Field scale evaluation of biostimulation in the near source zone of the former S3 ponds at Oak Ridge

Stanford University

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

Miami Univ

Matthew Fields

Universität Stuttgart

Olaf Cirpka
Frank-Andreas Weber

Oak Ridge National Laboratories

Craig Brandt
Scott Brooks
Sue Carroll
Matthew Fields
Baohua Gu
Philip Jardine
Tonia Mehlhorn
Terry Gentry
Ye-Kyoung Ku
Ken Lowe
Lynda Campbell
Jeff Riggs
Jizhong Zhou
Yul Roh
Jack Carley
Bobette Nourse

NABIR Field Research Center

David Watson

Retec

Robert Hickey
Raj Rajan
Dan Wagner

LBNL

Susan Hubbard
Ken Williams

Argonne

Ken Kemner

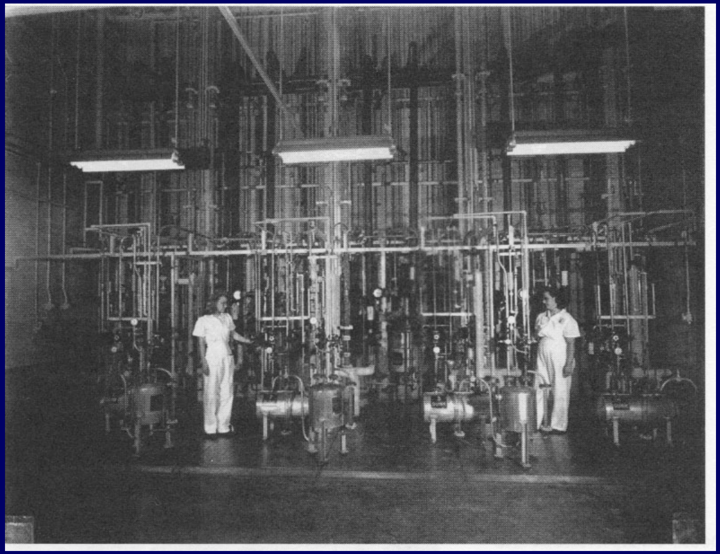
INEEL

Gill Geesey
David Cummings

Michigan State University

Terry Marsh

The Oak Ridge S3 pon

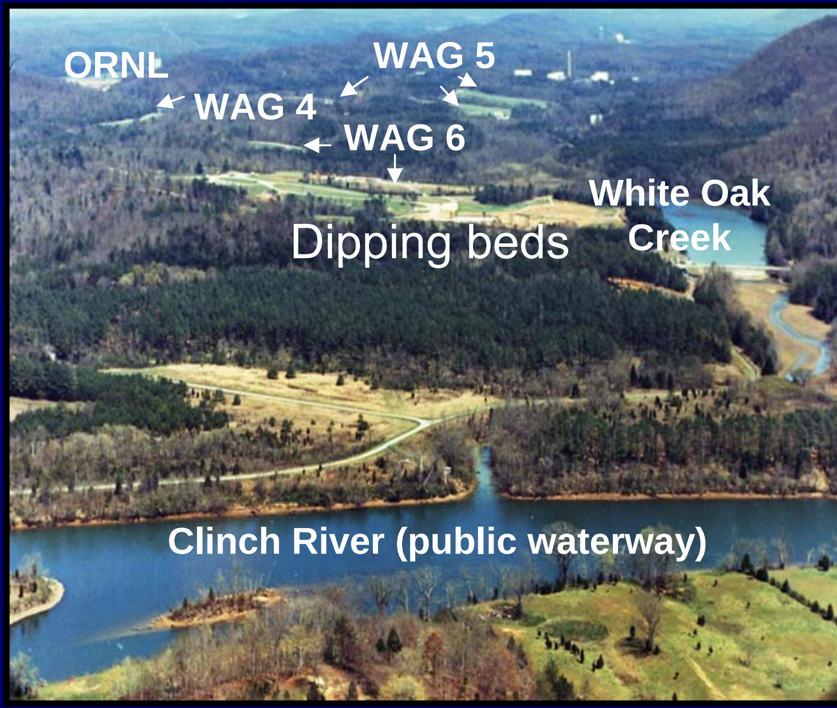


- Depleted uranium
- Strong acids (HNO_3 and H_2SO_4)
- Halogenated solvents
- Heavy metals

1951-1984 : wastes stored in unlined ponds

Pore scale

Field meso-scale



Watershed and regional scale

Close-up of structured saprolite. cm scale matrix blocks surrounded by fractures

Convergent flow and formation of empherial and perennial streams

SCALE OF INTEREST FOR THIS WORK

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.

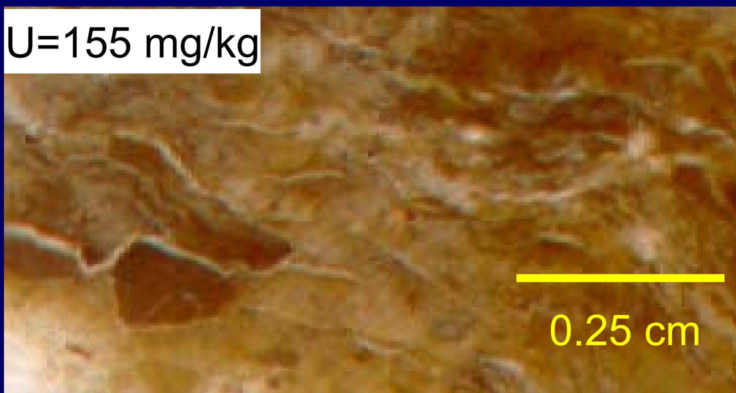
• The fractures surround a high porosity, low permeability matrix that is a source and sink for contaminants.

Overlying Saprolites

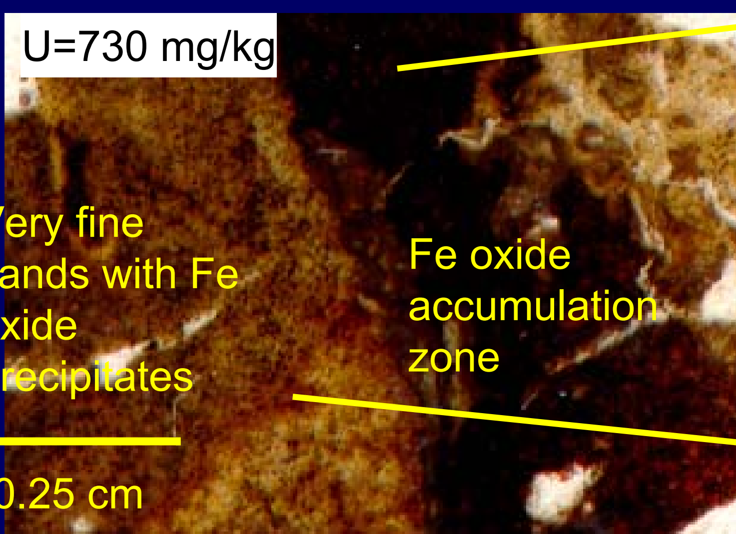
Underlying Bedrock

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

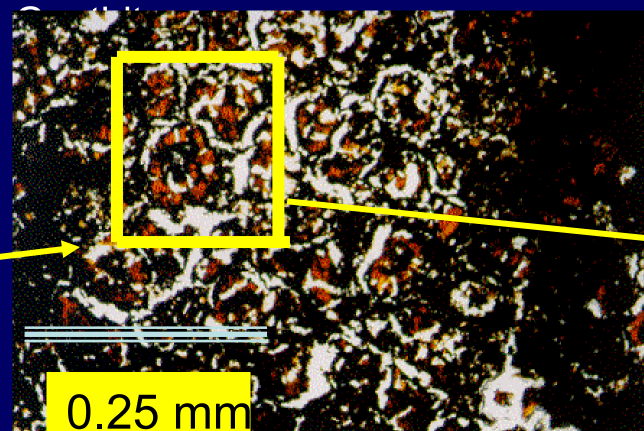


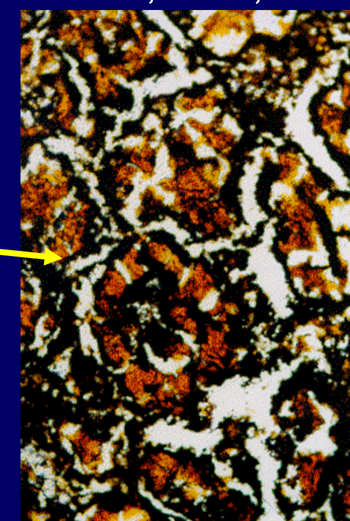
A high U zone was detected in the center of the test cell at a depth of 46'.

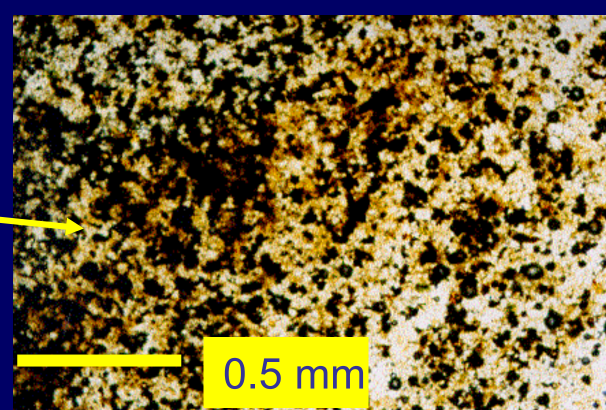
XRD results:

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

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







Phillips/Watson, 2003

Study area

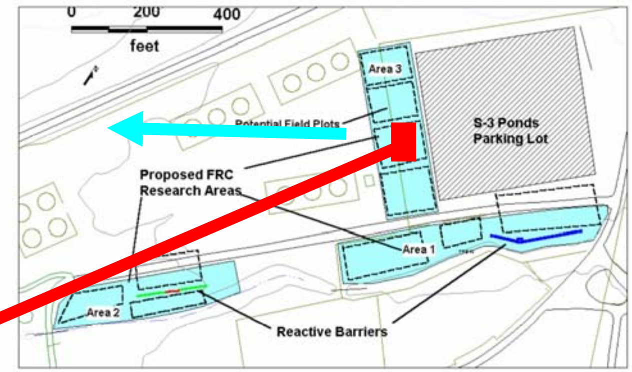


Figure A1. Location of potential field plots within Areas 1, 2, and 3

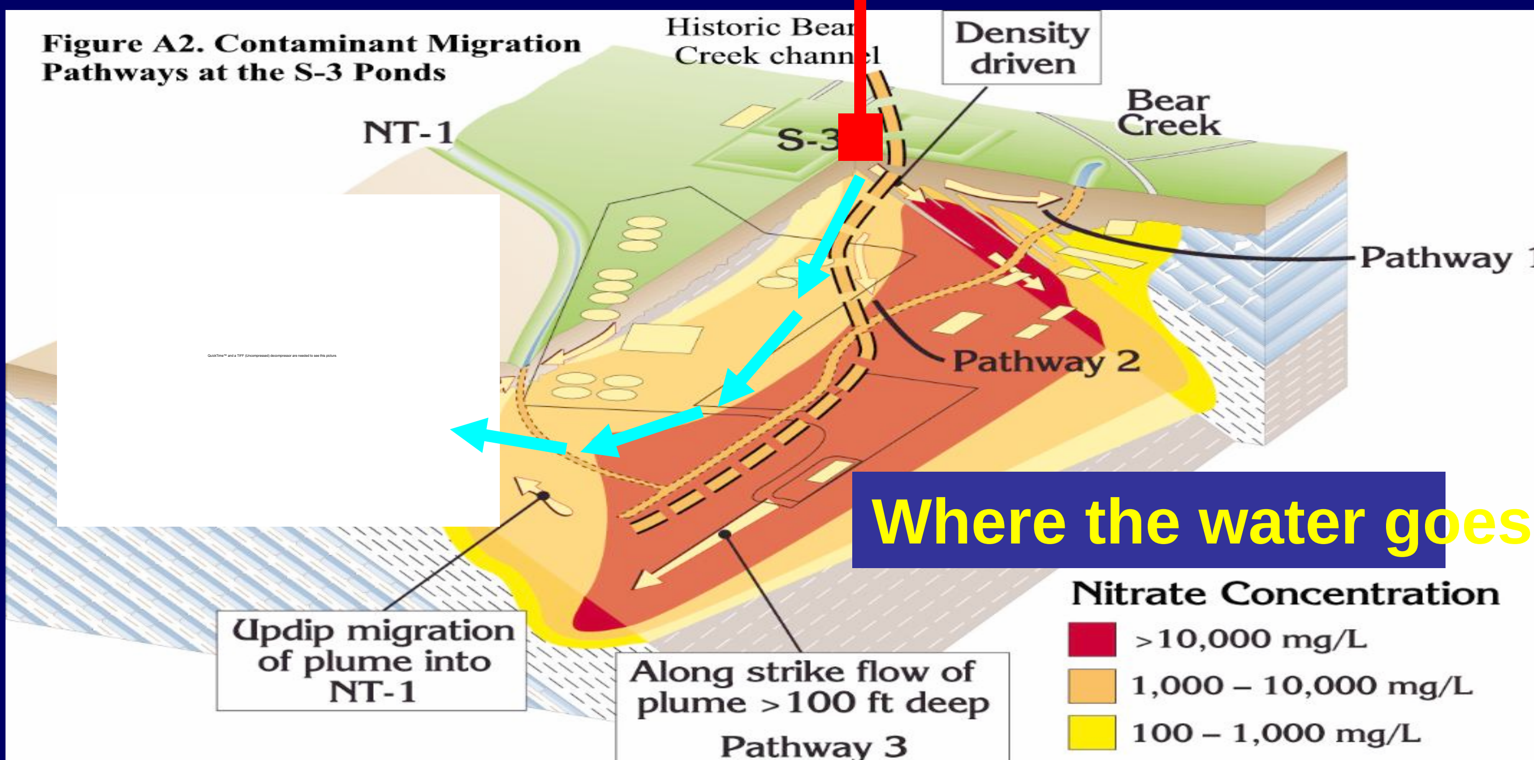


Figure A2. Contaminant Migration Pathways at the S-3 Ponds

Where the water goes

Contaminants in groundwater near the S3 p

Inorganic Constituents	Concentrations	Organic Constituents	Concentrations
pH	3.4-3.6		
	202-401 mg/L		
	249-298 mg/L		
	843-1116 mg/L		
	7500-8963 mg/L		
	Low		
	42-51 mg/L		
	35-40 nCi/L		2100-3300 µg/L
	(80-89 dpm/ml)		
			94-130 µg/L
	0.45 mg/L		
	541±47 mg/L		
	931±74 mg/L		
	174±11 mg/L		
	130±9 mg/L		
	<0.003 mg/L		
	0.17 mg/L		
	0.03 mg/L		
	0.02 mg/L		

- estimated value
- values for MLS FW 100, 40’ depth.

Rationale for work near the source zo

The source zone is a reservoir of U(VI) for long-term groundwater and surface water 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

PRIMARY OBJECTIVE

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

$$UO_2(CO_3) + H^+ + 2e^- = UO_2 + HCO_3^-$$

- 119 mg U are reduced for every mmol of electrons transferred
- This is equivalent to 119 mg U reduced/mg H_2
- It is also equivalent to 15 mg U reduced/ mg COD

Hypotheses

- Biological reduction of U(VI) in the S-3 soils is a multistep process: desorption/dissolution of U(VI), followed by uptake/reductive mineralization.

- Desorption/dissolution will typically limit the reduction rate.

- Both metal- and sulfate-reducing bacteria will play a role.

Chemistry considerations

Low pH (~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+}:

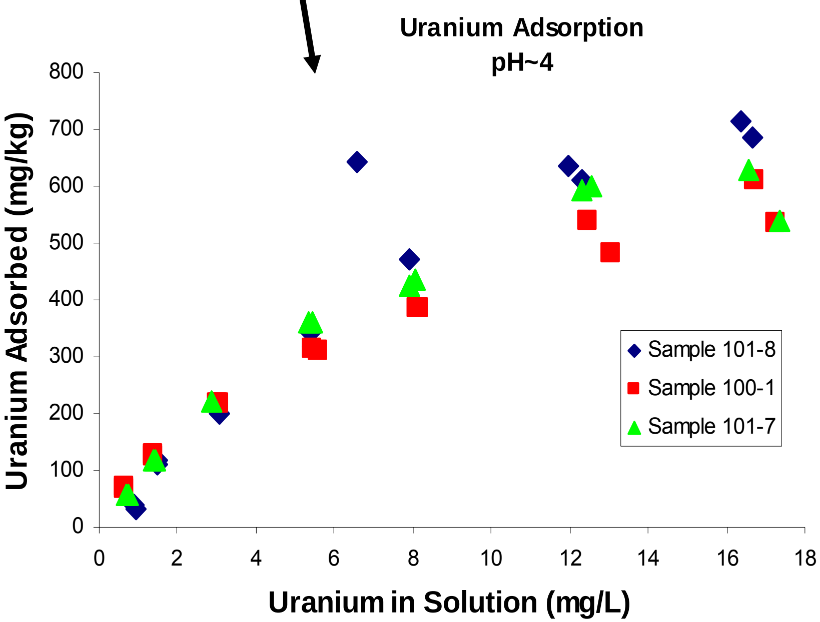
~20 mM in groundwater - Ca^{2+} inhibits U(VI) reduction at 5 mM (Brooks et al., 2003)

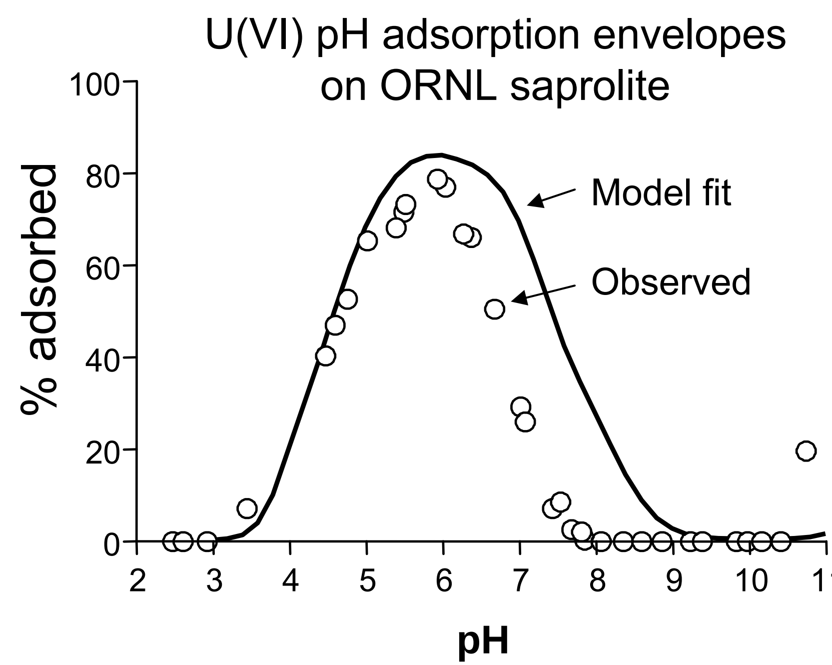
$UO_2(CO_3) + H^+ + 2e^- = UO_2 + HCO_3^-$ E°' = +0.105 V

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

Uranium adsorption

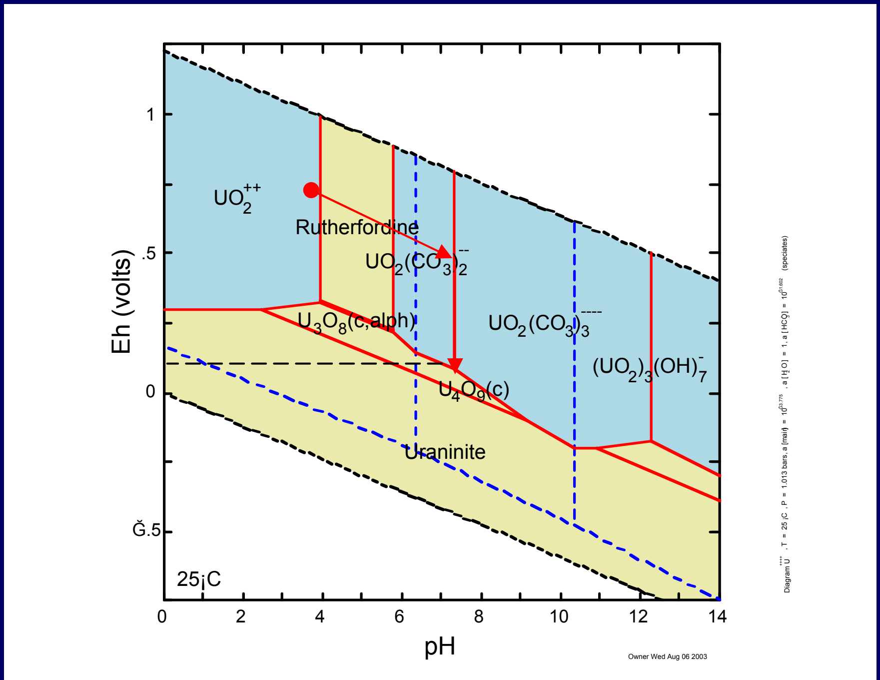
U sorption is concentration dependent
It is also strongly pH dependent.



