
2. Remove NO_3^- by denitrification in FBR
3. Vacuum strip to remove VOCs and N_2

✓ ***In-situ* reduction of uranium**

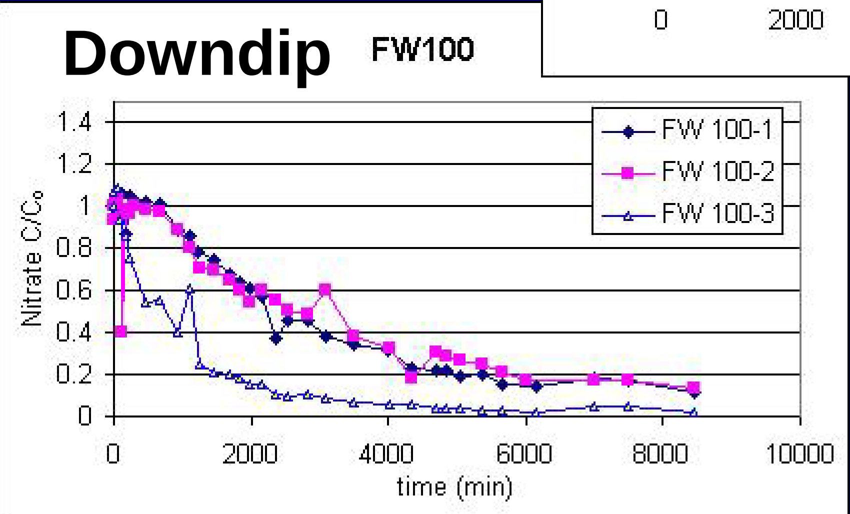
1. ✓ Flush to remove Al and initial nitrate. Bulk of uranium remains on soil.
2. Inject FBR effluent into outer cell to protect inner cell from background water.
3. Neutralize inner cell.
4. Add electron donor to inner cell to reduce U.