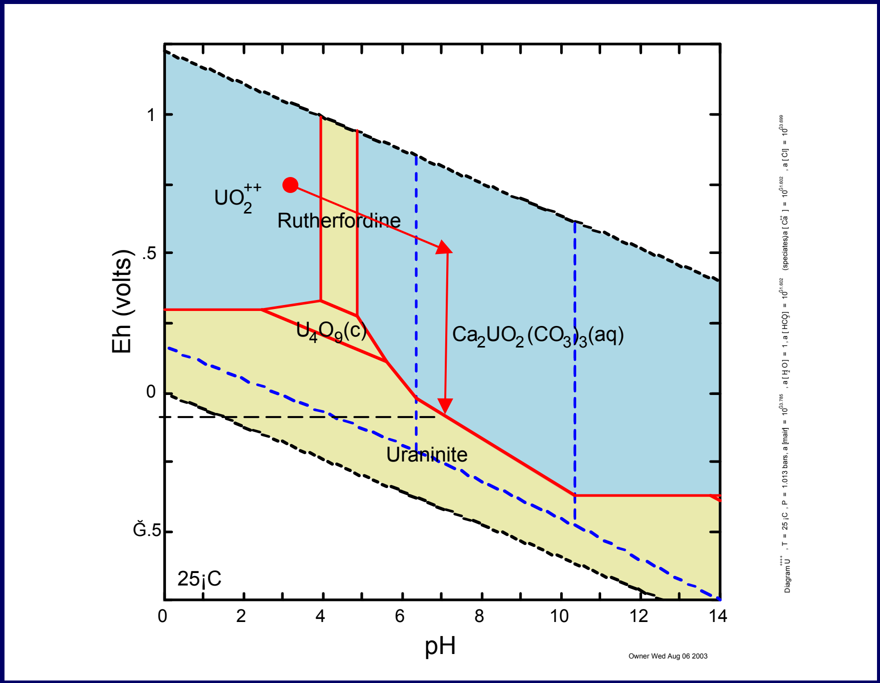


Eh/pH Plot of Uranium Speciation (300 mg/L TIC, 40 mg/L U)

No Ca

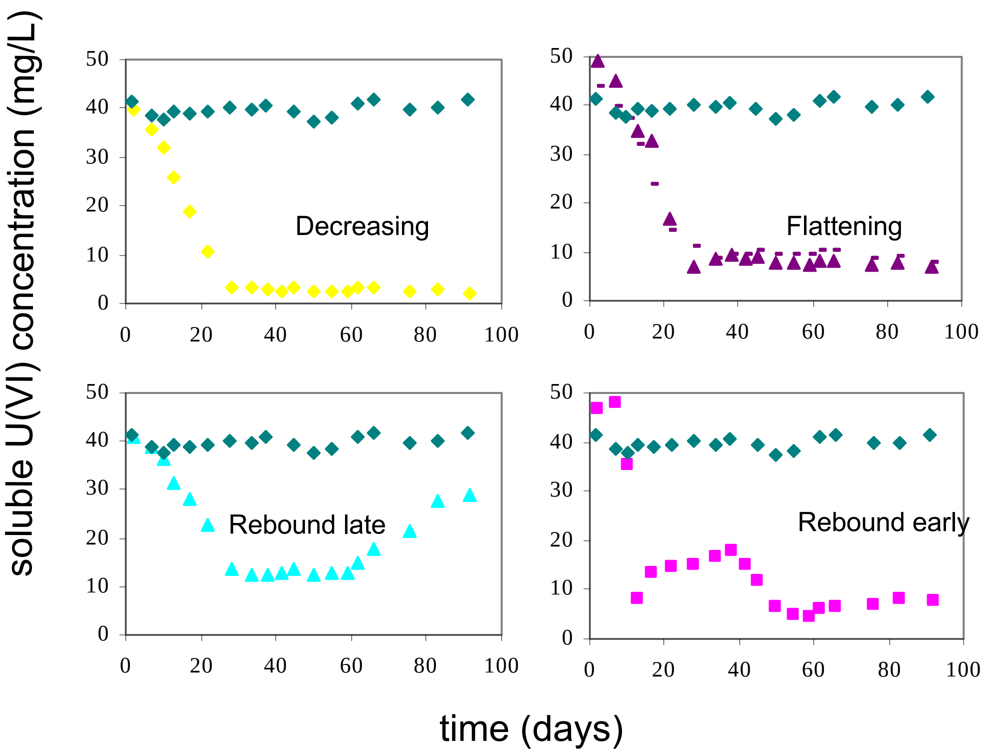


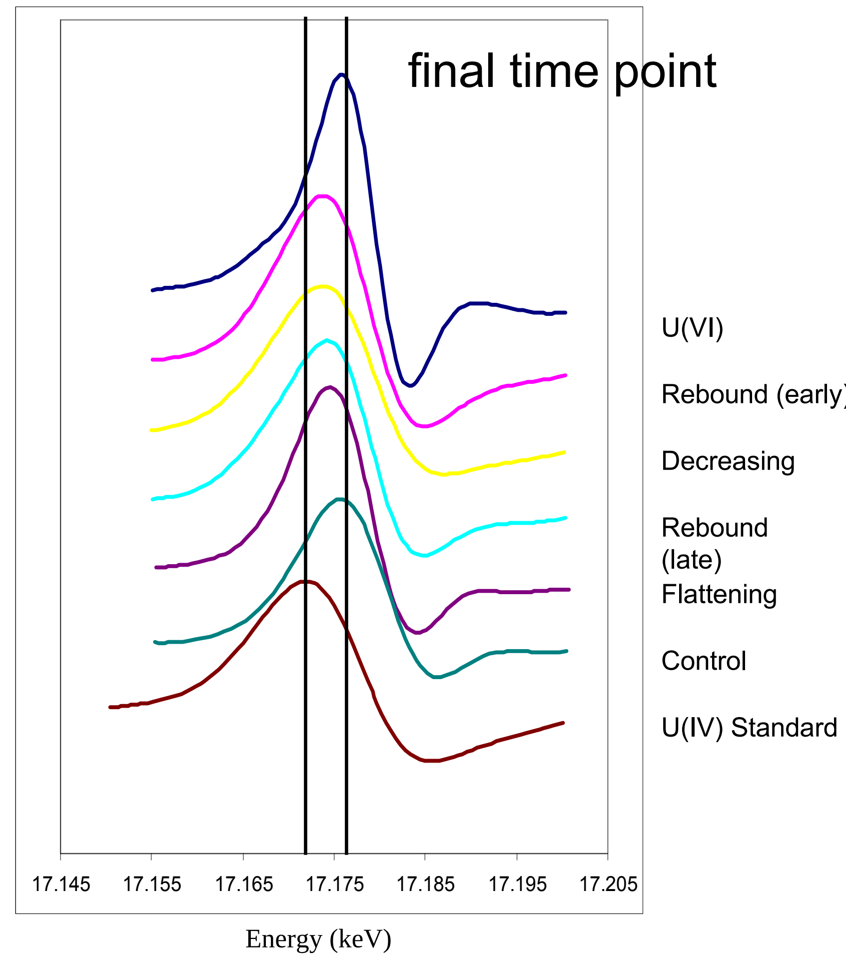
+ 20 mM Ca



Batch microcosms: ethanol biostimulated U reduction in the presence of contaminated sediment

Variation in pattern of **soluble** uranium concentration over time:



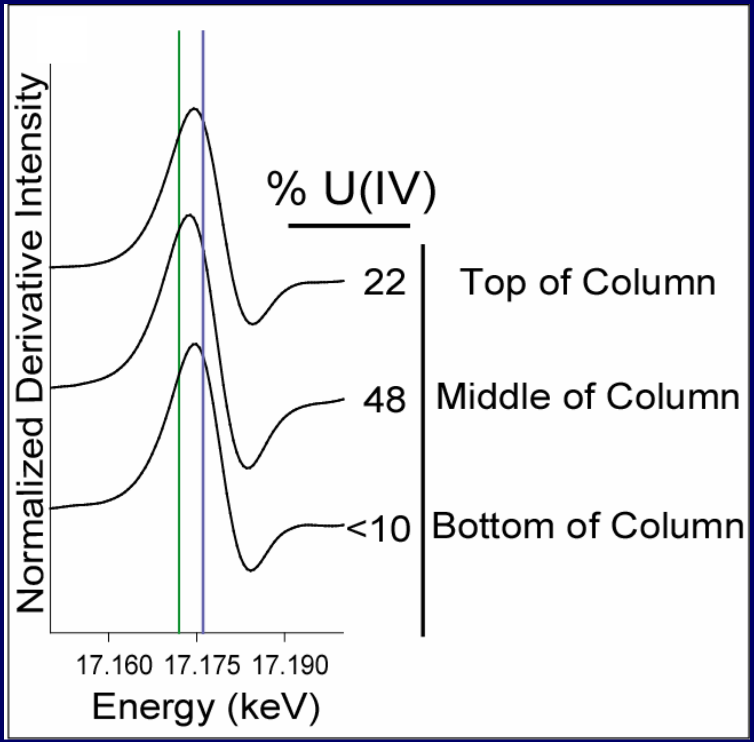


X-ray absorption spectroscopy shows the reduction of **solids-associated** uranium in viable, but not control, microcosms.

Column microcosm

Before

After



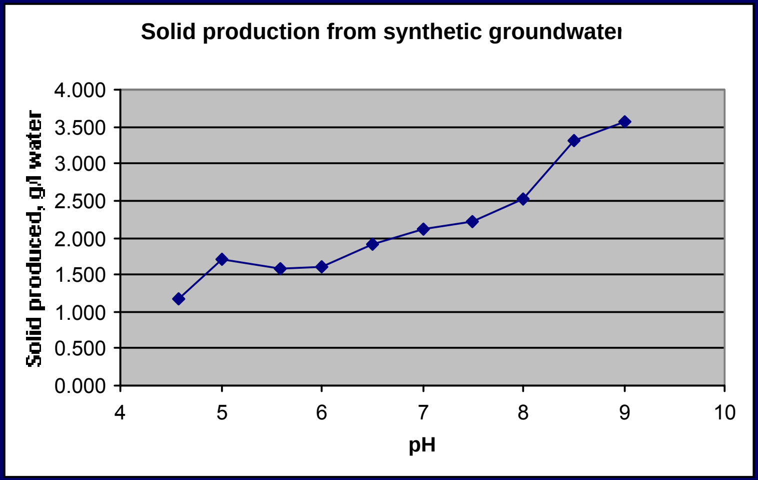
Clogging agents

- 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.

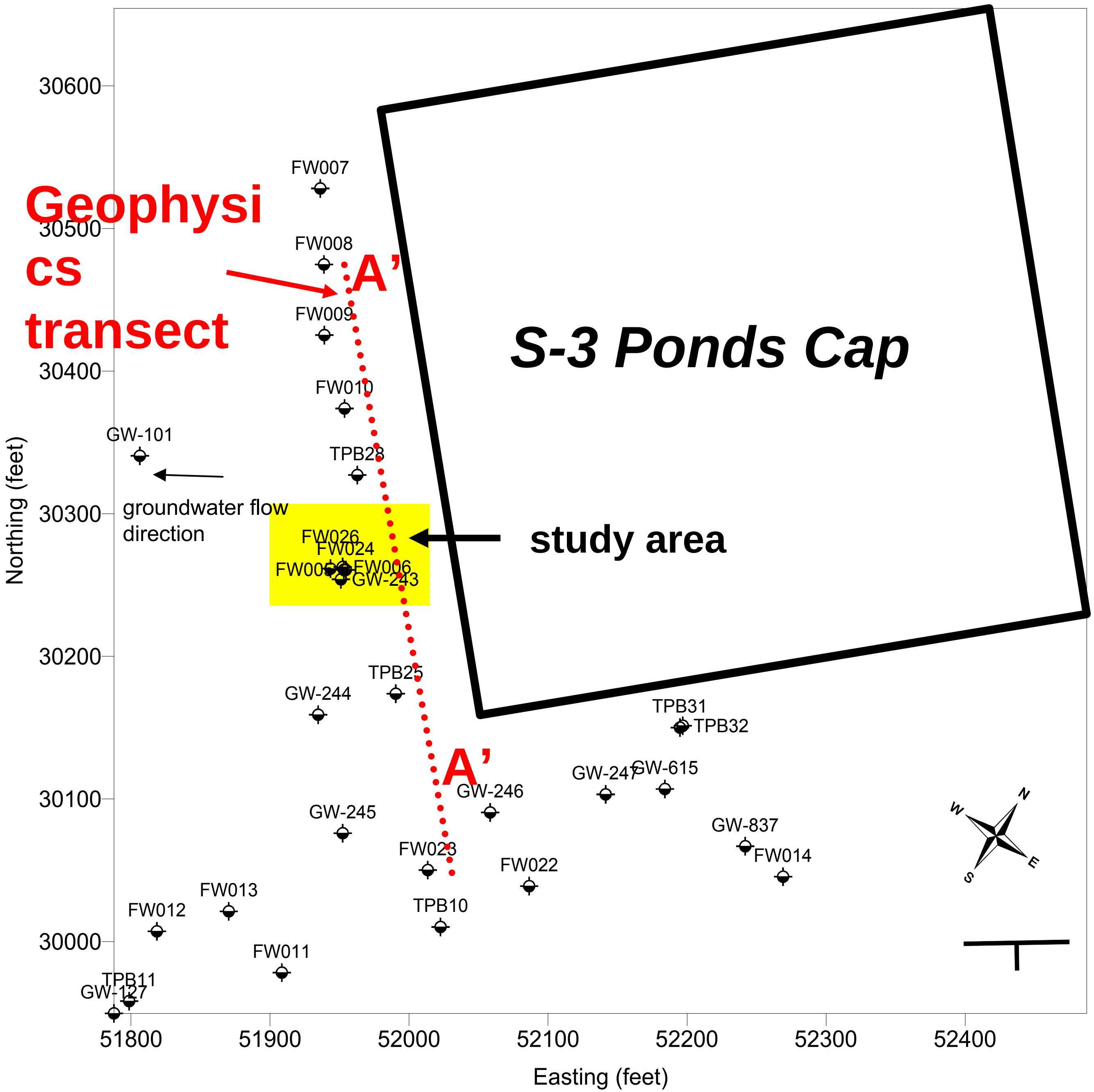
pH adjusted to 7 with 50% liquid from denitrifying batch cultures

pH adjusted to 7 with Na_2CO_3

pH adjusted to 7 with KOH



2 g/L solids produced



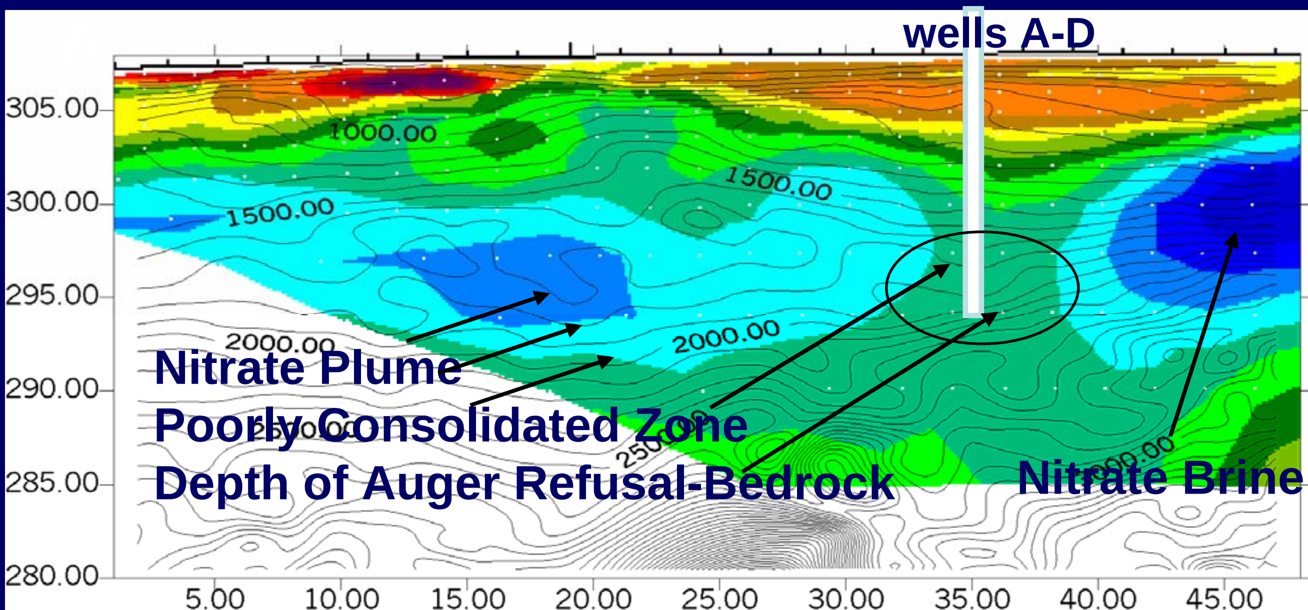
Geophysics transect
A'
A'
S-3 Ponds Cap
study area
groundwater flow direction
FW007
FW008
FW009
FW010
GW-101
TPB28
FW026
FW024
FW006
GW-243
TPB25
GW-244
TPB31
TPB32
GW-247
GW-615
GW-246
GW-245
GW-837
FW014
FW023
FW022
FW013
FW012
TPB10
FW011
TPB11
GW-127
N
E
S
W
Northing (feet)
30600
30500
30400
30300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

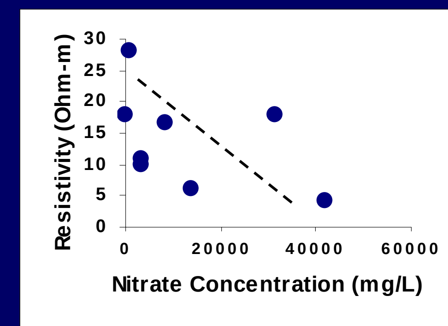
Geophysics was used to identify areas of contaminant tran

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

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

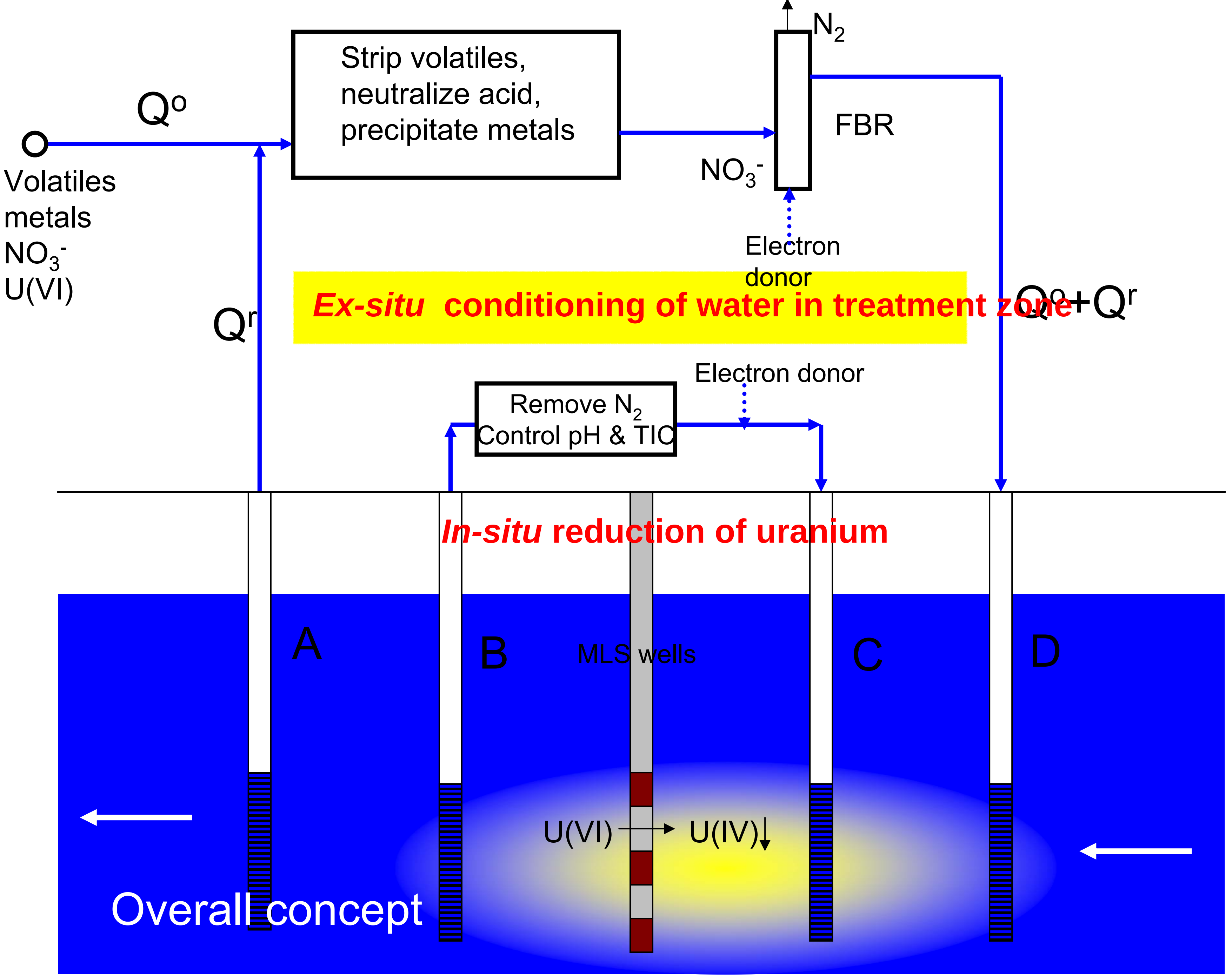
A’ A’





Low Resistivity ~ High Nitr

Contour Lines: Seismic
Velocity (m/s)



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

The “Big Top” where extracted groundwater is treated to enable metal reduction *in-situ*

Tanker for chemical sludge disposal

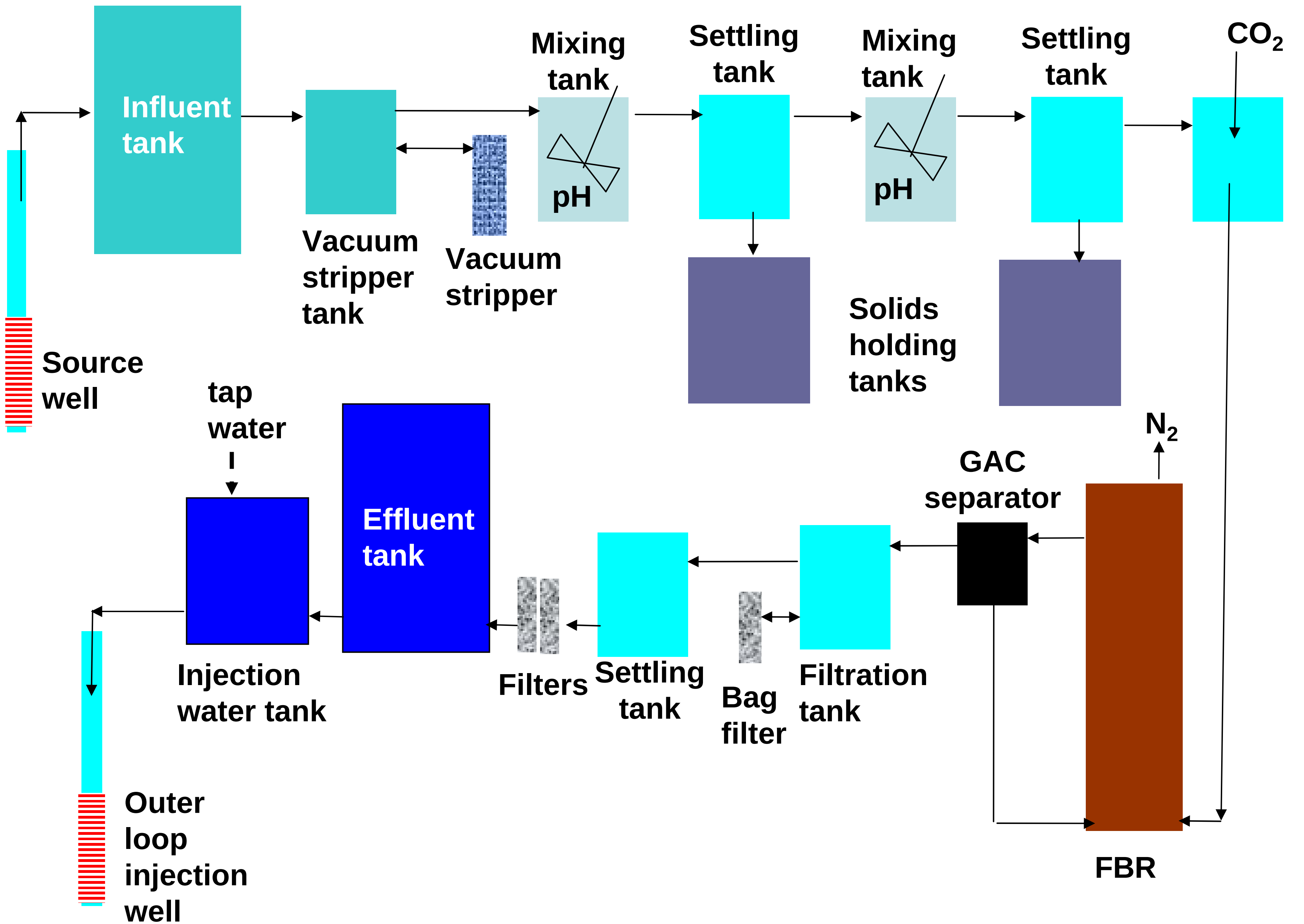
Bag filters for disposal of biomass

Inside the Big Top

Ex-situ conditioning of water in treatment

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

ABOVEGROUND PROCRESS TRAIN



The aboveground treatment train

Vacuum stripper

Two-step
chemical precipitation

Fluidized bed reactor
(FBR)

FBR sampling and characteriza

Phylogenetic analyses
Functional gene microarray
Functional monitoring

Well TPB16 enrichment

innoculum

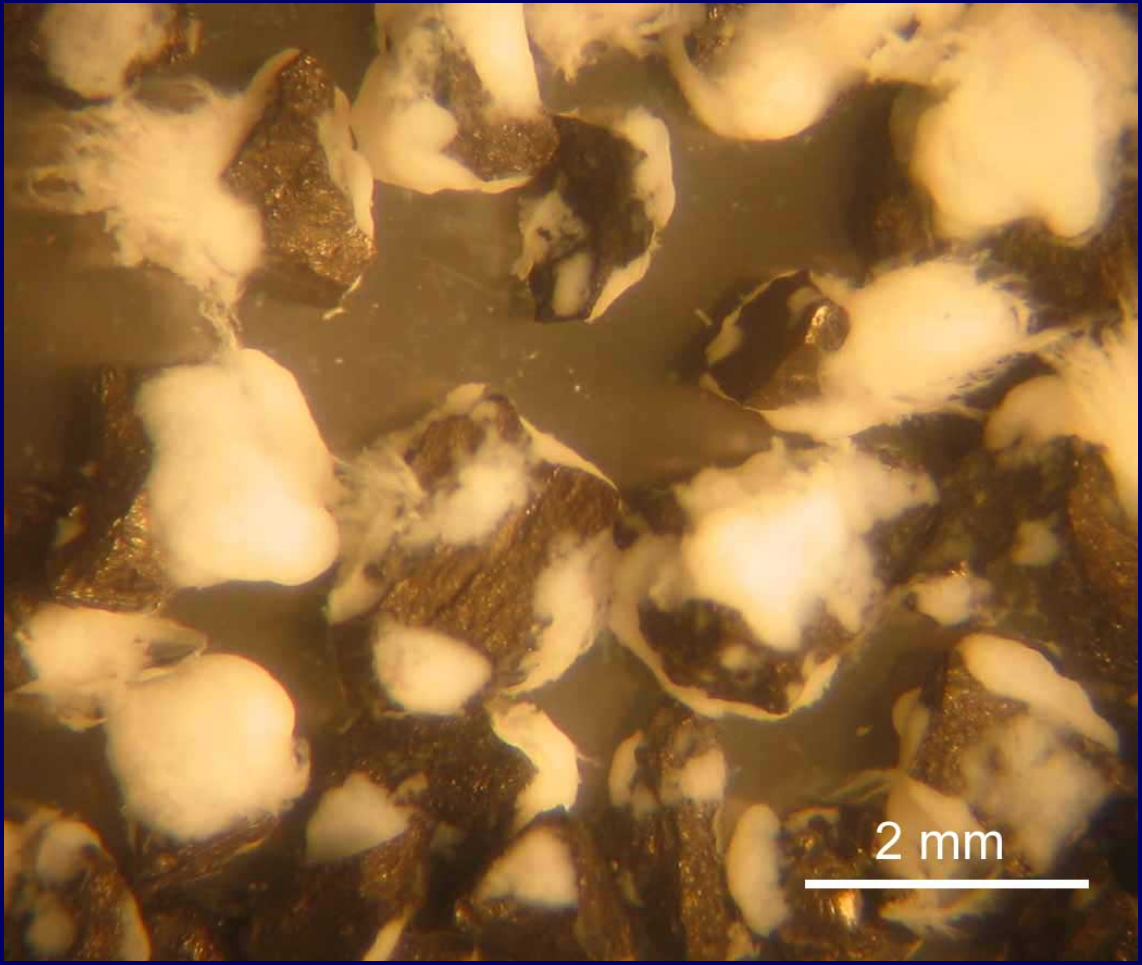
innoculum

Two piilot scale FBRs

Full scale FBR

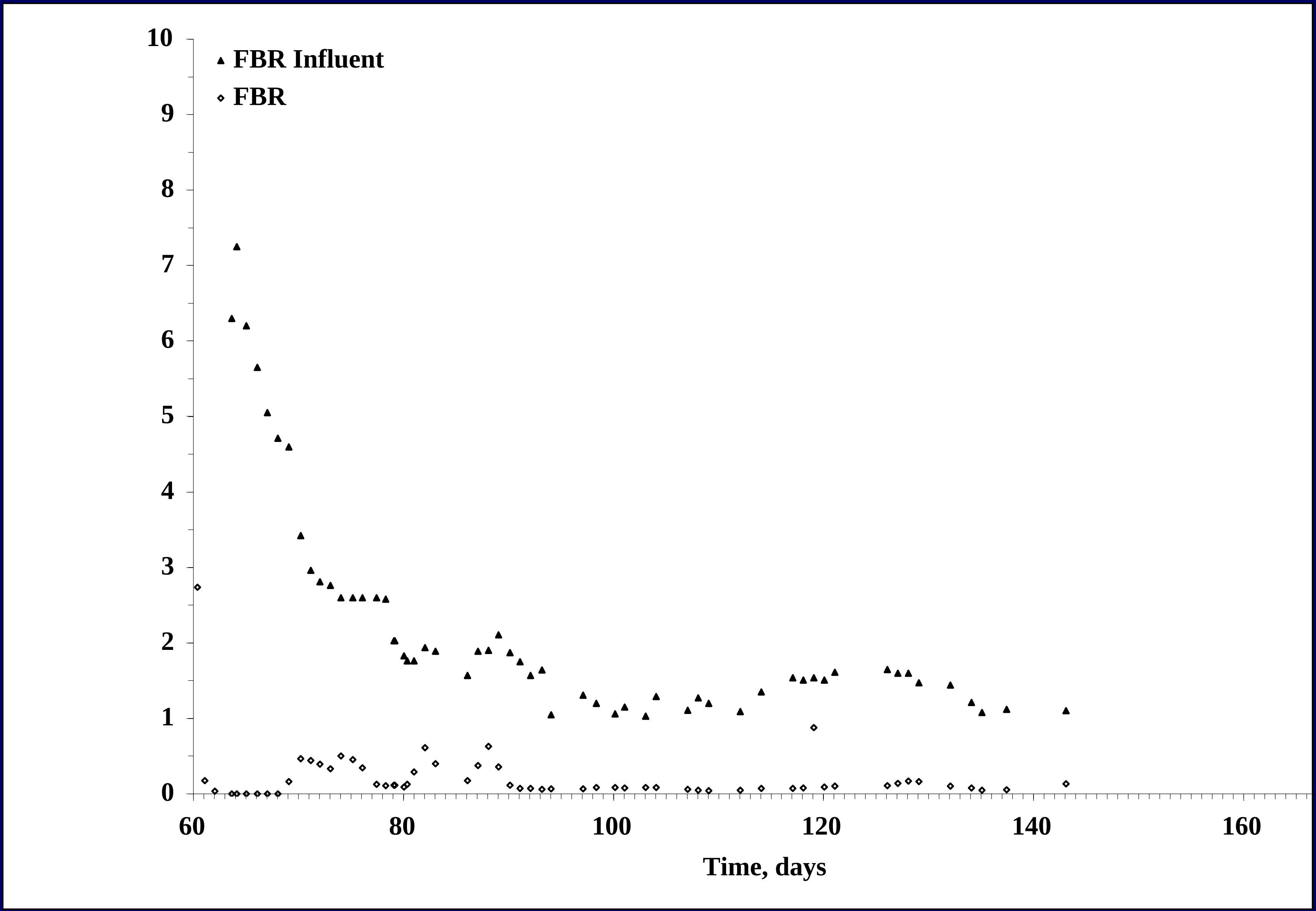
Fluidized Bed Reactor

- Removes NO_3^- as N_2
- Efficient
- Cheap
- Raises pH
- Demonstrated in two continuous pilot-scale systems (pH 7.4 and 9.2)

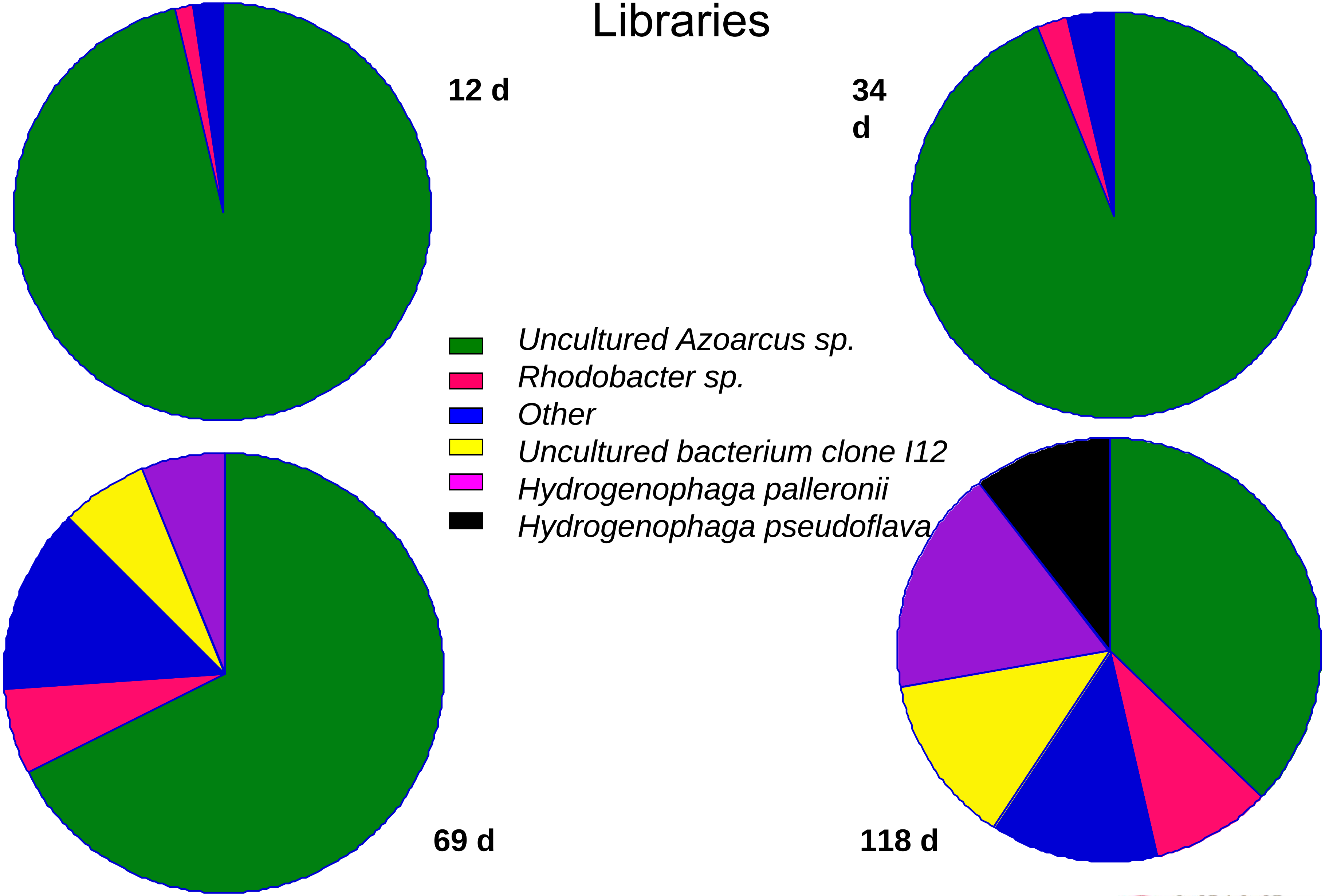


Denitrifying biofilms growing on granular activated carbon in pilot scale FBR at Stanford. Some of the bacterial general found in this community include *Zoogloea*, *Xanthomonas*, *Dechloromonas, Dechlorosoma, and Sporumosa*.