Clean water flush: Effect of flush on nitrate in MLS wells



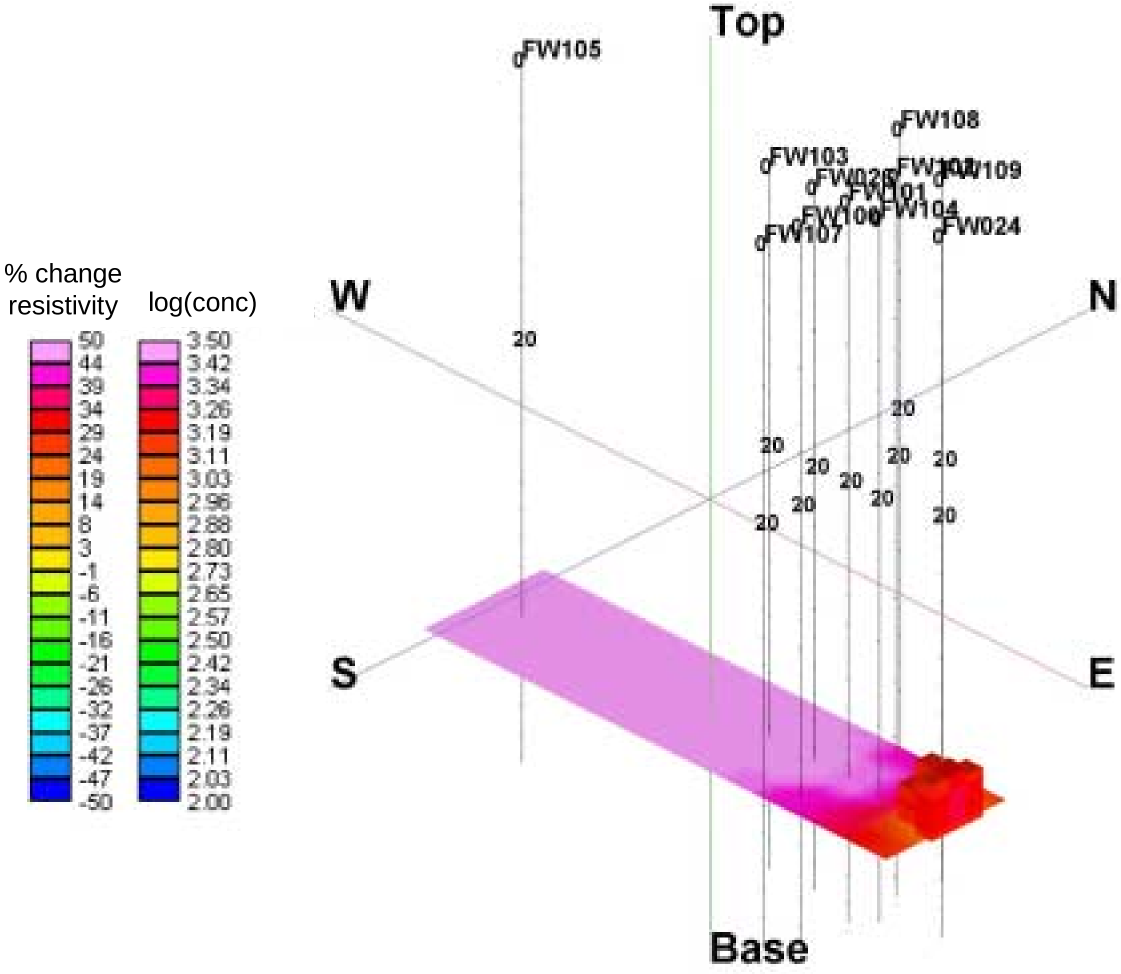


Mid-depths were flushed well
Bottom depth was poorly flushe



All depths were flushed

Time 014 hrs

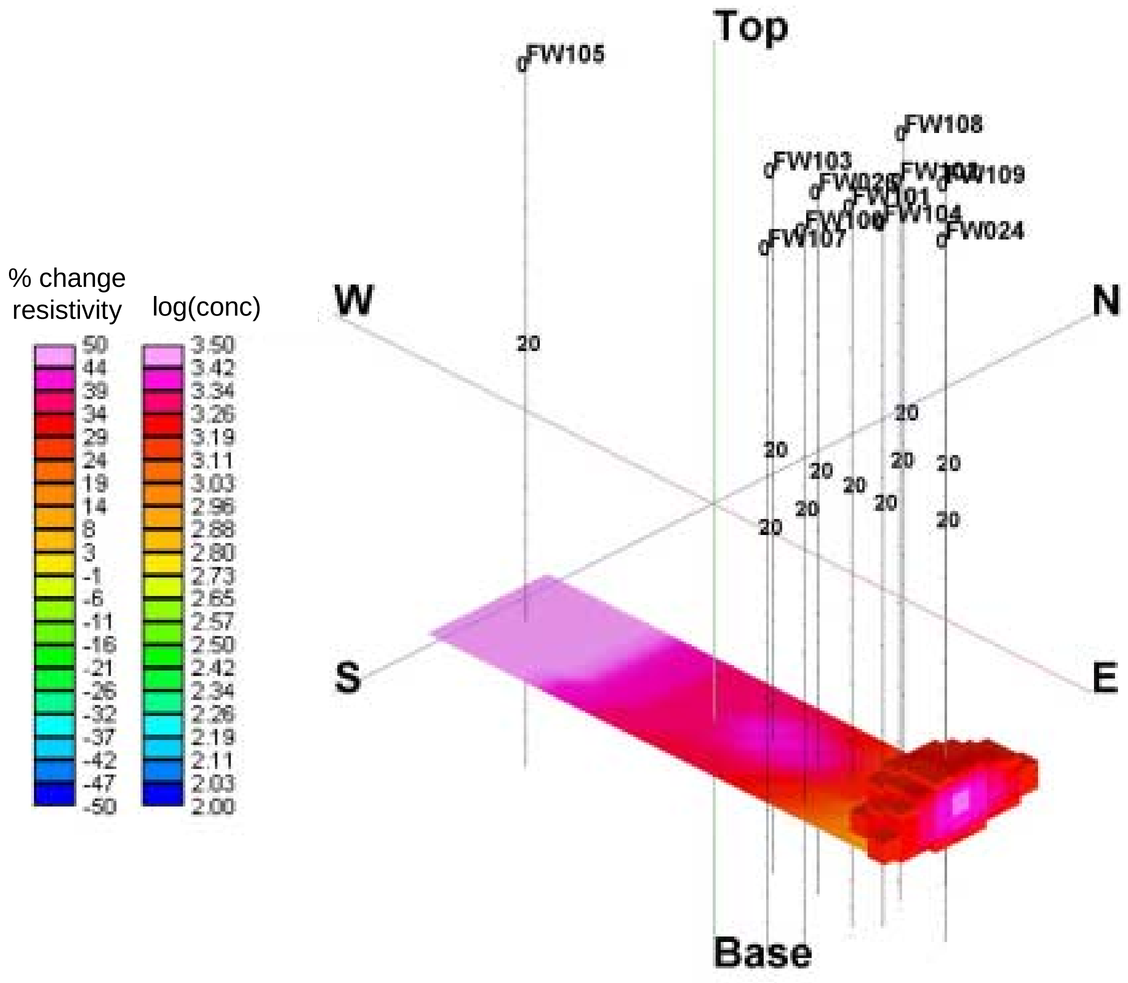


Gamey and Beard

3D: +30% change in resistivity

2D: log(NO_3 concentration) in mg/l

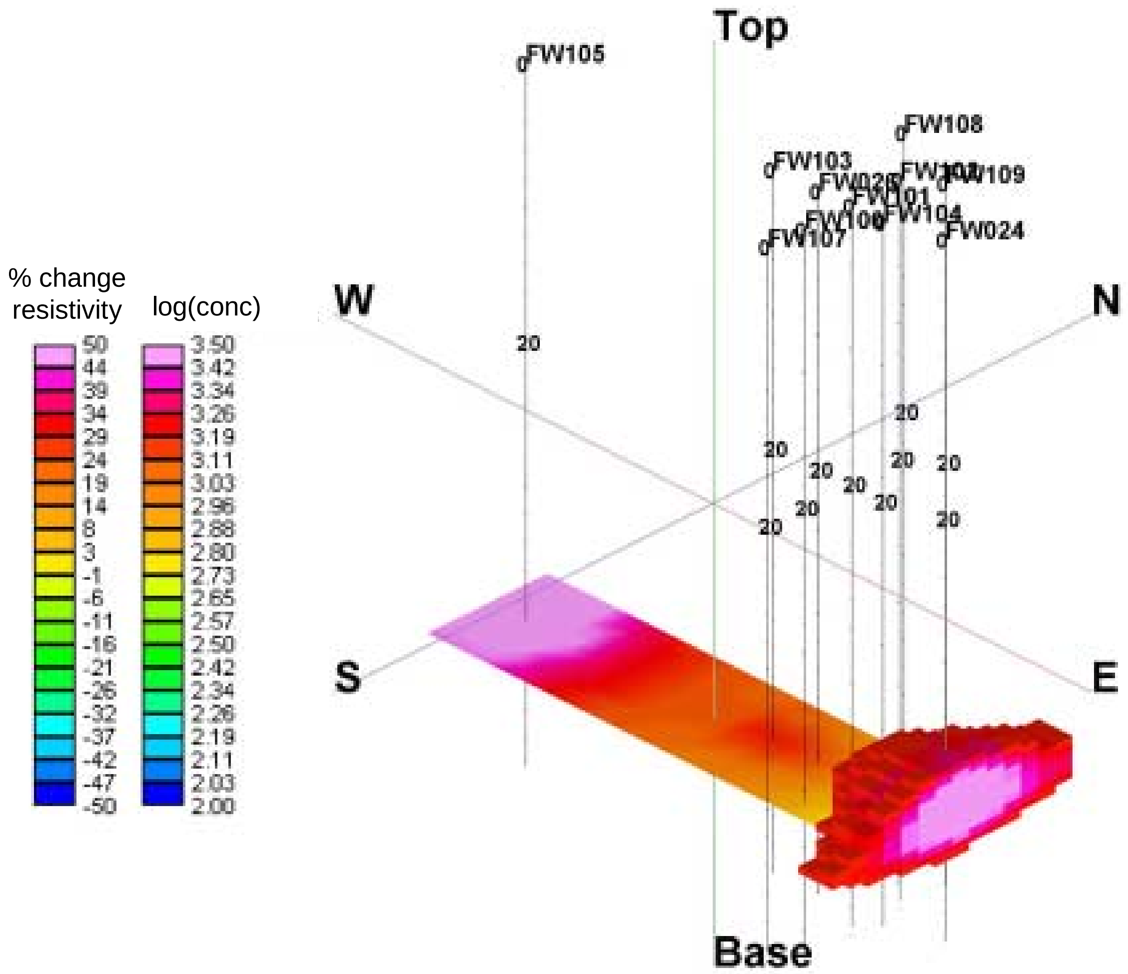
Time 028 hrs



3D: +30% change in resistivity

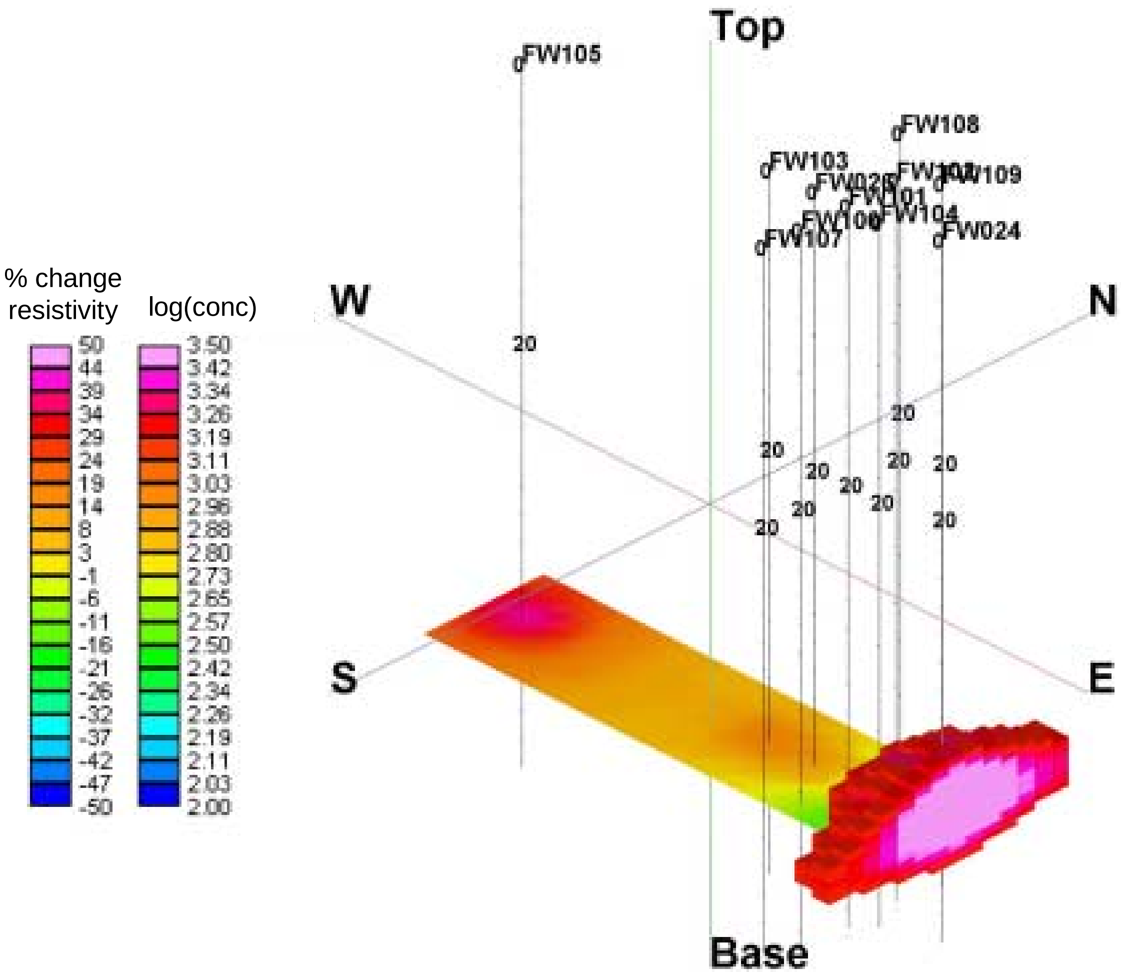
2D: log(NO_3 concentration) in mg/l

Time 046 hrs



3D: +30% change in resistivity

2D: log(NO_3 concentration) in mg/l

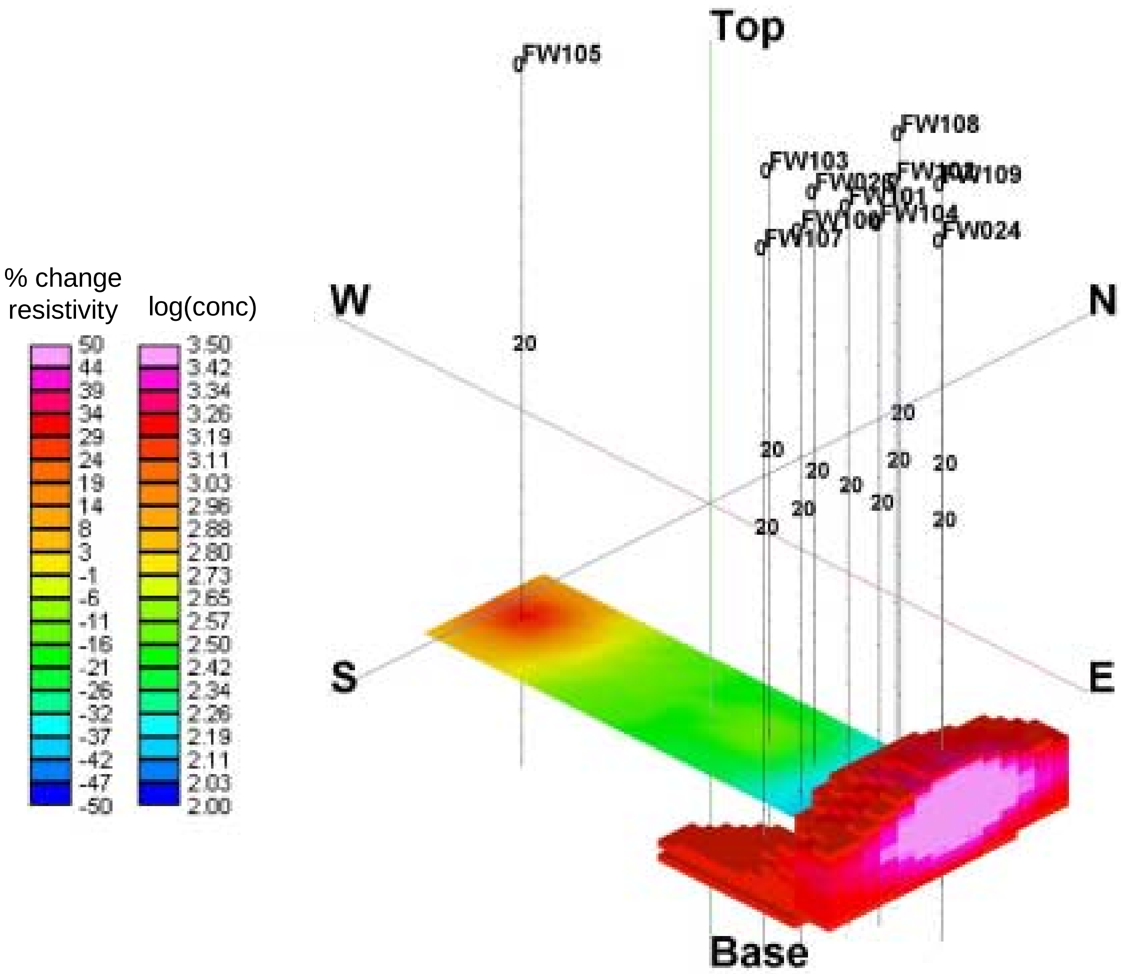


Time 062 hrs

3D: +30% change in resistivity

2D: log(NO_3 concentration) in mg/l