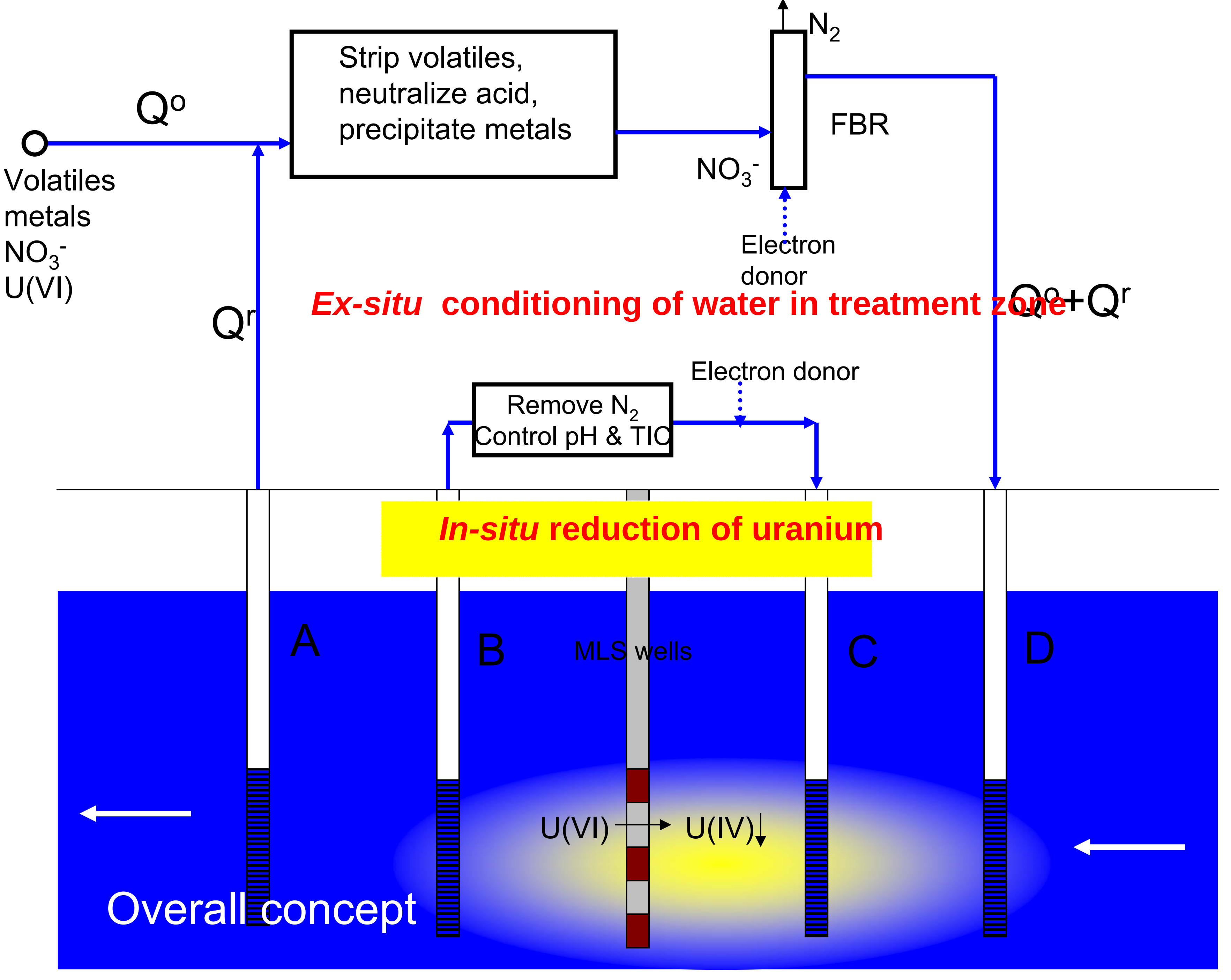
FBR: nitrate removal



Community Analysis Based Upon SSU rRNA Gene Libraries



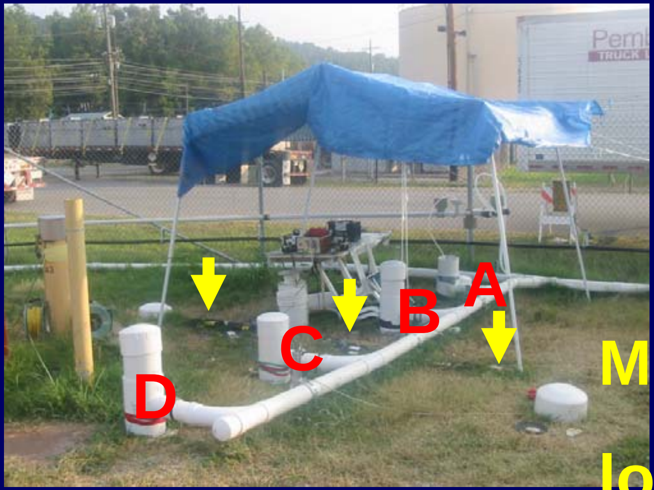
MIAMI UNIVERSITY



Strip volatiles, neutralize acid, precipitate metals
N2
FBR
NO3-
Electron donor
Qo
Volatiles
metals
NO3-
U(VI)
Qr
Ex-situ conditioning of water in treatment zone
Qo+Qr
Electron donor
Remove N2
Control pH & TIC
In-situ reduction of uranium
A
B
MLS wells
C
D
U(VI)
U(IV)
Overall concept

Well layout

before plumbing

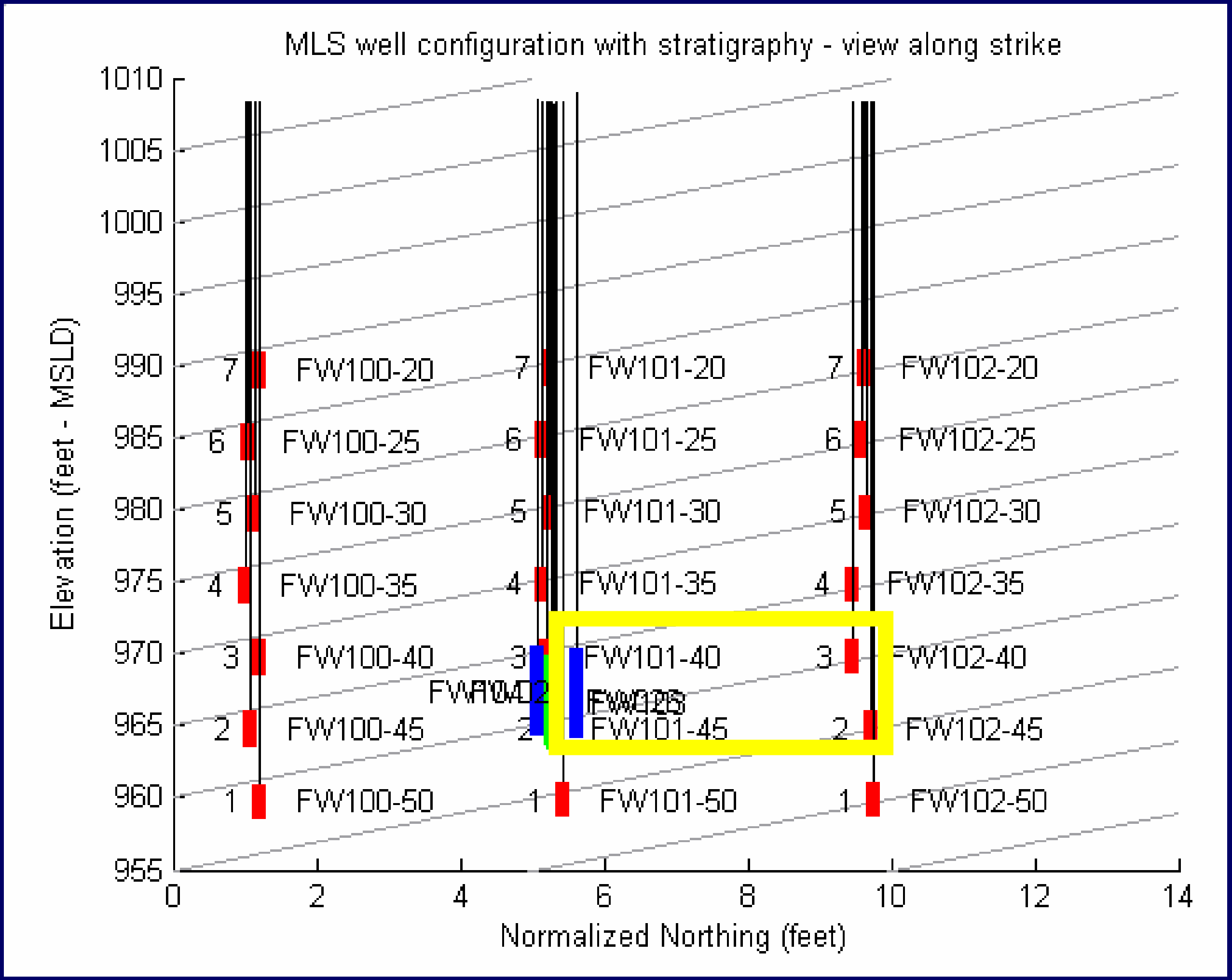


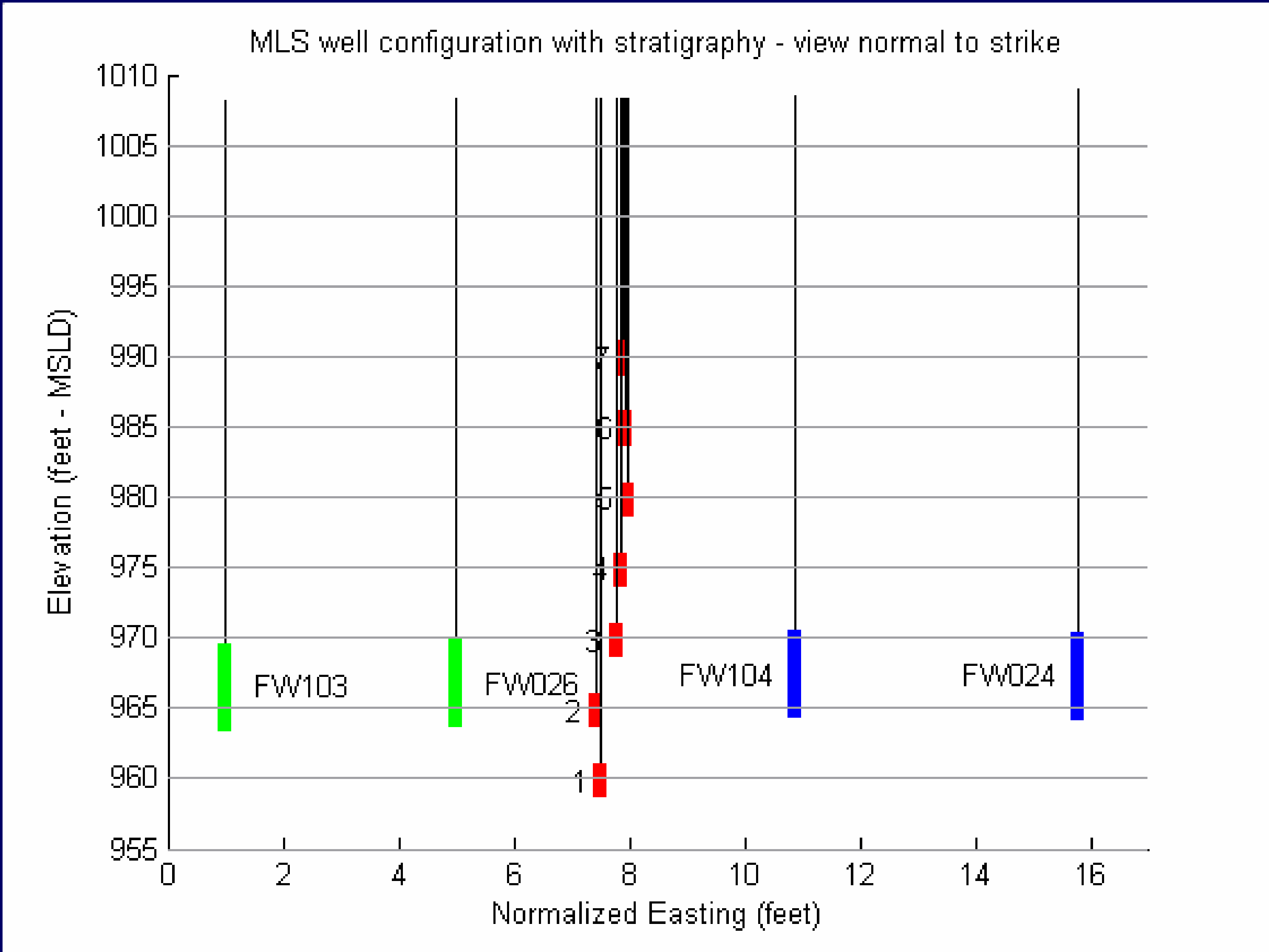
MLS well locations

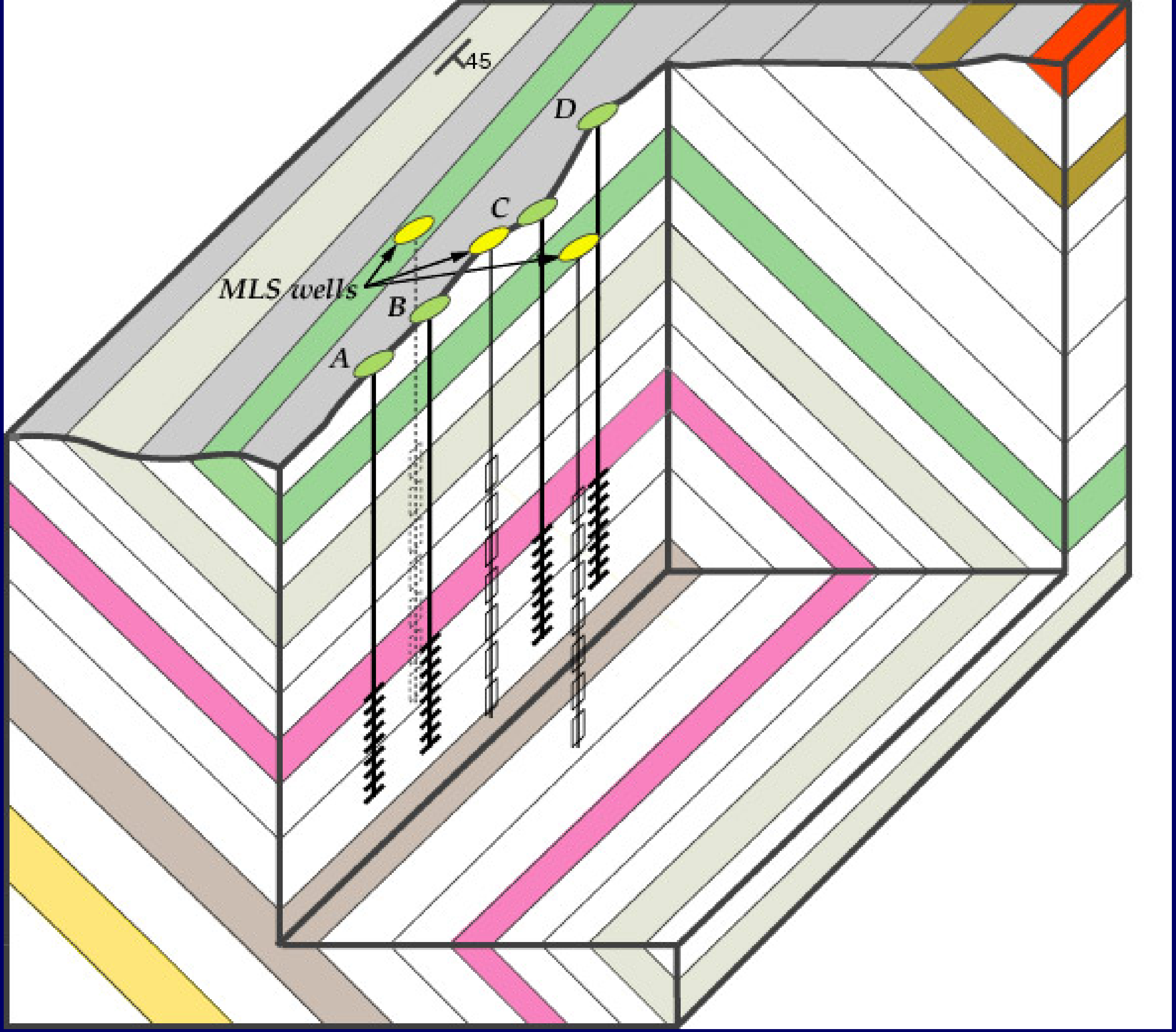
after plumbing

Skid with pumps and meters for wells
inside Big Top

Multilevel sampling wells



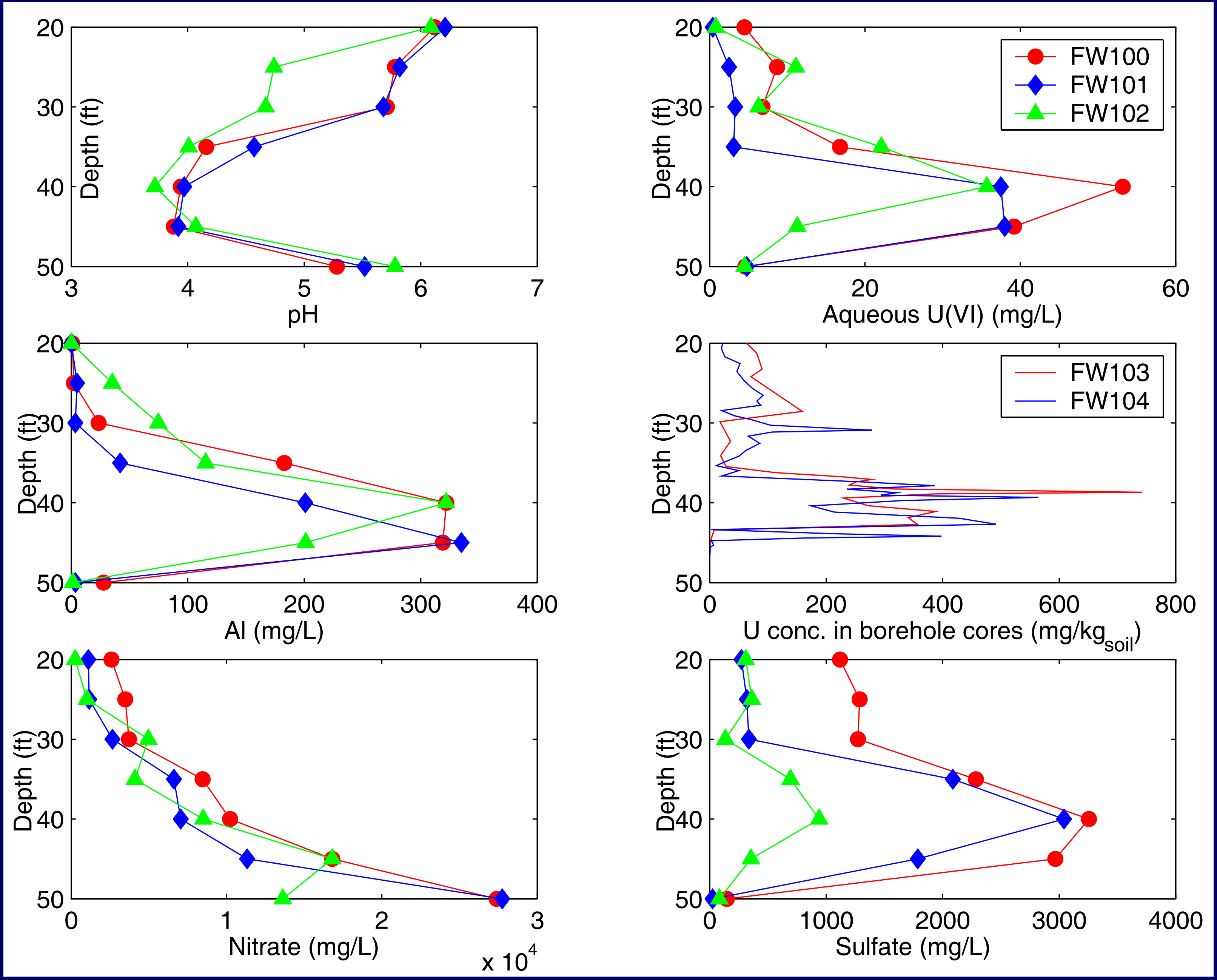

MLS well configuration with stratigraphy - view normal to strike
Elevation (feet - MSLD)
1010
1005
1000
995
990
985
980
975
970
965
960
955
0
2
4
6
8
10
12
14
16
Normalized Easting (feet)
FW103
FW026
FW104
FW024
1
2
3
4
5
6
7



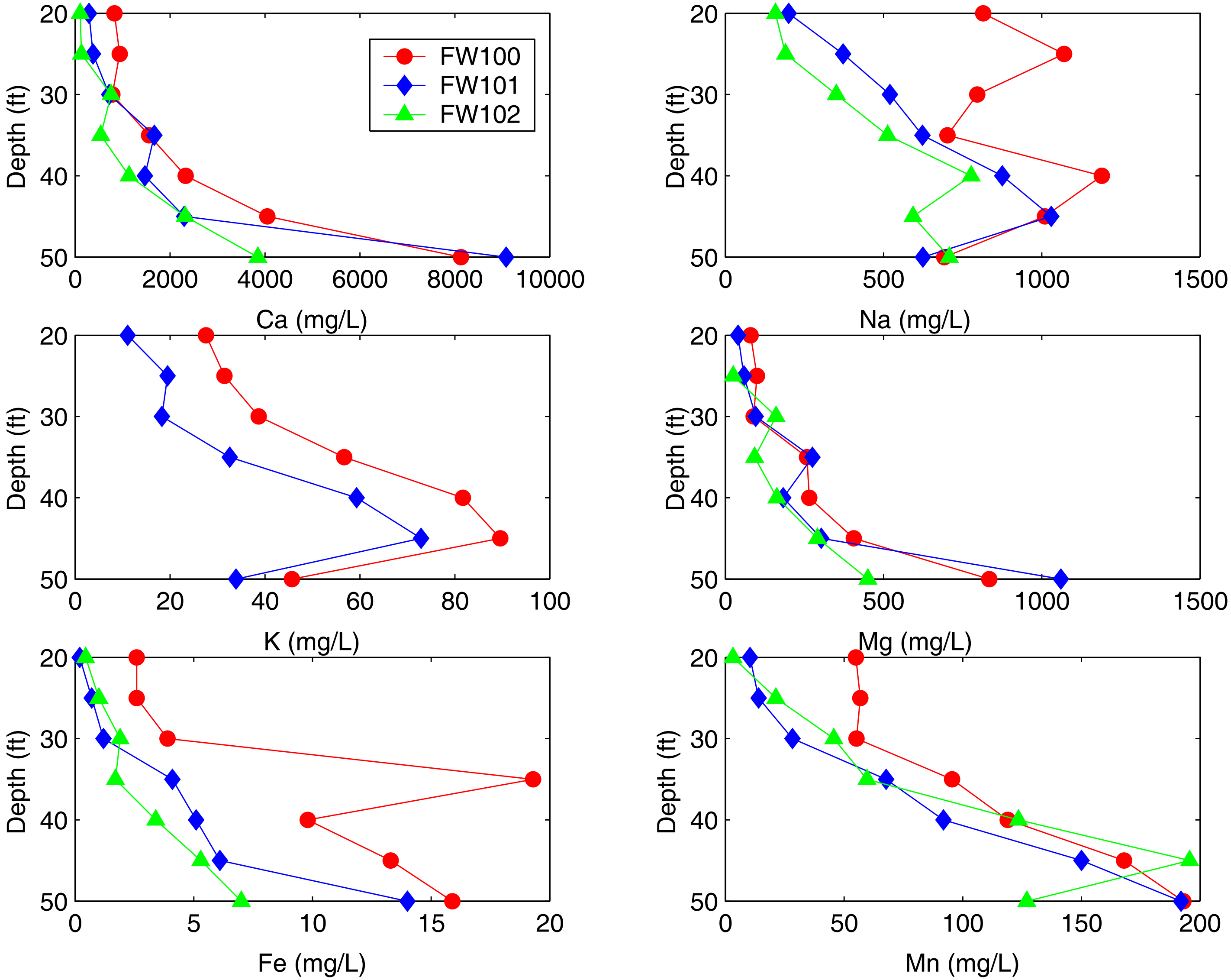
Screened Interval = 38-45’

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

Chemical profiles with depth at the MLS wells - before biosti

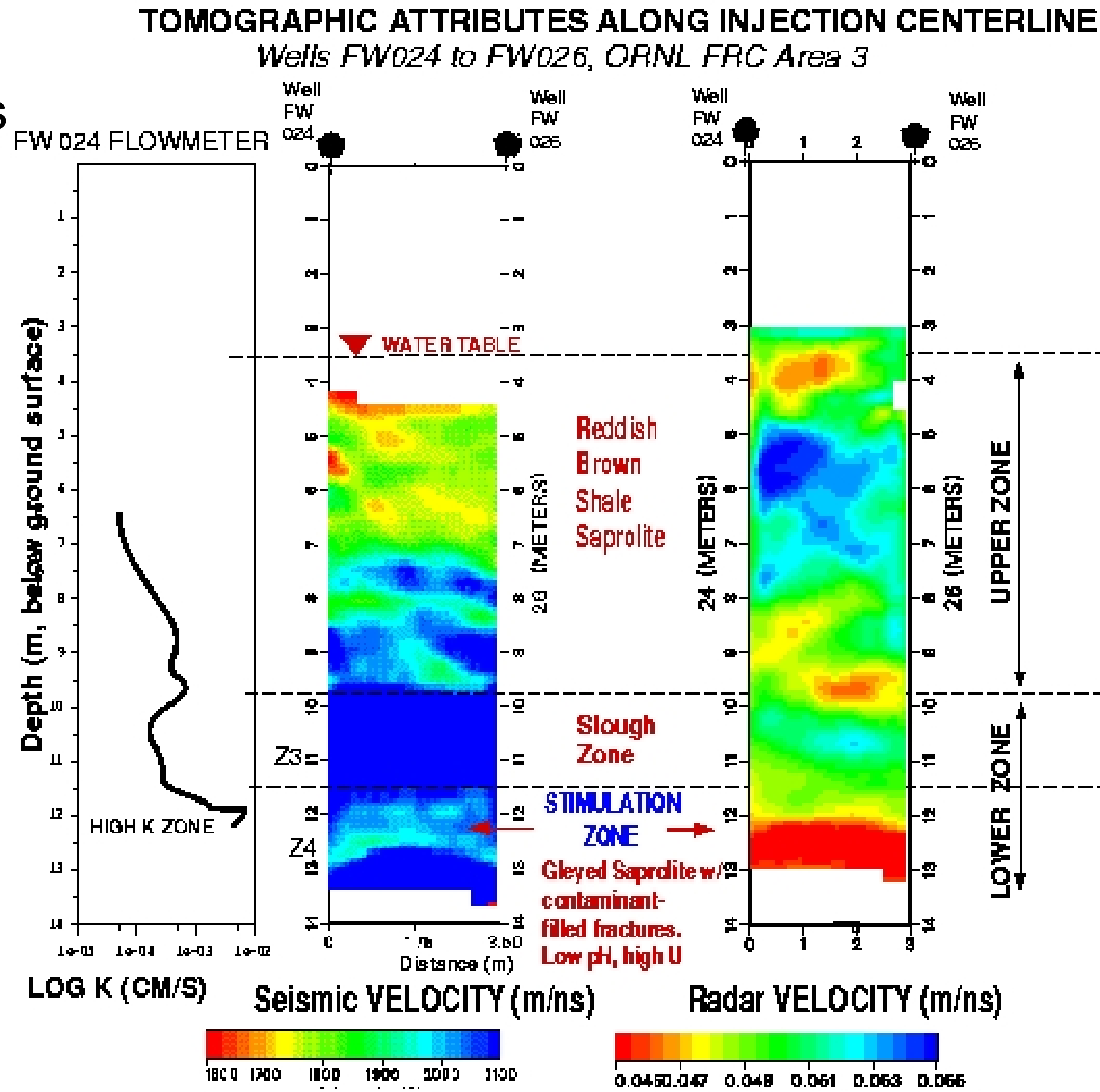


Chemical profiles with depth at the MLS wells - before biosti

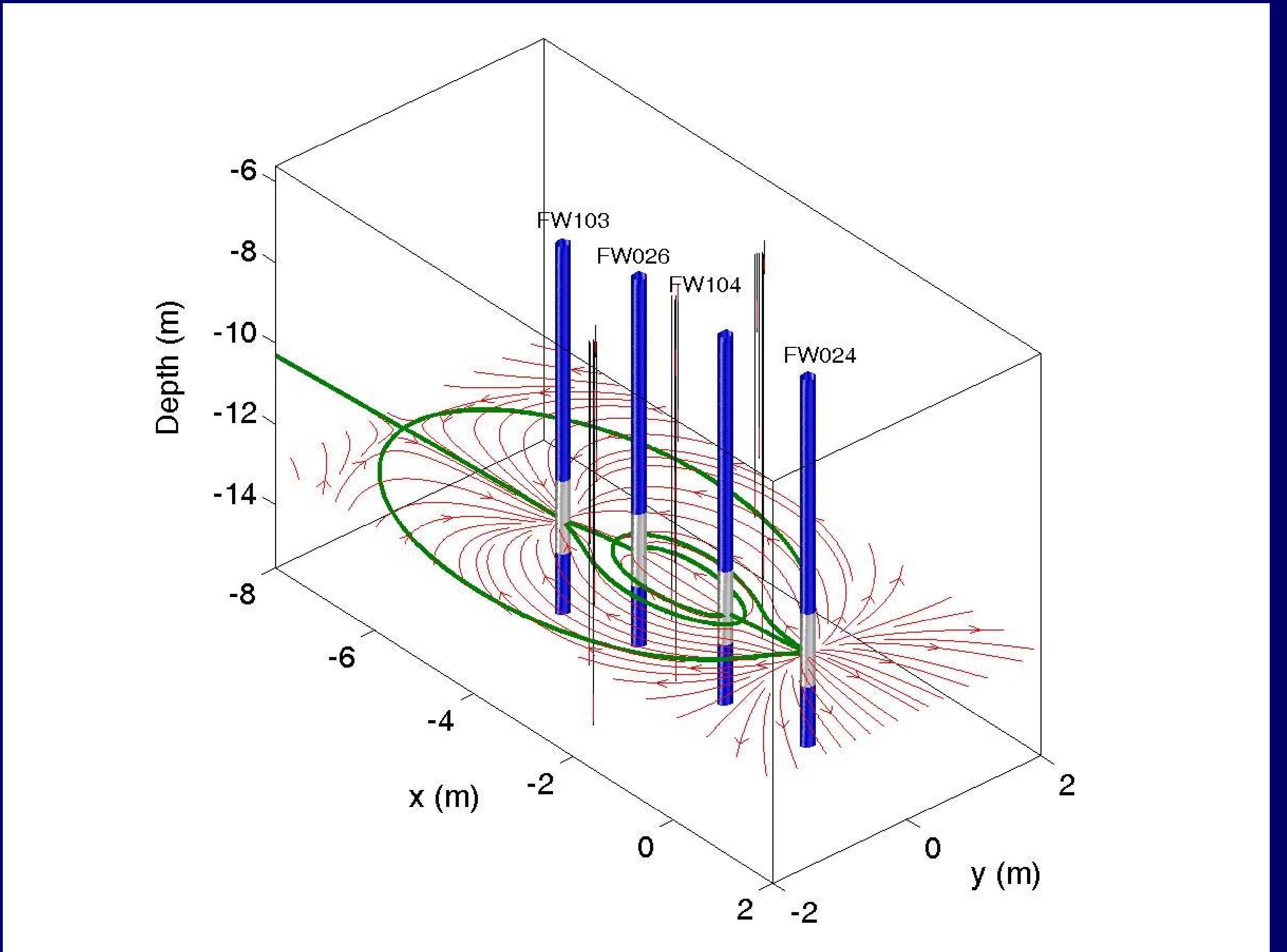


Seismic and Radar Tomography

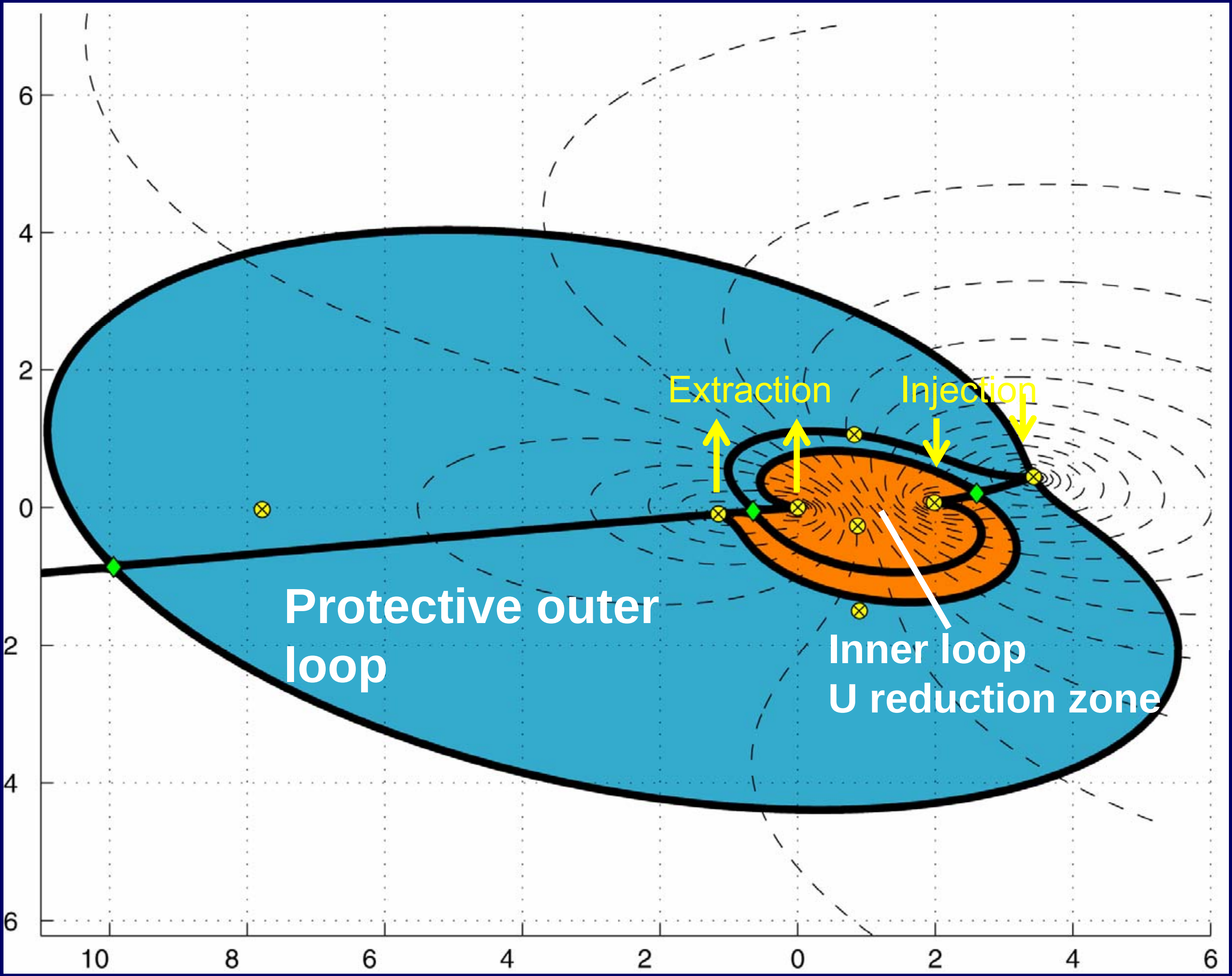
Mapping subsurface material heterogeneities using cross-borehole techniques.