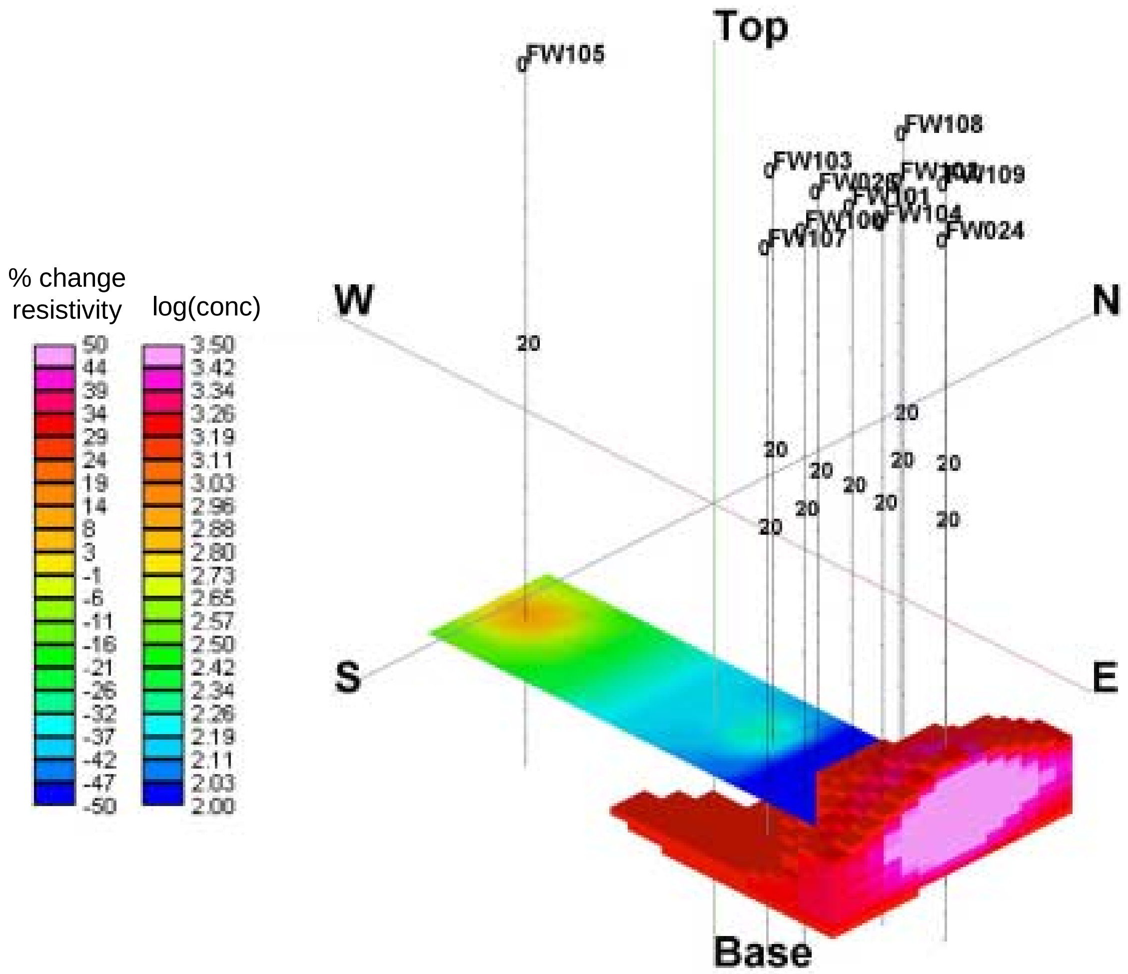
Time 078 hrs



3D: +30% change in resistivity

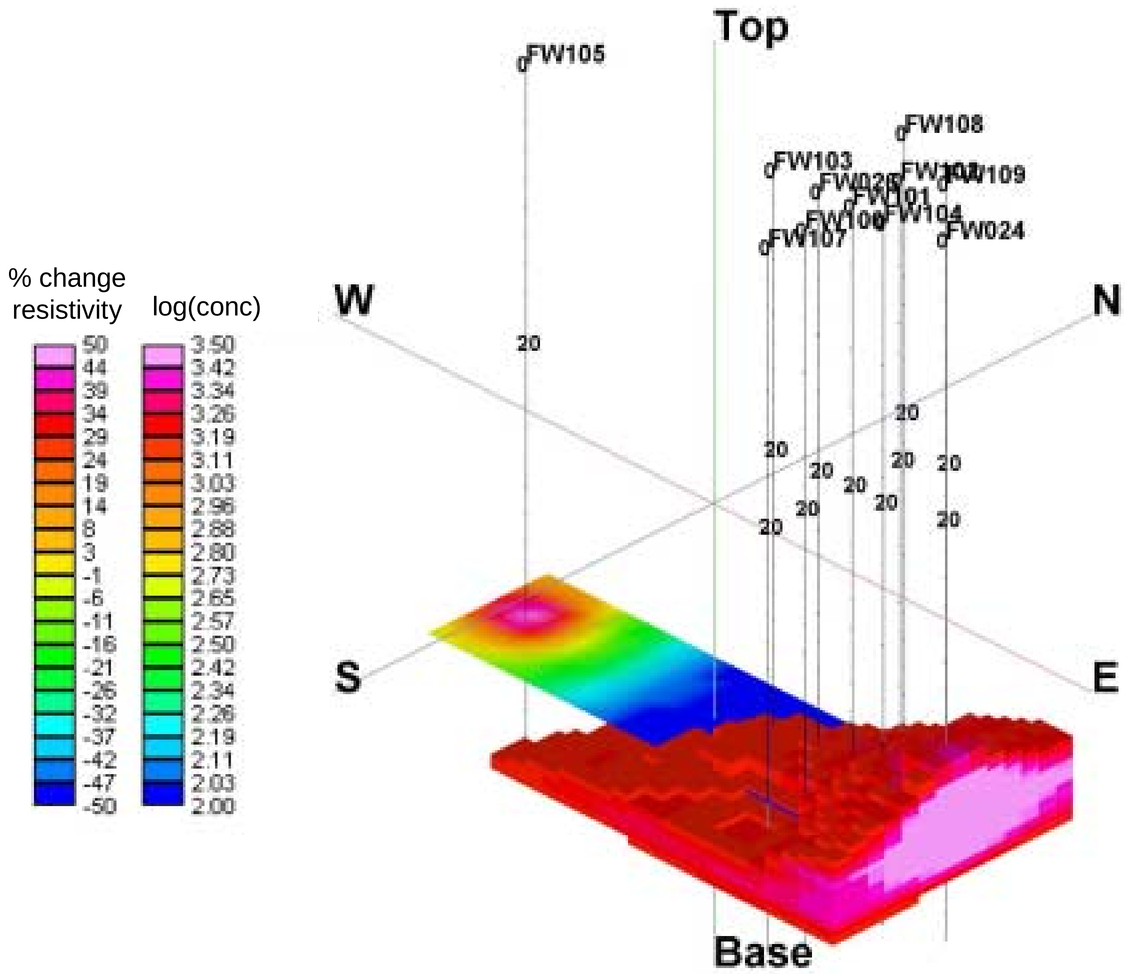
2D: log(NO_3 concentration) in mg/l

Time 095 hrs



3D: +30% change in resistivity

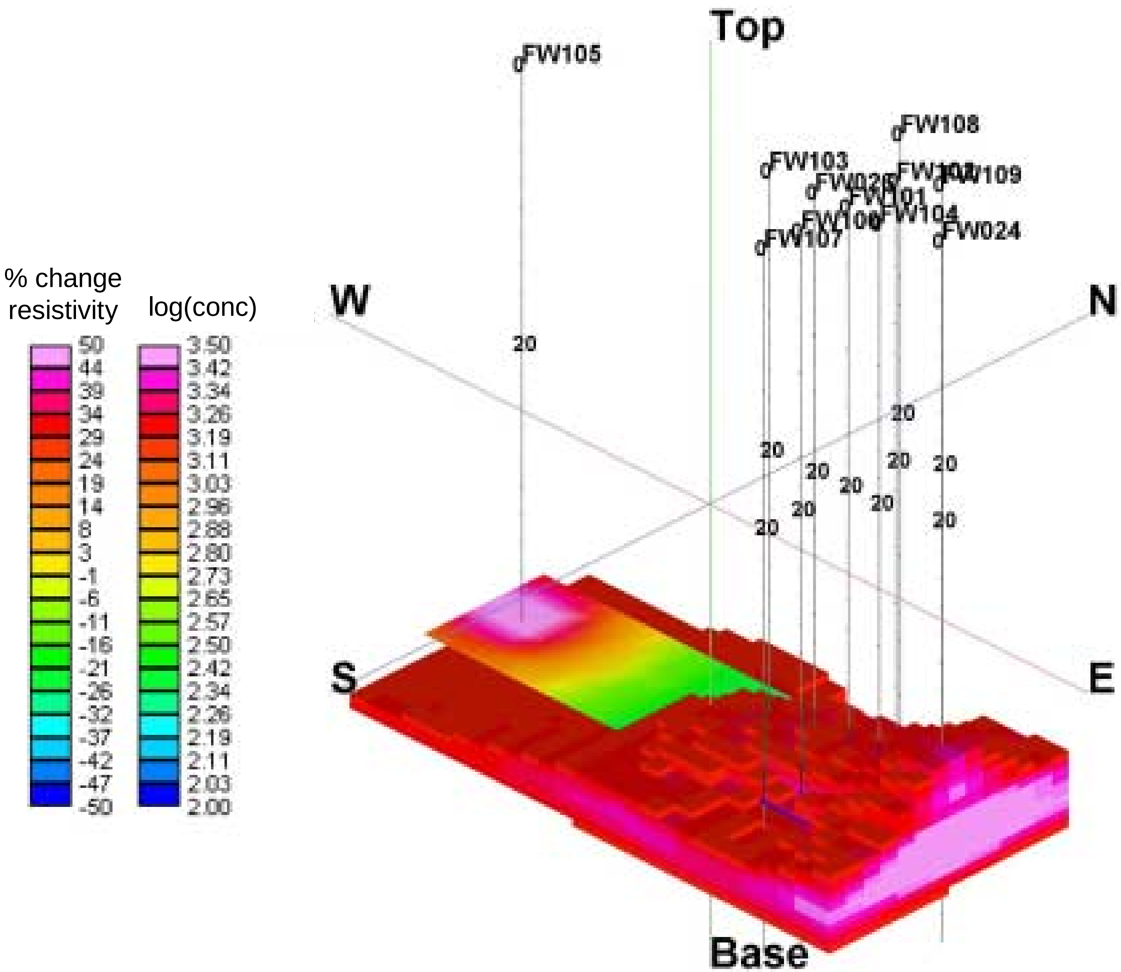
2D: log(NO_3 concentration) in mg/l



Time 119 hrs

3D: +30% change in resistivity

2D: log(NO_3 concentration) in mg/l



Time 143 hrs

3D: +30% change in resistivity

2D: log(NO_3 concentration) in mg/l

Microbiology

FBR sampling and characterization (denitrifers)

Phylogenetic analyses - Zhou, Fields, Criddle

Functional gene microarrays - Zhou, Fields

Functional monitoring

Monitoring of microbial succession in subsurface (uranium reducing populations)