Hubbard et al., 2003


FW103
FW026
FW104
FW024
Depth (m)
-6
-8
-10
-12
-14
-8
-6
-4
-2
0
2
x (m)
-2
0
2
y (m)

Regions of the subsurface



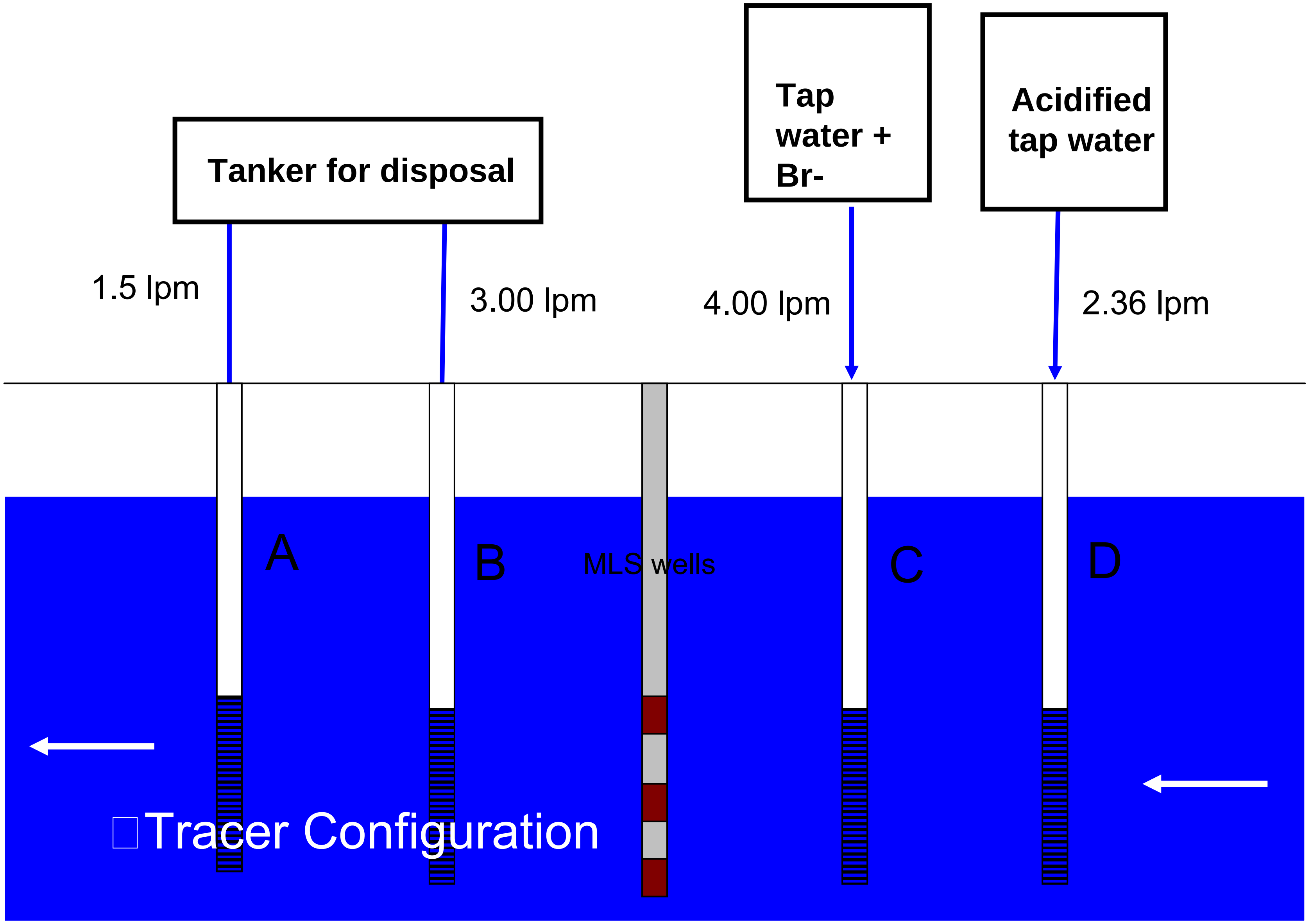
Overall Strategy

1. Perform a tracer study to determine connectivity of wells and residence time distribution. Obtain desorption rates from the rebound.

2. Flush outer and inner cell with clean water at pH 4 to remove Al, Ca, and most of the nitrate. Follow with flush at pH 5-6 to prepare for denitrification.

3. Stimulate denitrification *in-situ* and vacuum strip N_2 to remove residual nitrate.

4. Increase pH of inner cell to mobilize U(VI)



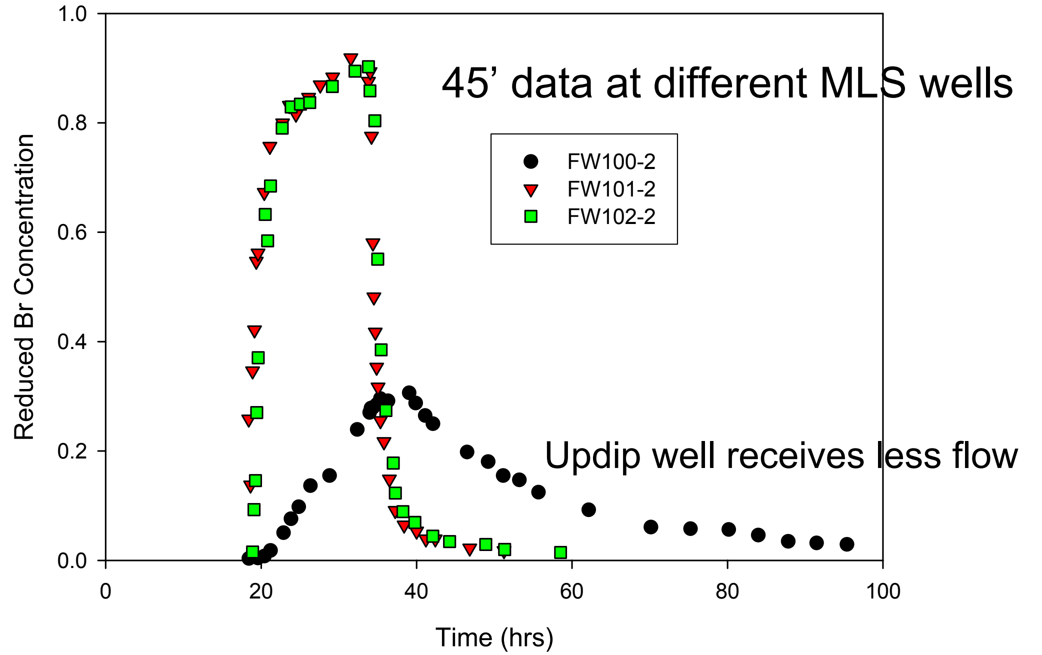
Tanker for disposal
Tap water + Br-
Acidified tap water
1.5 lpm
3.00 lpm
4.00 lpm
2.36 lpm
A
B
MLS wells
C
D
Tracer Configuration

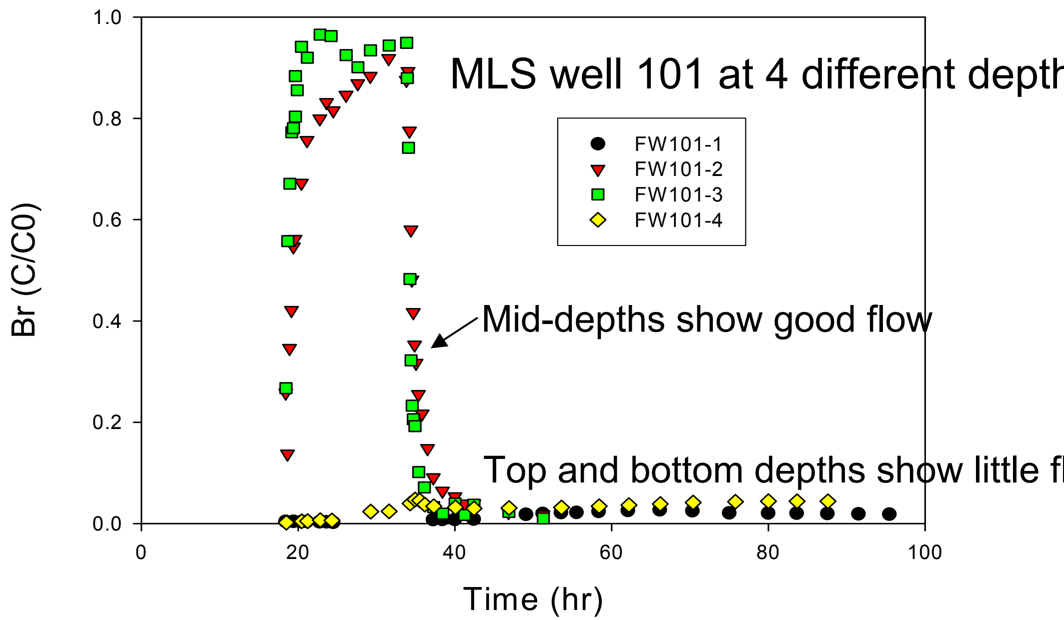
Tracer study of the Inner loop

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.

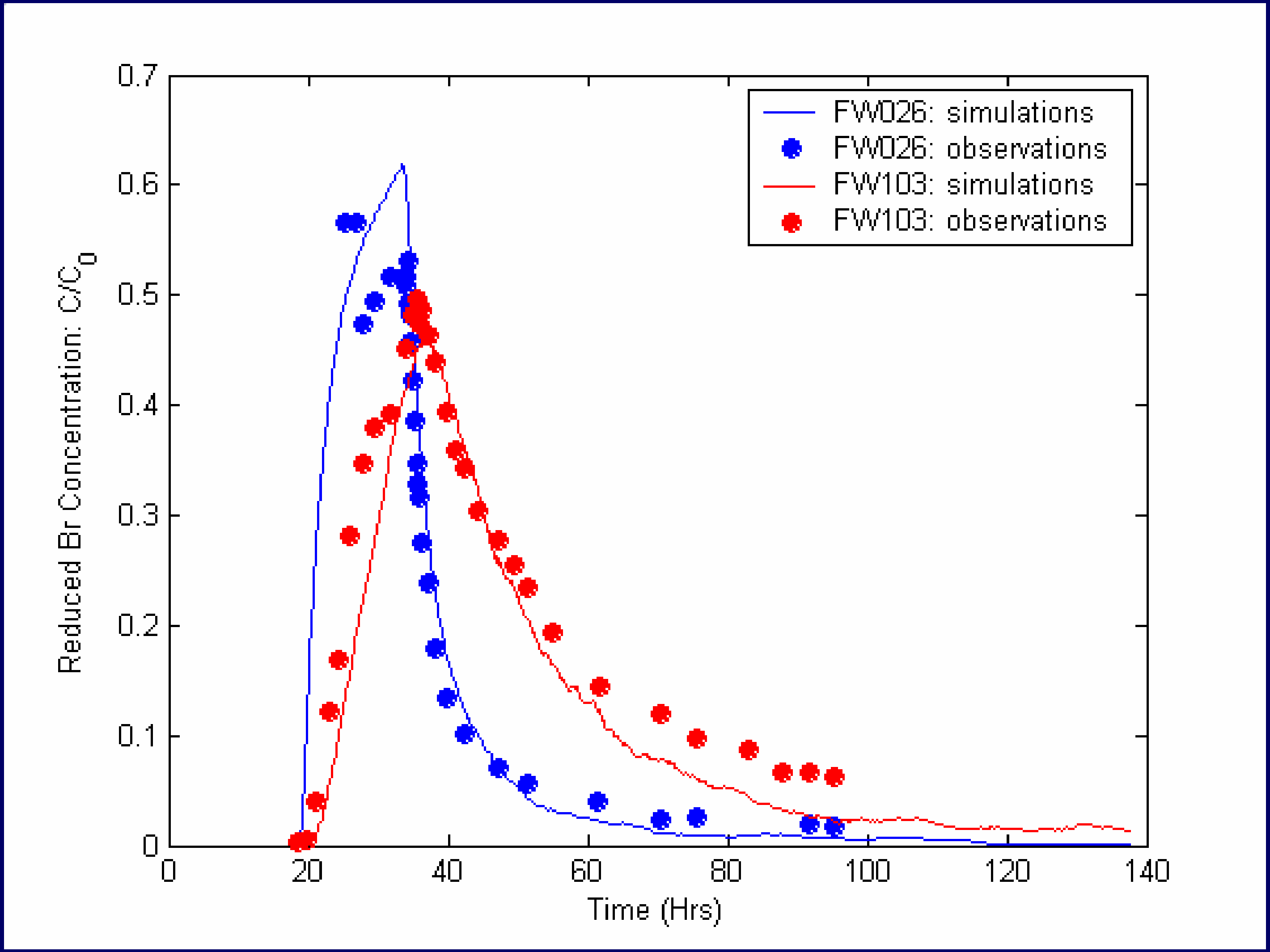
Results confirmed location and transport features of preferential flow regimes and slow flowing matrix regimes.

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

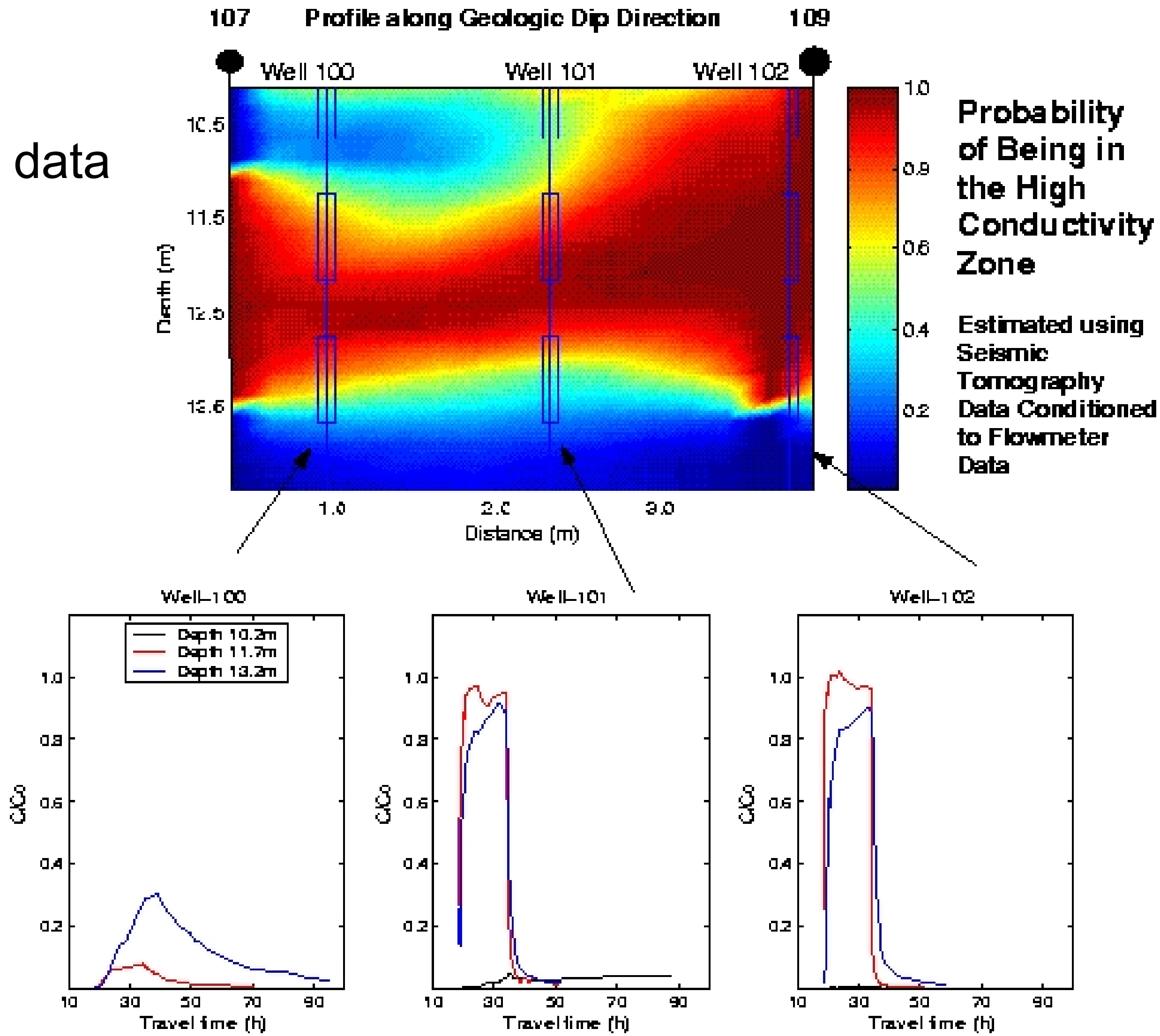




Tracer study simulations



Seismic tomography data complements tracer measurements.