Baseline analysis - Zhou, Fields, Geesey, Marsh

Slides on inner loop sidestream - Geesey

Small packed columns on inner loop sidestream

Filtered samples from inner loop - Zhou, Fields

U-reducing enrichment characterization - phylogeny, kinetics

Phylogenetic analyses - Fields, Marsh, Nyman, Criddle

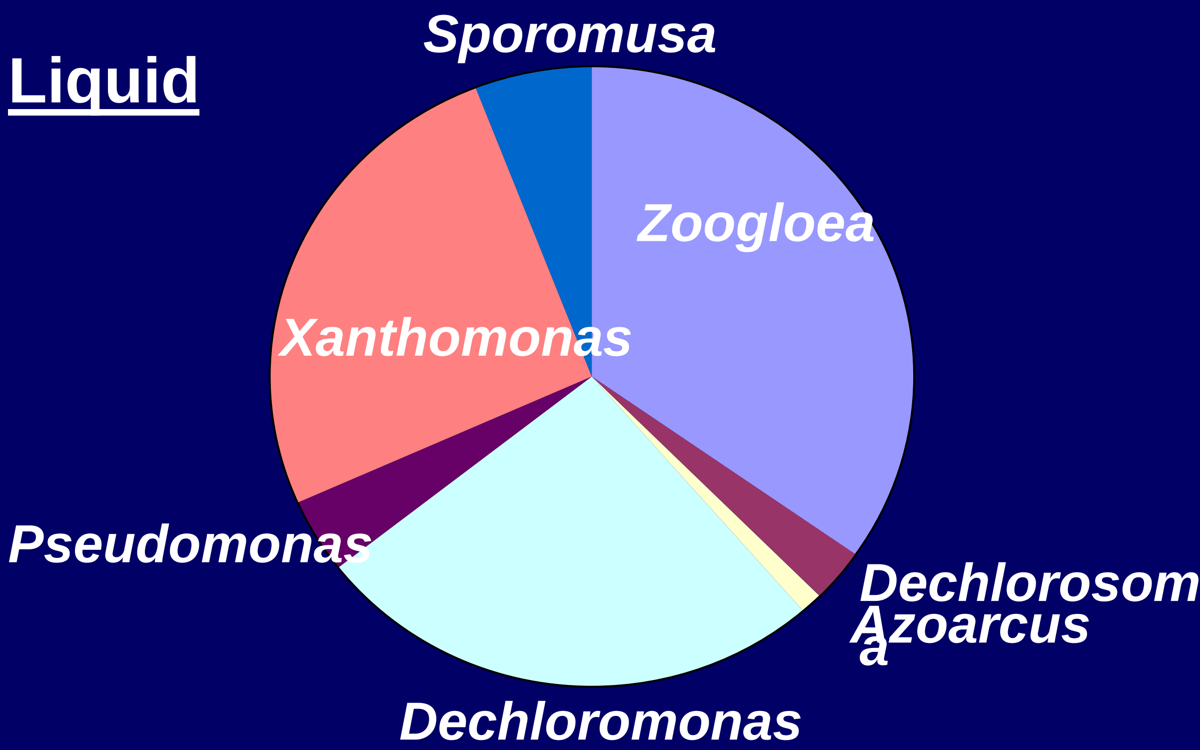
Pilot scale FBR was innoculated with enrichment from Well TPB16

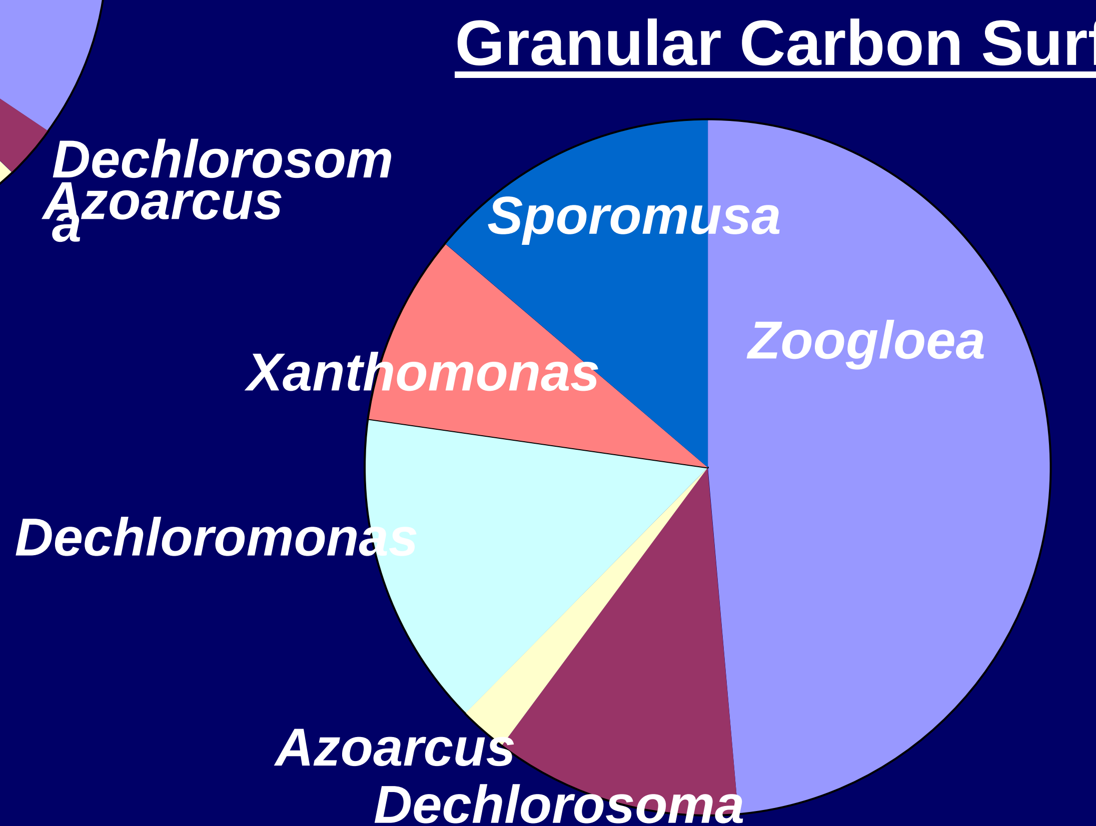
Denitrifying biofilms growing on granular activated carbon in pilot scale FBR

Fluidized Bed Reactor

- Removes NO_3^- as N_2
- Efficient
- Cheap
- Raises pH
- Demonstrated in two continuous pilot-scale systems (pH 7.4 and 9.2)
- Pilot FBR biomass as innoculum for the field FBR

Community Structure of Pilot FBR Used as Inoculum (SSU rDNA

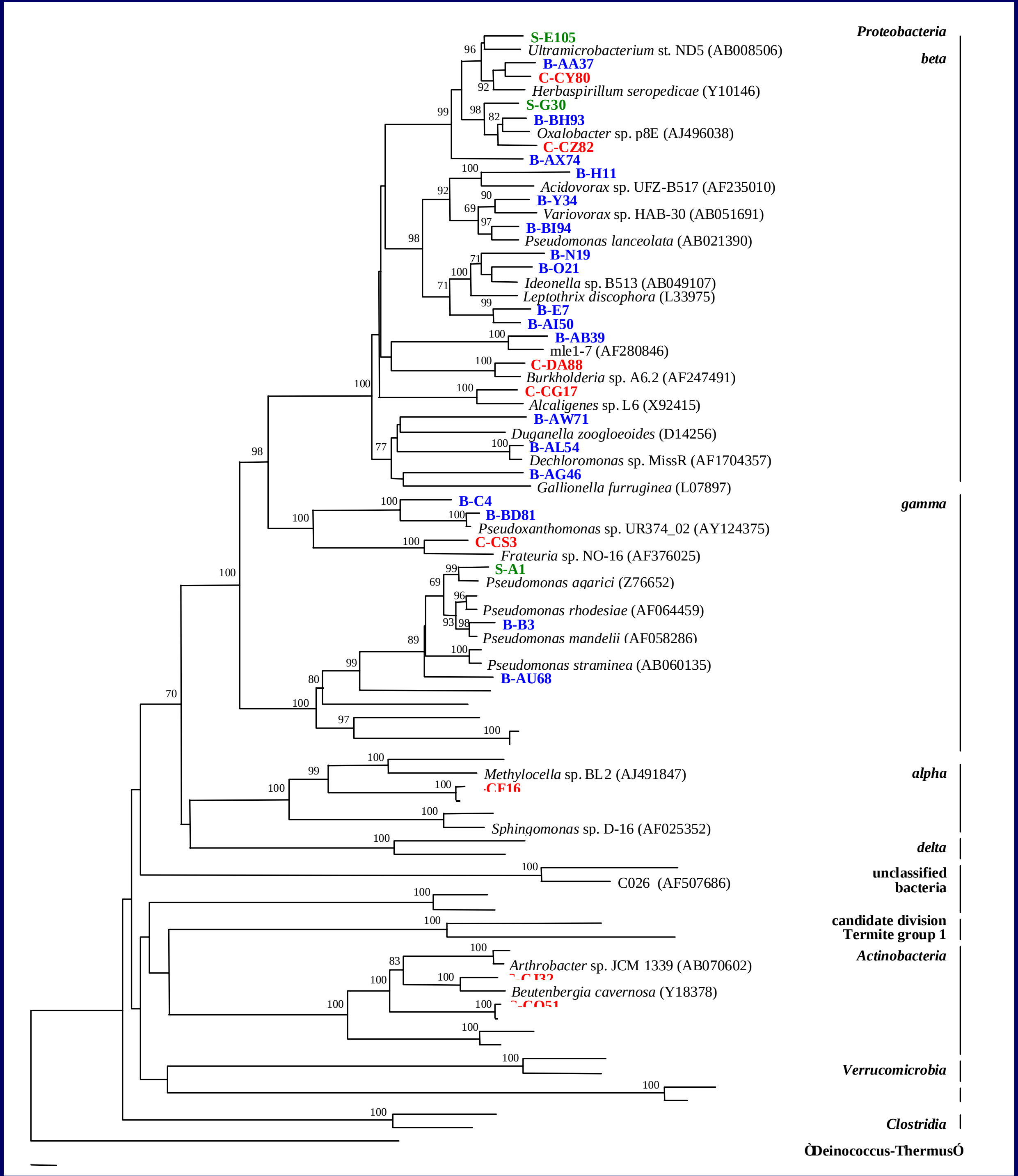




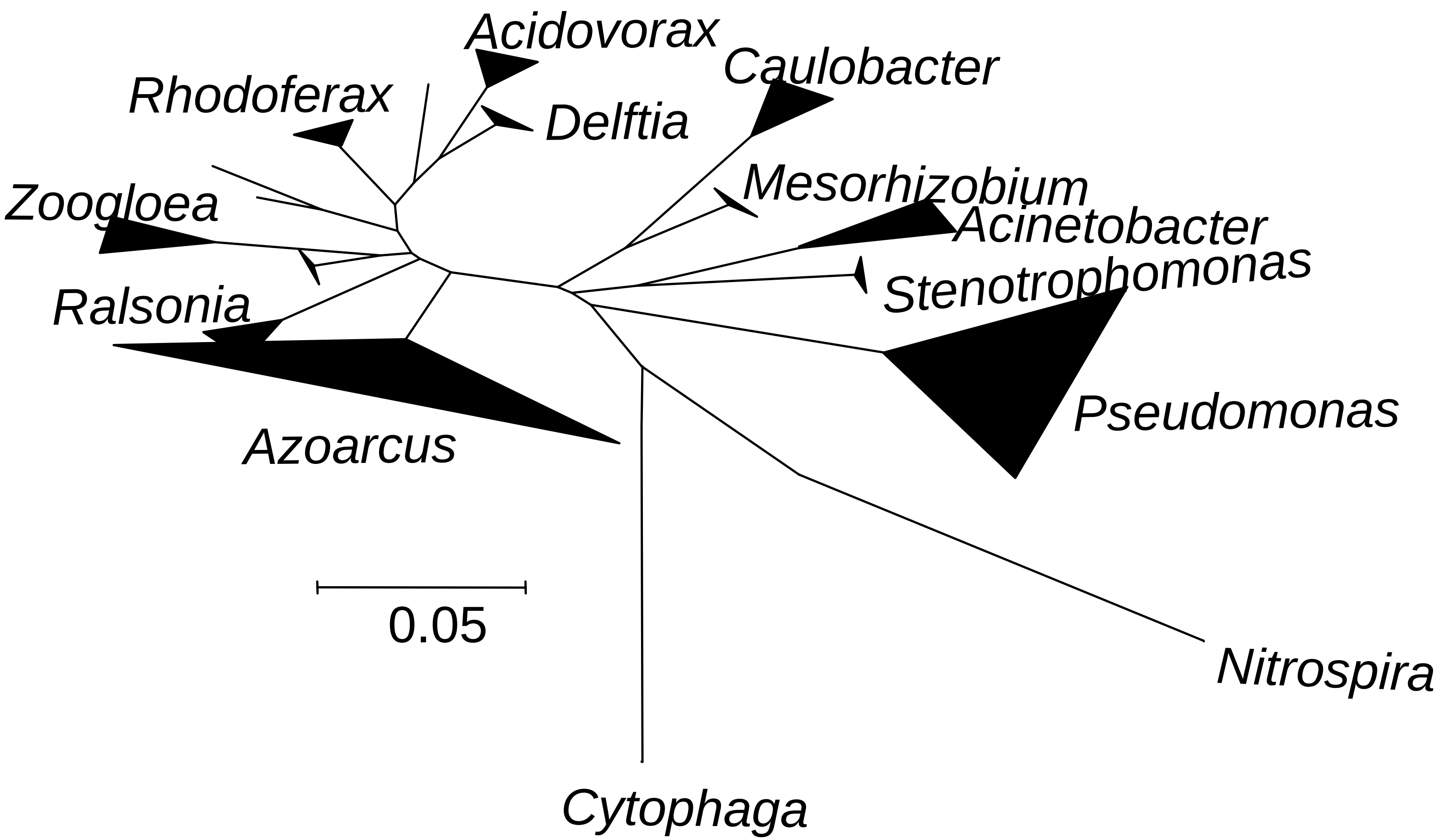
Baseline characterization slides in wells (INEEL):

Many β proteobacteria, including *Acidovorax* and *Burkholderia*; γ proteobacteria, including *Pseudomonas*.

Others: *Microbacteriu*



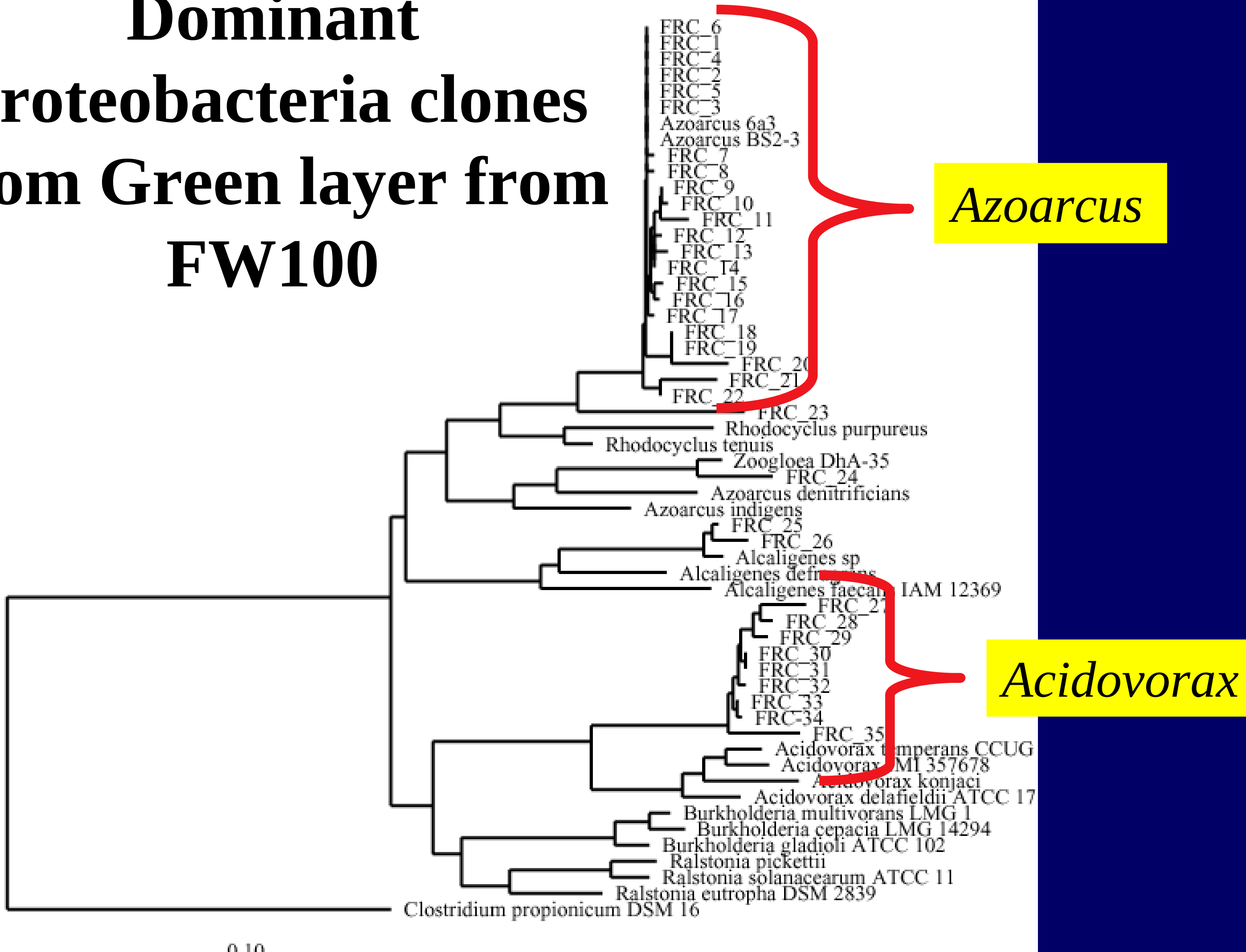
Phylogenetic analysis of groundwater 16S rRNA clonal library. β-*Proteobacteria* appeared to be a predominant sub-division (60% of library), represented by *Azoarcus*, *Zoogloea*, *Acidovorax*, and *Ralstonia*-like species. Iron, nitrate, and sulfate reducing organisms have also been isolated with the later shown to effectively reduce uranium.



Fields and Zhou

Marsh

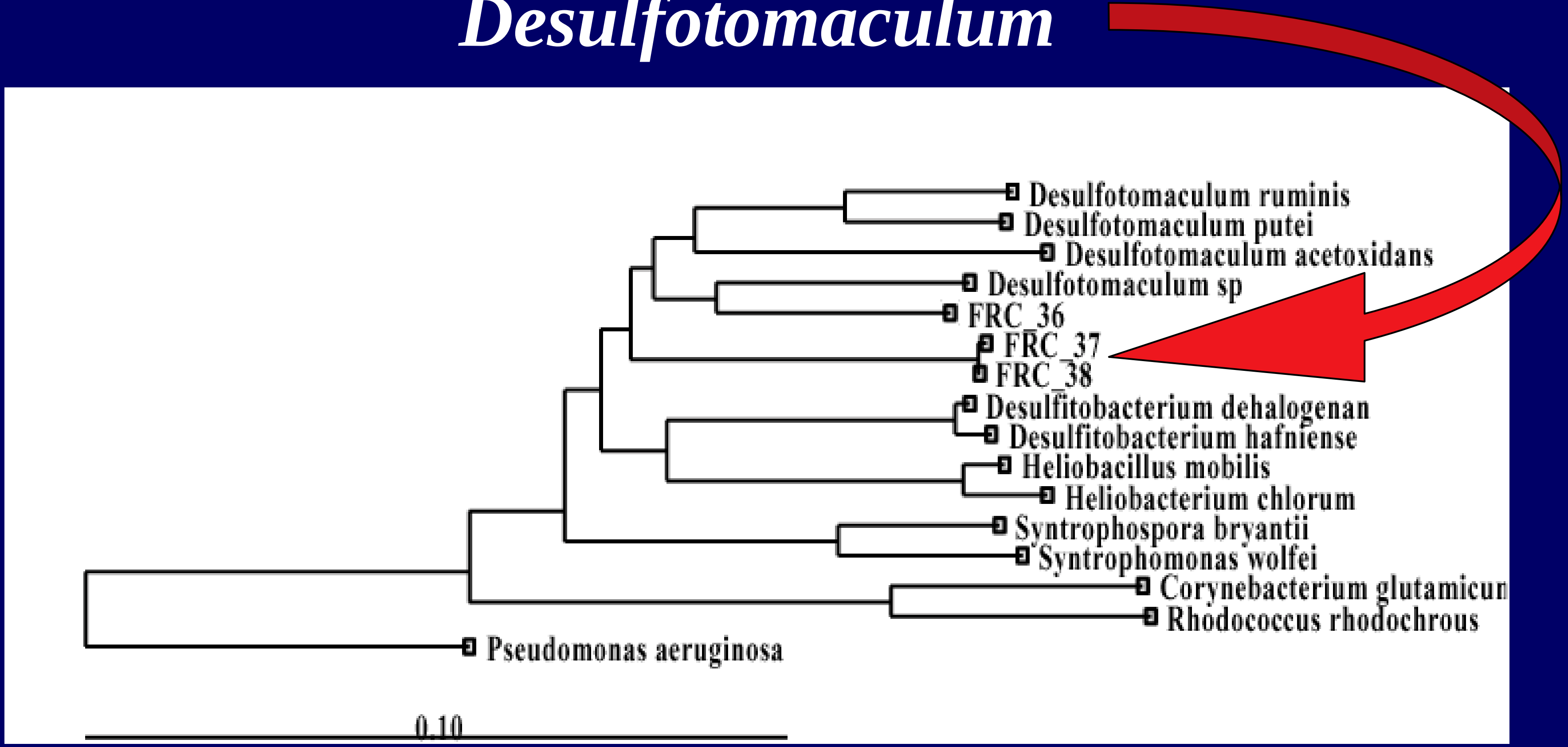
Dominant Proteobacteria clones from Green layer from FW100