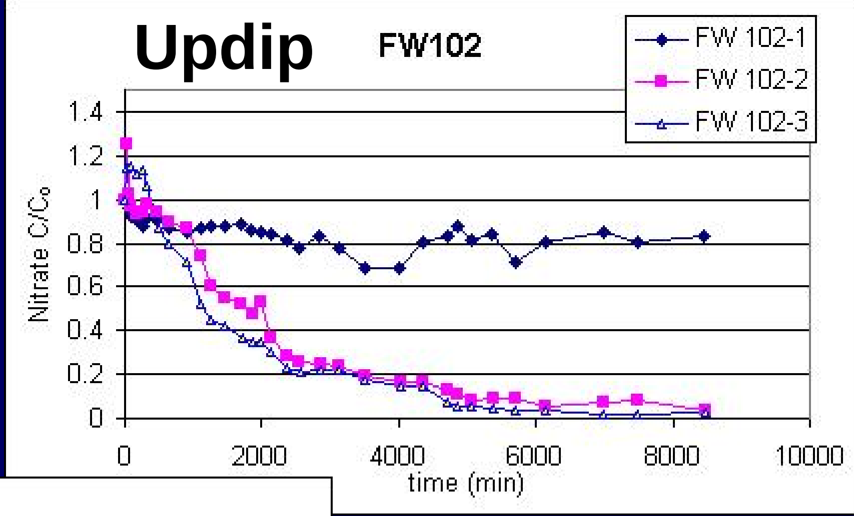


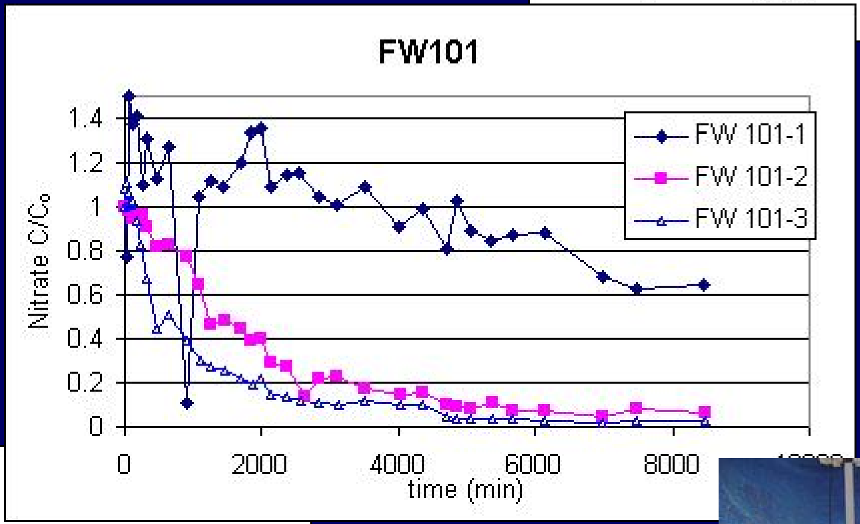
Tracer Breakthrough at 3 Multi-Level Samplers along Geologic Dip Direction

Hubbard et al., 2003

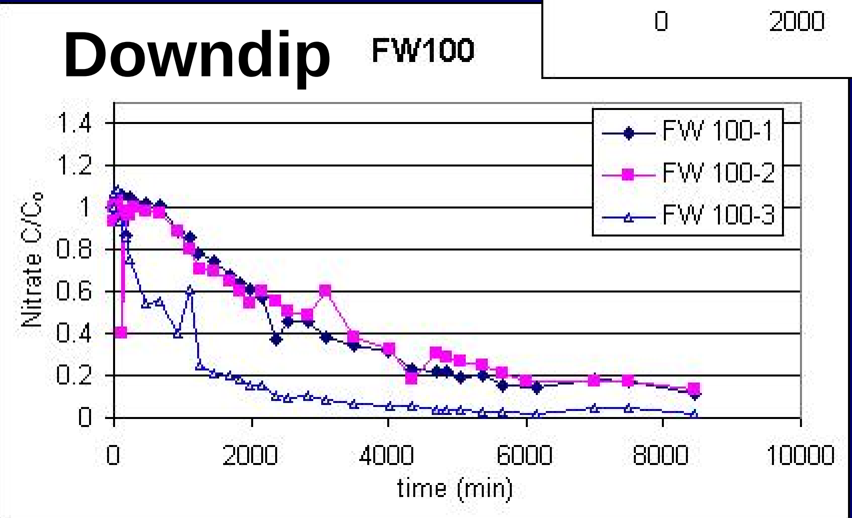
Mehlhorn et al., 2003

Effect of tracer clean water flush on nitrate in MLS wells

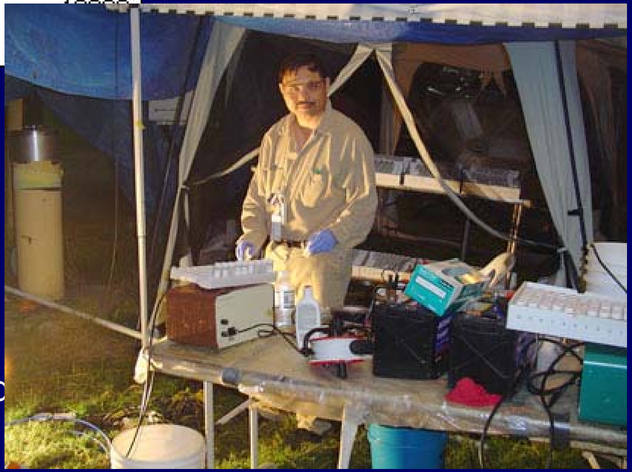




Mid-depths were flushed well
Bottom depth was poorly flushe



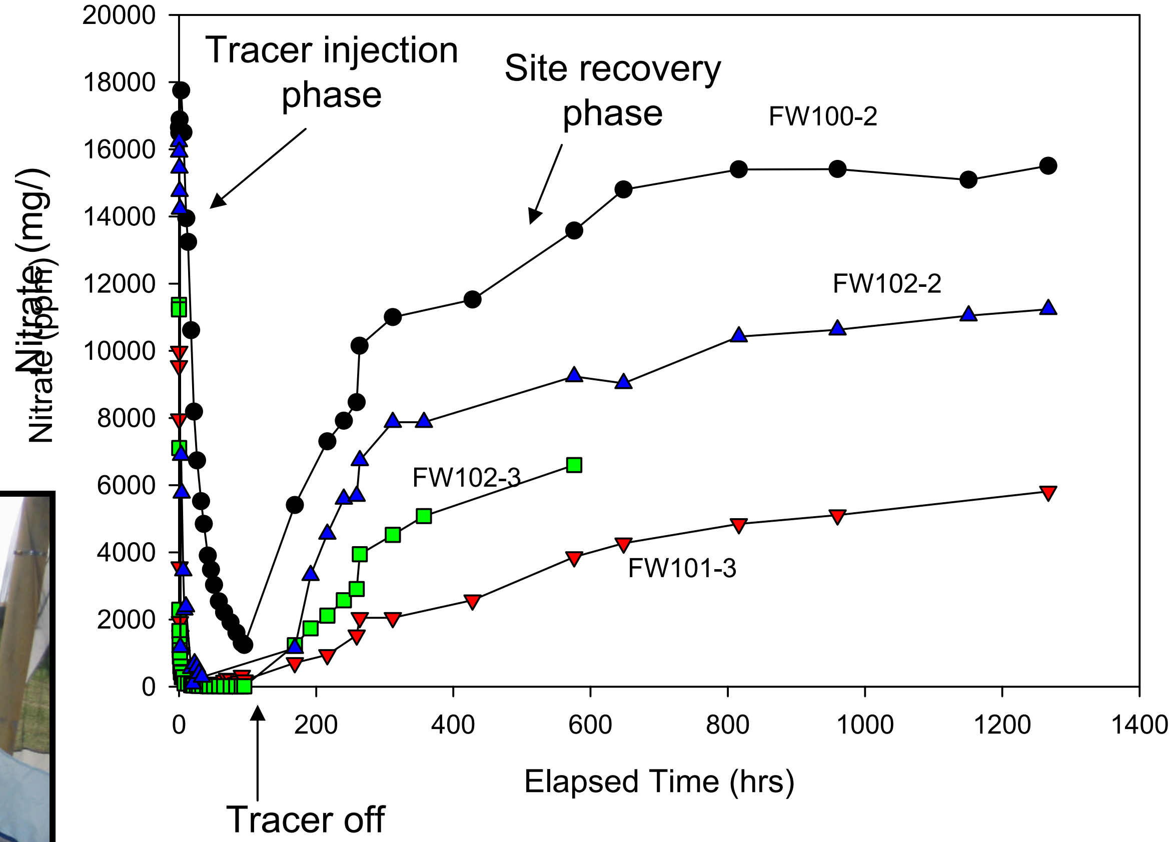
All depths were flushed

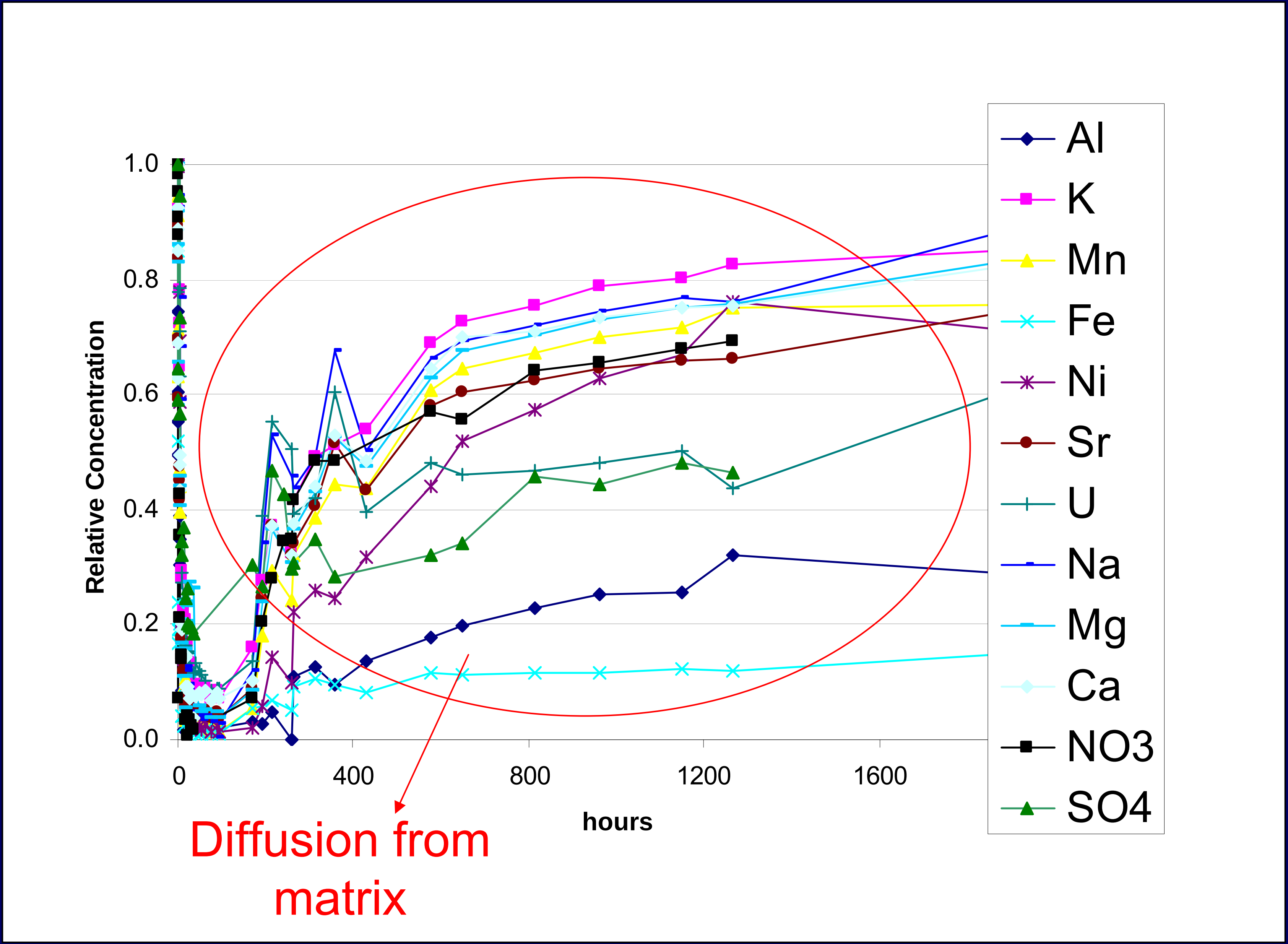


Natural gradient site recovery solute breakthrough

Natural gradient contaminant transport monitored during site recovery.

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





1.0
0.8
0.6
0.4
0.2
0.0
Relative Concentration
0
400
800
1200
1600
hours
Al
K
Mn
Fe
Ni
Sr
U
Na
Mg
Ca
NO3
SO4
Diffusion from matrix

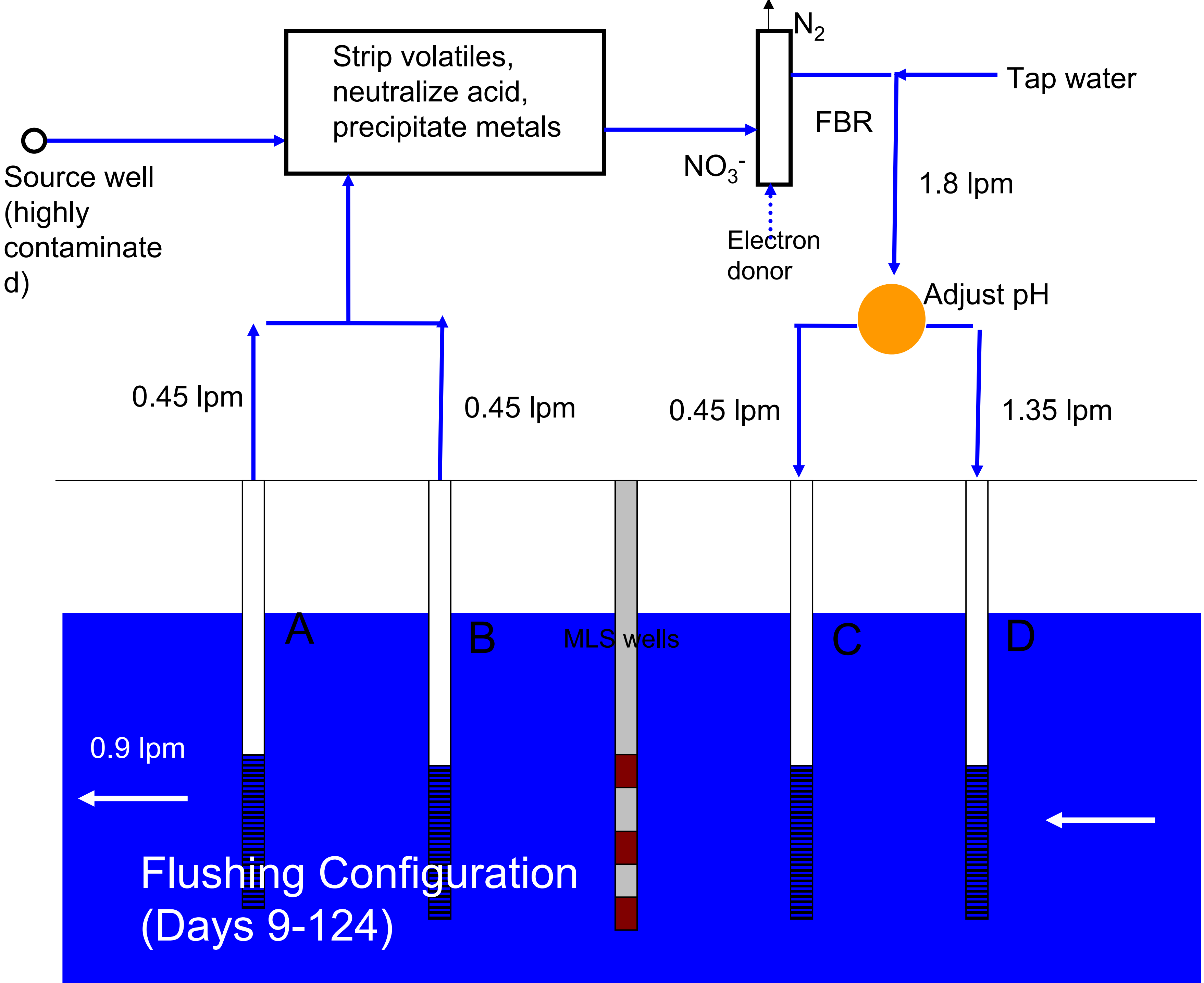
Overall Strategy

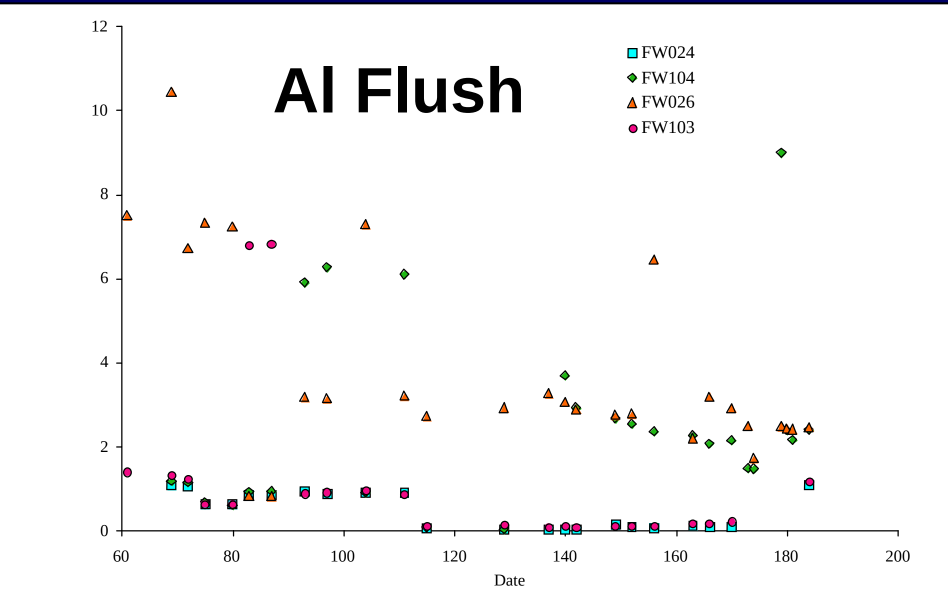
1. Perform a tracer study to determine connectivity of wells and residence time distribution. Obtain desorption rates from the rebound.

2. Flush outer and inner cell with clean water at pH 4 to remove Al, Ca, and most of the nitrate. Follow with flush at pH 5-6 to prepare for denitrification.

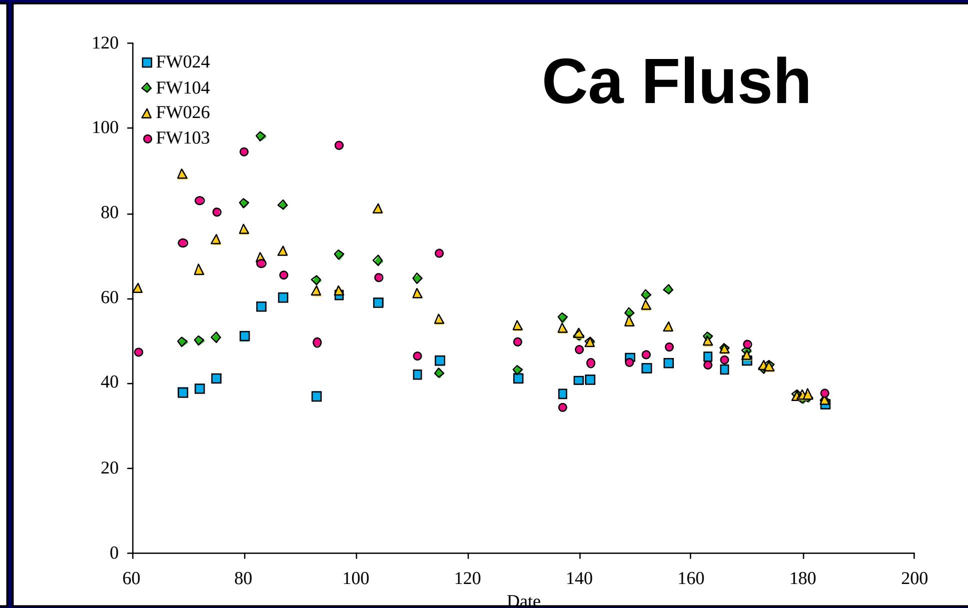
3. Stimulate denitrification *in-situ* and vacuum strip N_2 to remove residual nitrate.