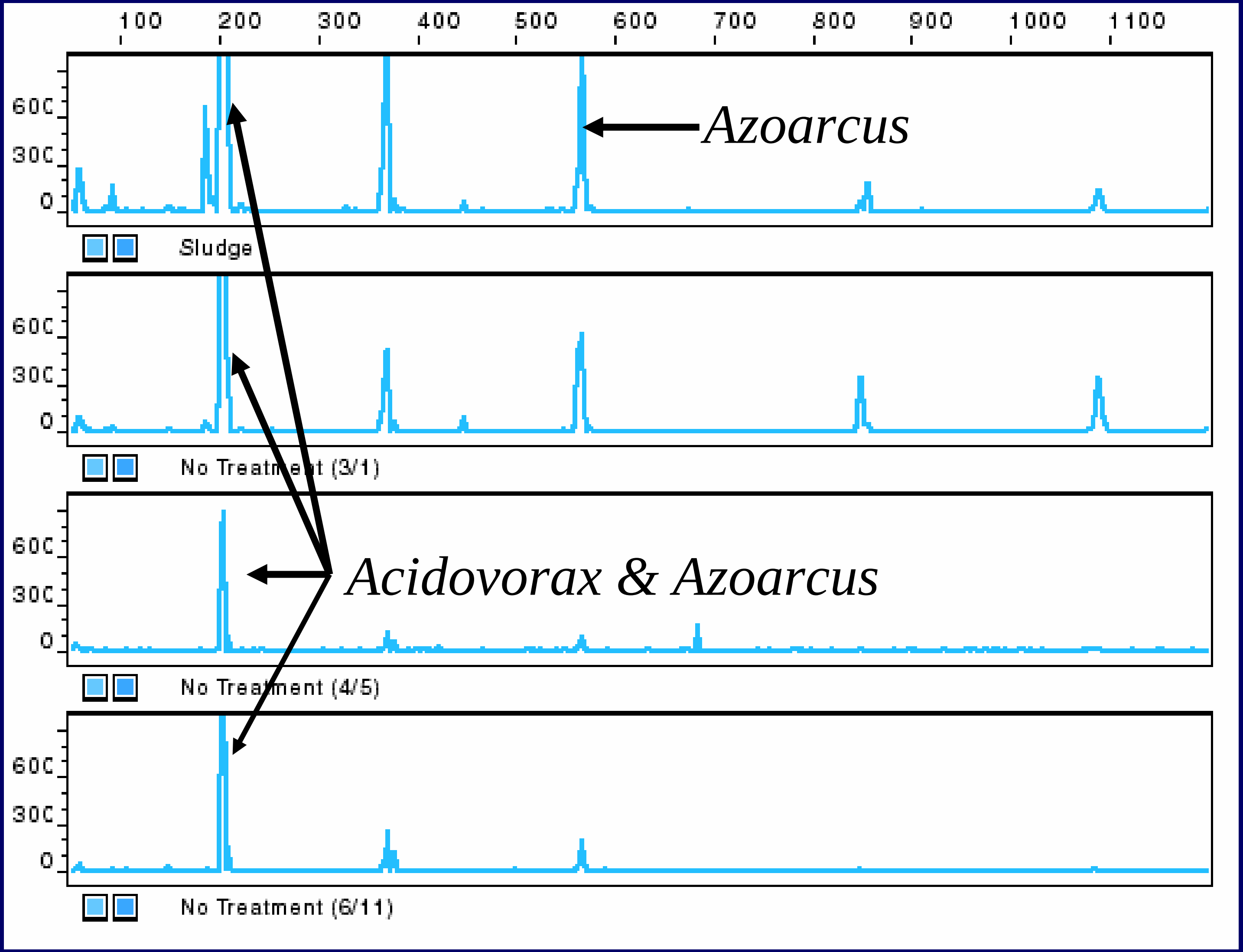
Marsh

Gram+ clones Detected in Green Layer (high flow zone)

Desulfotomaculum



16S rRNA T-RFLP analysis; Black layer



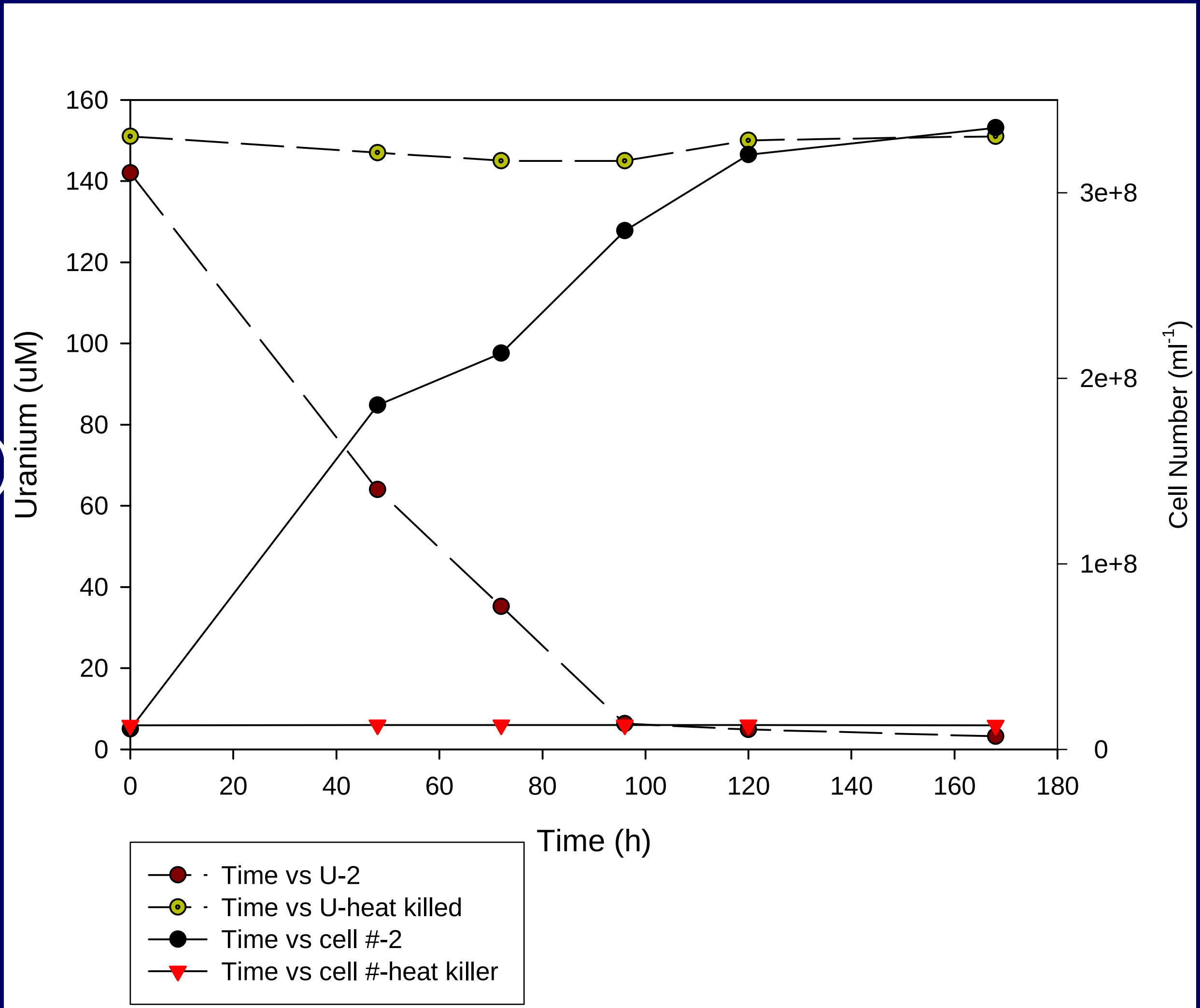
Background levels of denitrifiers, metal-reducers, and sulfate-reducers on sediment (MPN/g)

	Nitrate reducers	Ferric citrate reducers	Sulfate reducers
FW-107 (13.2 m)	3500	46	240
FW-109 (15.4 m)	5400	1700	1100

Fields

Uranium reduction by sulfate-reducing enrichment from Area 3 (FW-

U (µM)



Fields

Lactate (10 mM)
Medium - artifical gw + yeast extract

Bench-scale studies

- **Column studies of geochemistry - Jardine**

  Tracer + Sorption/Desorption profiles

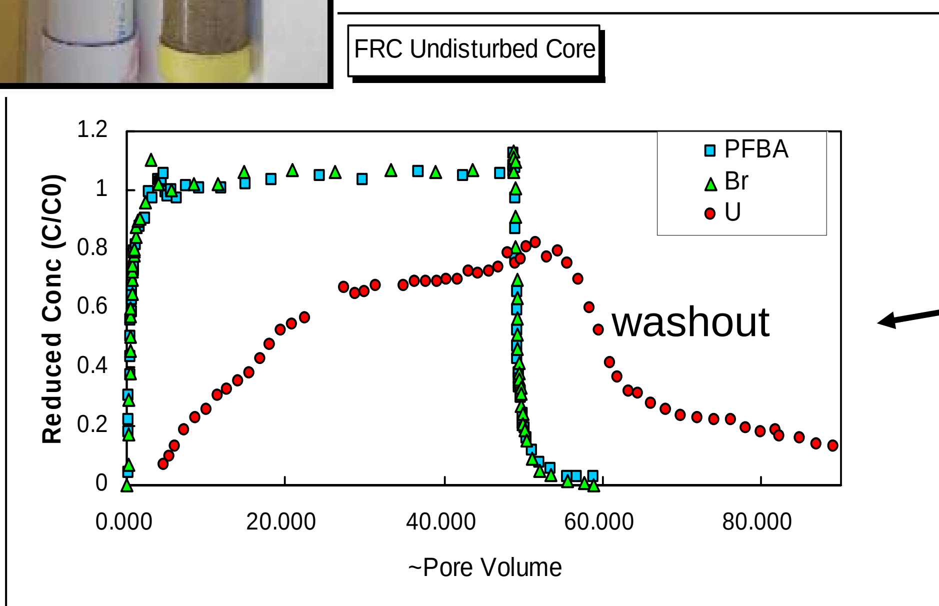
  Modeling to obtain mass transfer rates - Luo, Kitanidis, Cirpka

- **Microcosm experiments - Wu, Nyman, Criddle**

- **Column biostimulation study - Wu, Gu, Criddle**

Undisturbed column from treatment zone (42 ft. depth)

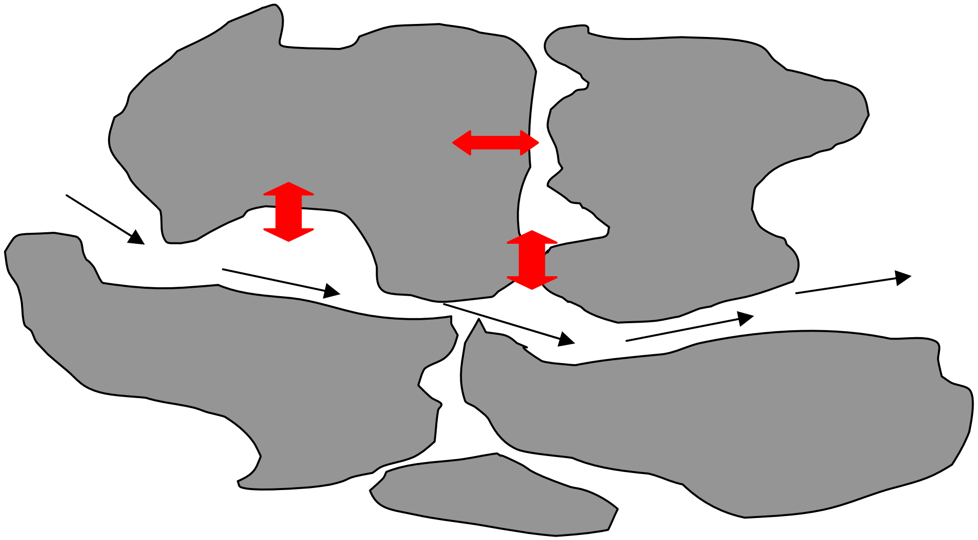
Current experiments are designed to quantify solute mass transfer kinetics. Planned experiments will examine bioreduction of uranium under dynamic flow conditions.



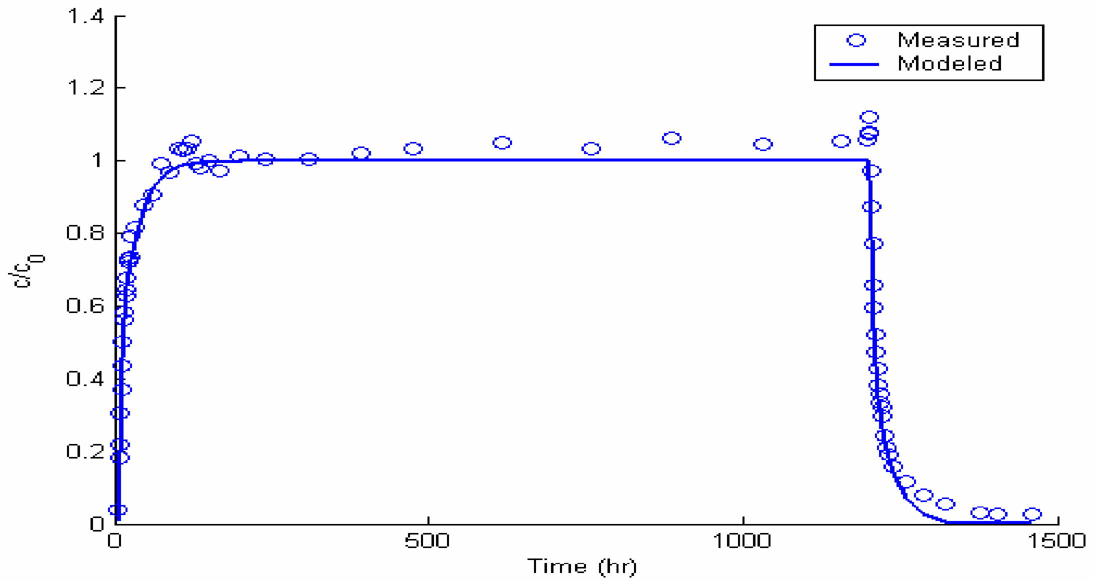
- **Kinetic Model**

  Assumptions

  - Kinetically controlled sorption/desorption
  - Kinetic mass transfer between two regions



- Tracer Transport

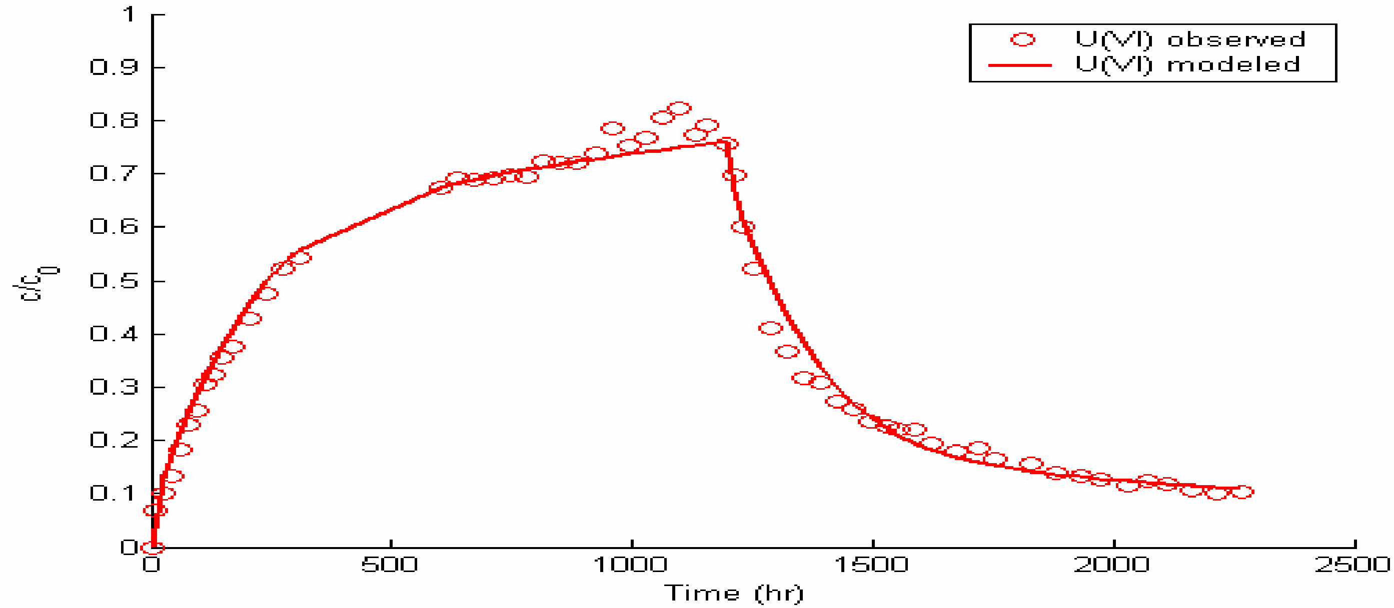


Simulation of conservative tracer transport

$$\theta_m = 0.198 \qquad \theta_{im} = 0.193$$

$$\lambda = 2.72 \times 10^{-6} / s \qquad D = 3.54 \times 10^{-8} m^2 / s$$

- U(VI) Transport



Simulation of U(VI) transport

$$\alpha_m = 5.2\times10^{-5} / s \qquad \alpha_{im} = 8.4\times10^{-5} / s$$

$$K_{d,m} = 12.2 \qquad K_{d,im} = 66.9$$

Screening Experiments

Anaerobic batch tubes were prepared containing:

- Denitrified synthetic groundwater

- Biomass from the FBR

- Effluent from the FBR

- Ethanol, lactate, or acetate

-50 mg/L uranyl

Soil test samples also contained:

- Sediment (washed with $CaCl_2$), from the MLS wells at the depth of the in-situ experiment

→ Addition of ethanol increased the rate of U(VI) removal from solution, but did not have much effect on the final level of reduction

Uranium Oxidation State in Biomass

1st Derivative XANES Spectra

U(VI) Standard ($UO_2(NO_3)_2 \cdot 6H_2O$)

U(IV) (FBR effluent, EtOH)

U(IV) (FBR effluent, Biomass)

U(IV) (FBR effluent, Biomass, EtOH)

U(IV) Standard (Uraninite)

SSRL

- Amendment of ethanol increased the rate of U(VI) removal from solution.
- A rebound of soluble U(VI) was observed in the Eff, EtOH tube.

Uranium Oxidation State in Sediment Samples

1st Derivative XANES Spectra

U(VI) Standard ($UO_2(NO_3)_2 \cdot 6H_2O$)

U(VI) (sediment)

U(IV) (sediment, FBR effluent)

U(IV) (sediment, FBR effluent, EtOH)

U(IV) (sediment, FBR effluent, biomass, E

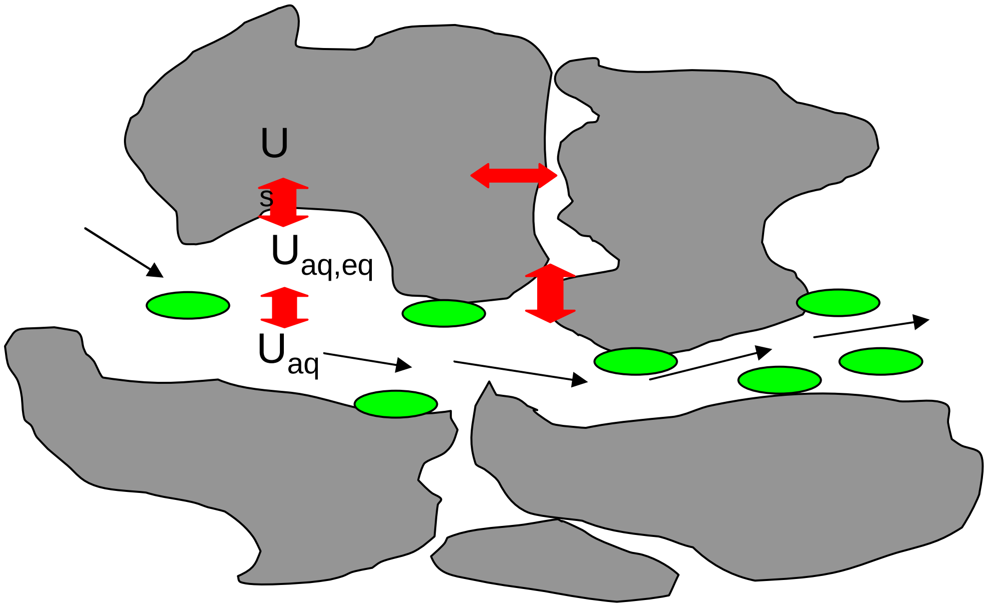
U(IV) Standard (Uraninite)

SSRL

- **Kinetic Model**

  Assumptions

  - Kinetically controlled sorption/desorption
  - Kinetic mass transfer between two regions
  - Microbial reduction of U(VI) in the mobile zone



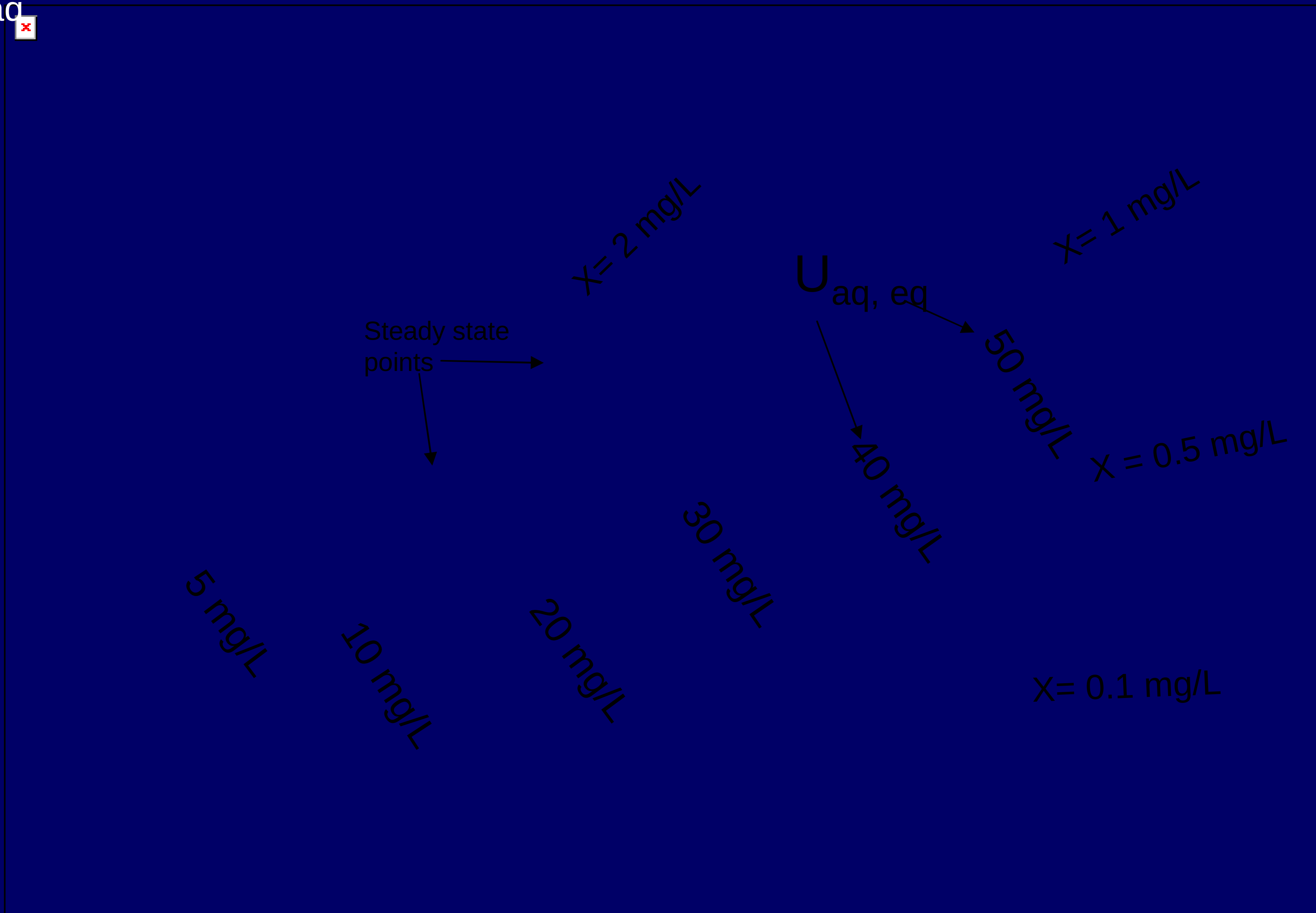
k_w is a lumped parameter accounting for mass transfer. It has units of time^{-1}. $U_{eq,aq}$ is the concentration of U in equilibrium with the solid phase concentration. It is a function of pH and TIC. X is biomass concentration, and k' is a pseudo second order rate coefficient, .

Rate of mass transfer = $k_w(U_{aq,\,eq} - U_{aq})$

Rate of reduction = $k'X\,U_{aq}$

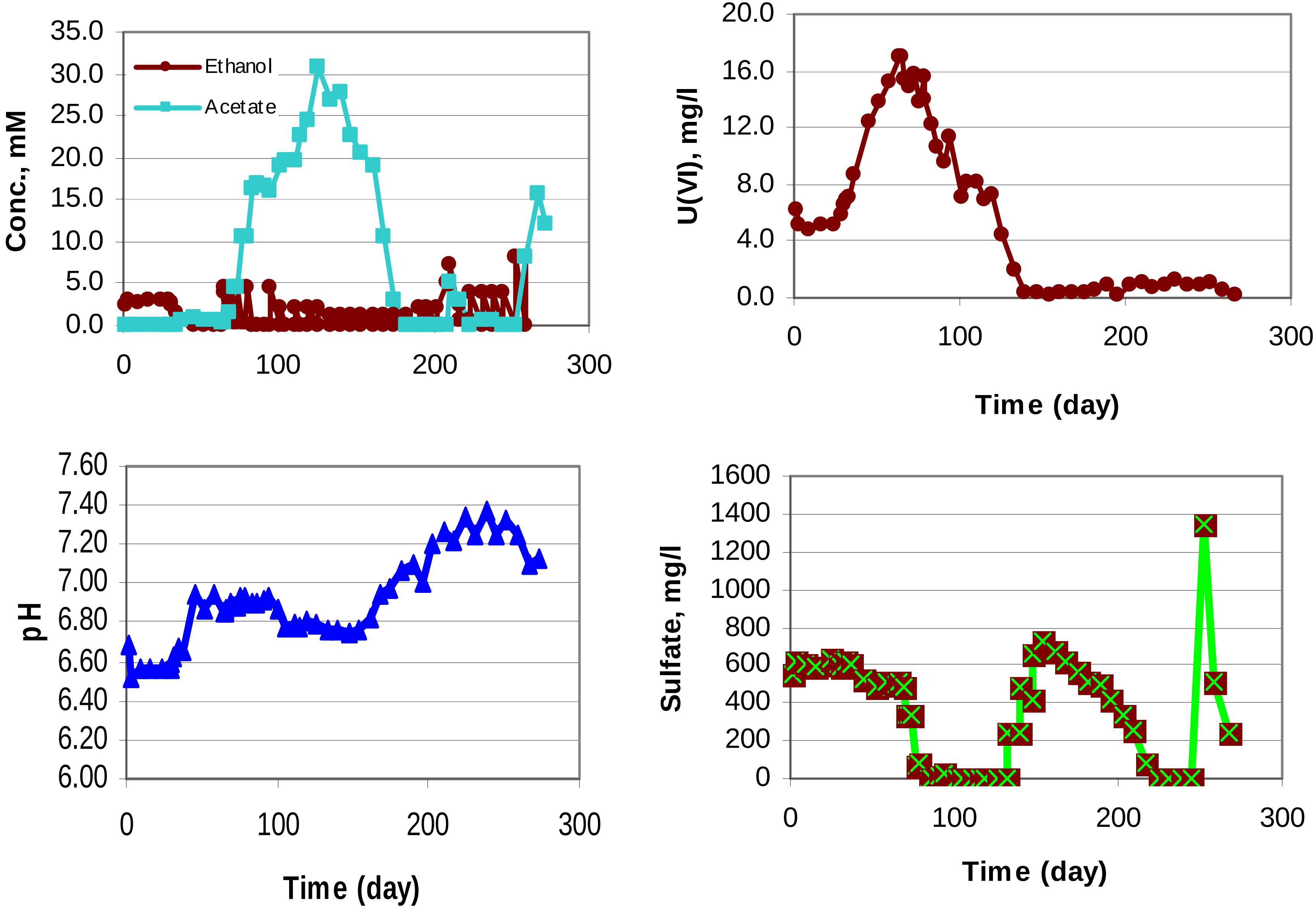
At steady state:

Rate of mass transfer = $k_w(U_{aq,eq} - U_{aq})$ = Rate of reduction = $k' X U_{aq}$



k_w= 6 x 10^{-6} s^{-1} (0.51 d^{-1})   k'= 0.2 L/mg-d

Biostimulation in FRC Soil Column



Ethanol
Acetate
Conc., mM
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
0
100
200
300
U(VI), mg/l
20.0
16.0
12.0
8.0
4.0
0.0
0
100
200
300
Time (day)
pH
7.60
7.40
7.20
7.00
6.80
6.60
6.40
6.20
6.00
0
100
200
300
Time (day)
Sulfate, mg/l
1600
1400
1200
1000
800
600
400
200
0
0
100
200
300
Time (day)

Key points

- Site characteristics: high acidity, high nitrate, high sulfate, high metals. Organisms identified repeatedly at low pH: *Acidovorax, Burkholderia, Pseudomonas, Microbacterium, Clostridia*.

- Aluminum buffers the system at low pH and precipitates when the pH is increased. It is removed ex-situ by precipitation.

- Nitrate inhibits U(VI) reduction. It is removed ex-situ in an FBR.

- Calcium inhibits U(VI) reduction. It is removed ex-situ by precipitation.

- A nested recirculation scheme is used to protect the treatment zone from aluminum, nitrate, and acidity.
- Addition of ethanol to the inner loop will begin once and nitrate is suffficiently removed from the treatment zone and the pH level has stabilized.

- Bench-scale study results:

Ethanol stimulates efficient U(VI) reduction

Desorption rates may be increased by increasing pH and TIC. This could prove to be a valuable tool for increasing rates that are mass transfer limited.

Sulfate addition may enable reduction to low levels.