4. Increase pH of inner cell to mobilize U(VI)

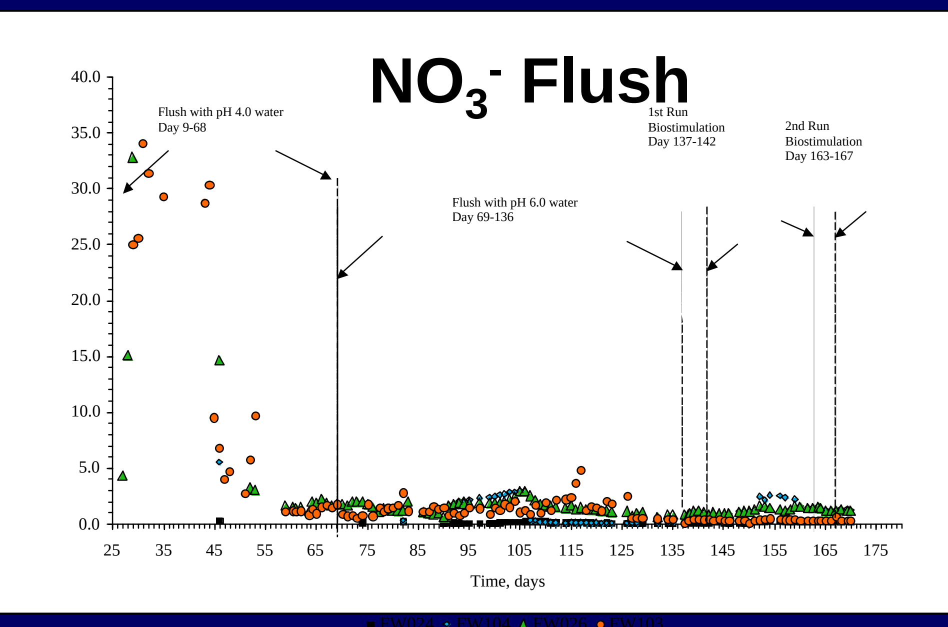

Strip volatiles, neutralize acid, precipitate metals
N2
Tap water
FBR
NO3-
1.8 lpm
Source well (highly contaminated)
Electron donor
Adjust pH
0.45 lpm
0.45 lpm
0.45 lpm
1.35 lpm
A
B
MLS wells
C
D
0.9 lpm
Flushing Configuration (Days 9-124)



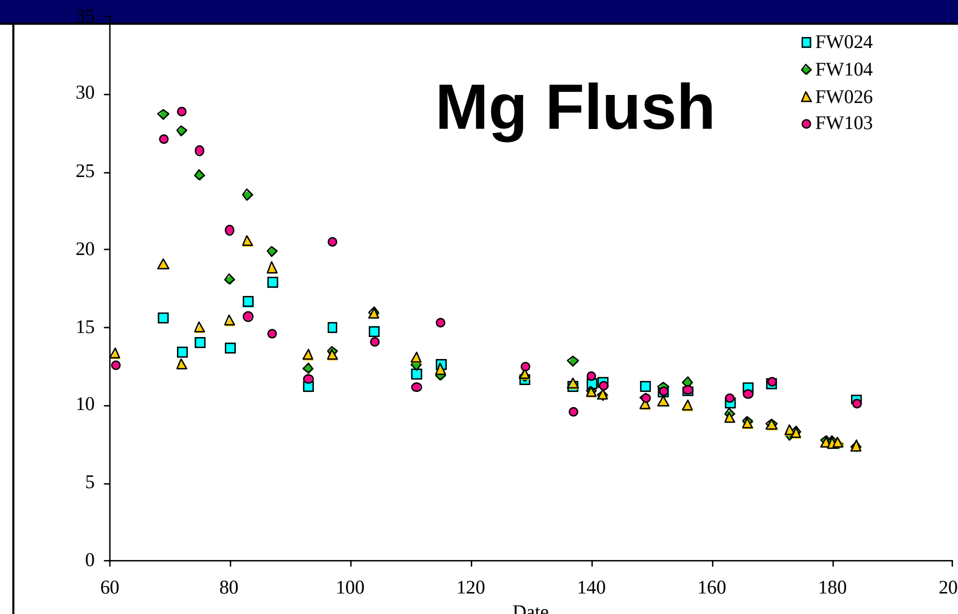
Al Flush
FW024
FW104
FW026
FW103
12
10
8
6
4
2
0
60
80
100
120
140
160
180
200
Date



Ca Flush
FW024
FW104
FW026
FW103
120
100
80
60
40
20
0
60
80
100
120
140
160
180
200
Date

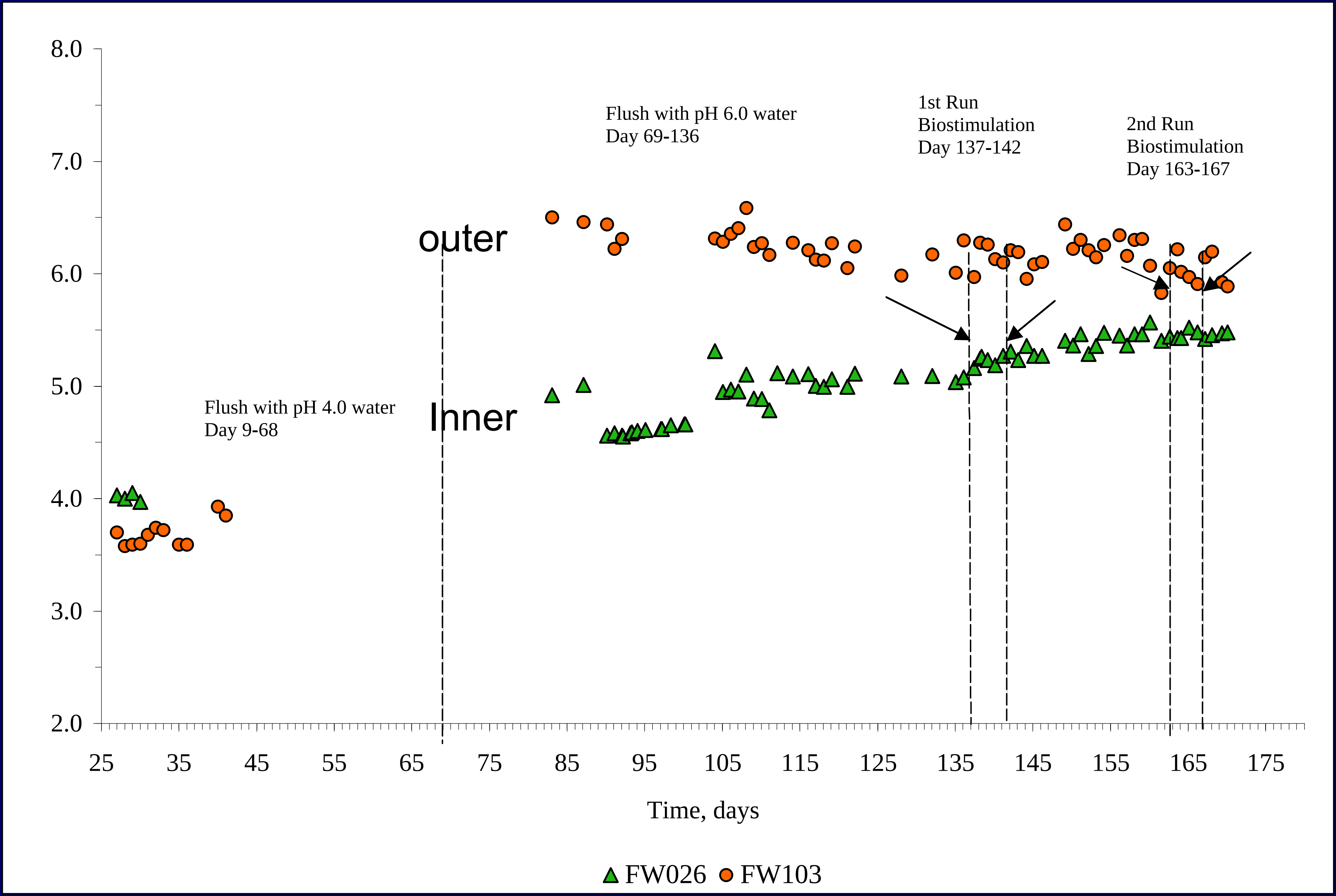


NO3- Flush
Flush with pH 4.0 water
Day 9-68
Flush with pH 6.0 water
Day 69-136
1st Run
Biostimulation
Day 137-142
2nd Run
Biostimulation
Day 163-167
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
25
35
45
55
65
75
85
95
105
115
125
135
145
155
165
175
Time, days
FW024 FW104 FW026 FW103



Mg Flush
FW024
FW104
FW026
FW103
35
30
25
20
15
10
5
0
60
80
100
120
140
160
180
200
Date

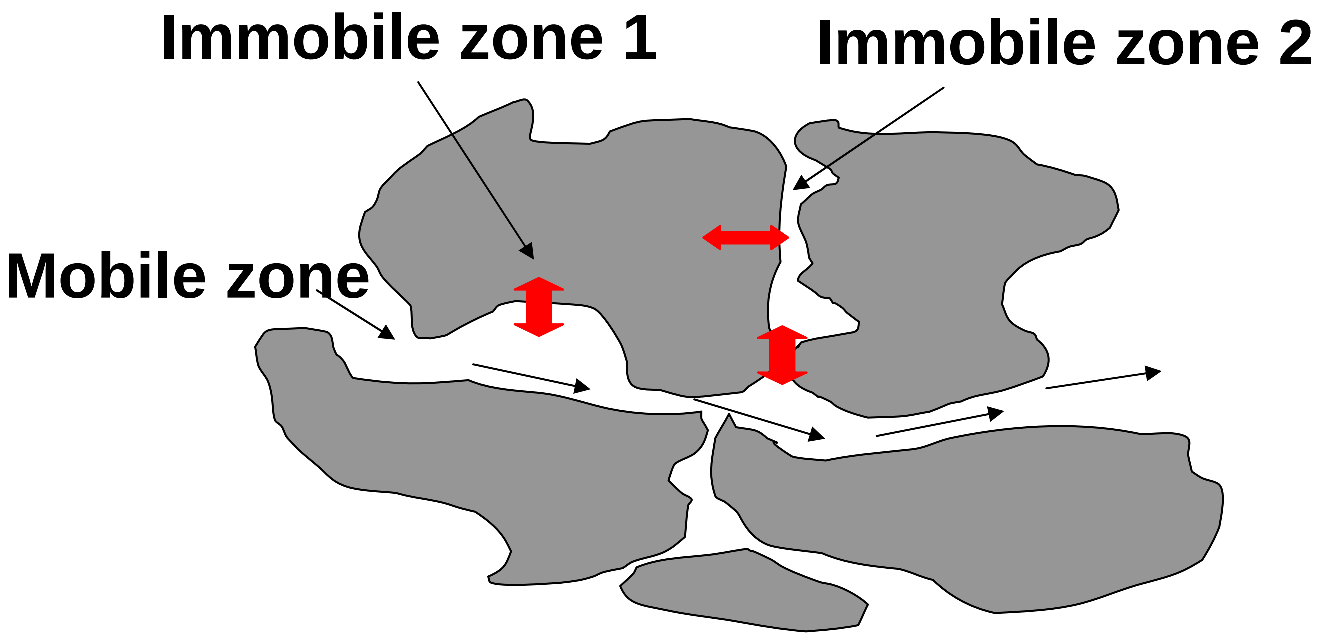
pH increase in inner and outer loop extraction well



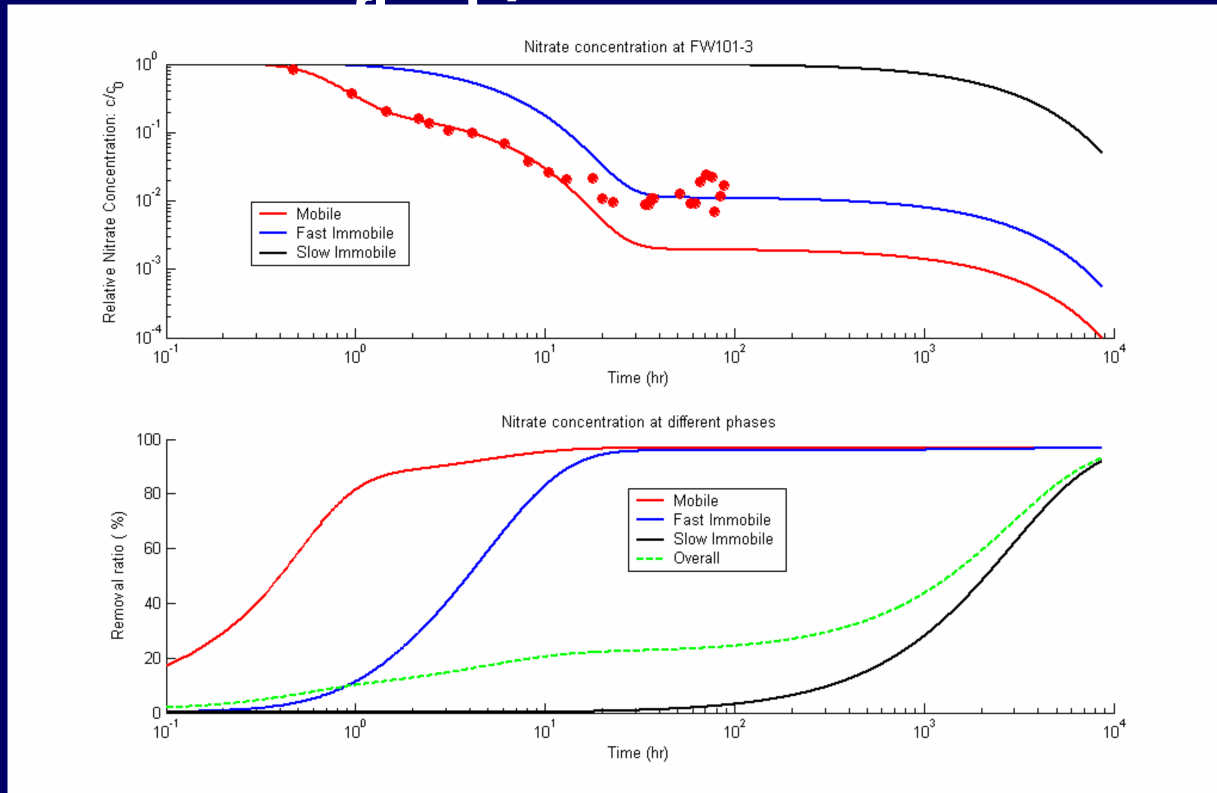
Mass transfer during the flush

Model assumptions:

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

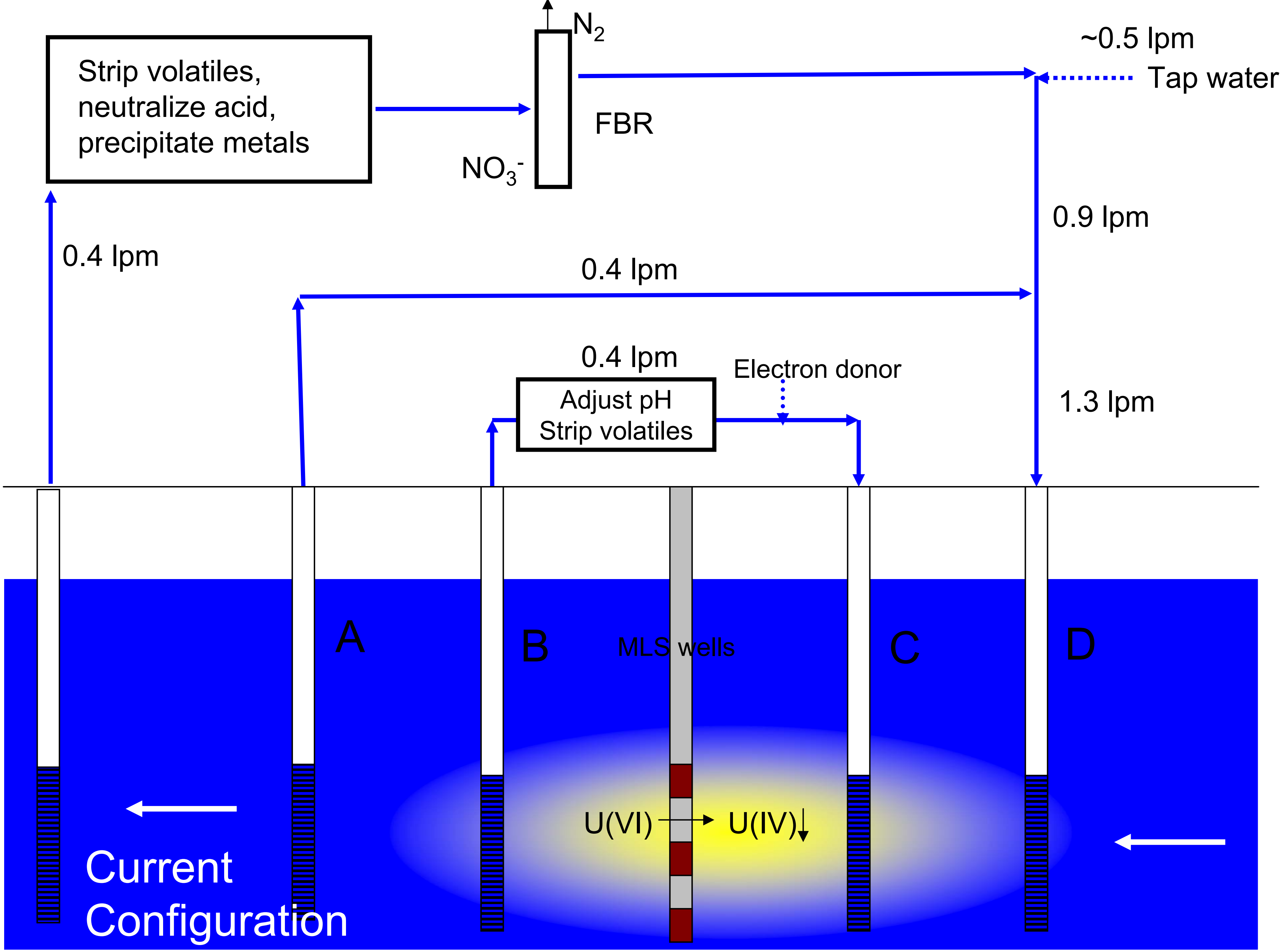


Modeling of



- The half-life of nitrate in the second immobile region is about 3 months. To deplete the second immobile zone would take about one year.

- The mobile region definitely responds to flushing and a low average Nitrate concentration can be maintained while removing the Nitrate as it enters the mobile zone.



Strip volatiles, neutralize acid, precipitate metals
N2
NO3-
FBR
~0.5 lpm
Tap water
0.9 lpm
0.4 lpm
0.4 lpm
0.4 lpm
Electron donor
Adjust pH
Strip volatiles
1.3 lpm
A
B
MLS wells
C
D
U(VI)
U(IV)
Current
Configuration

Overall Strategy

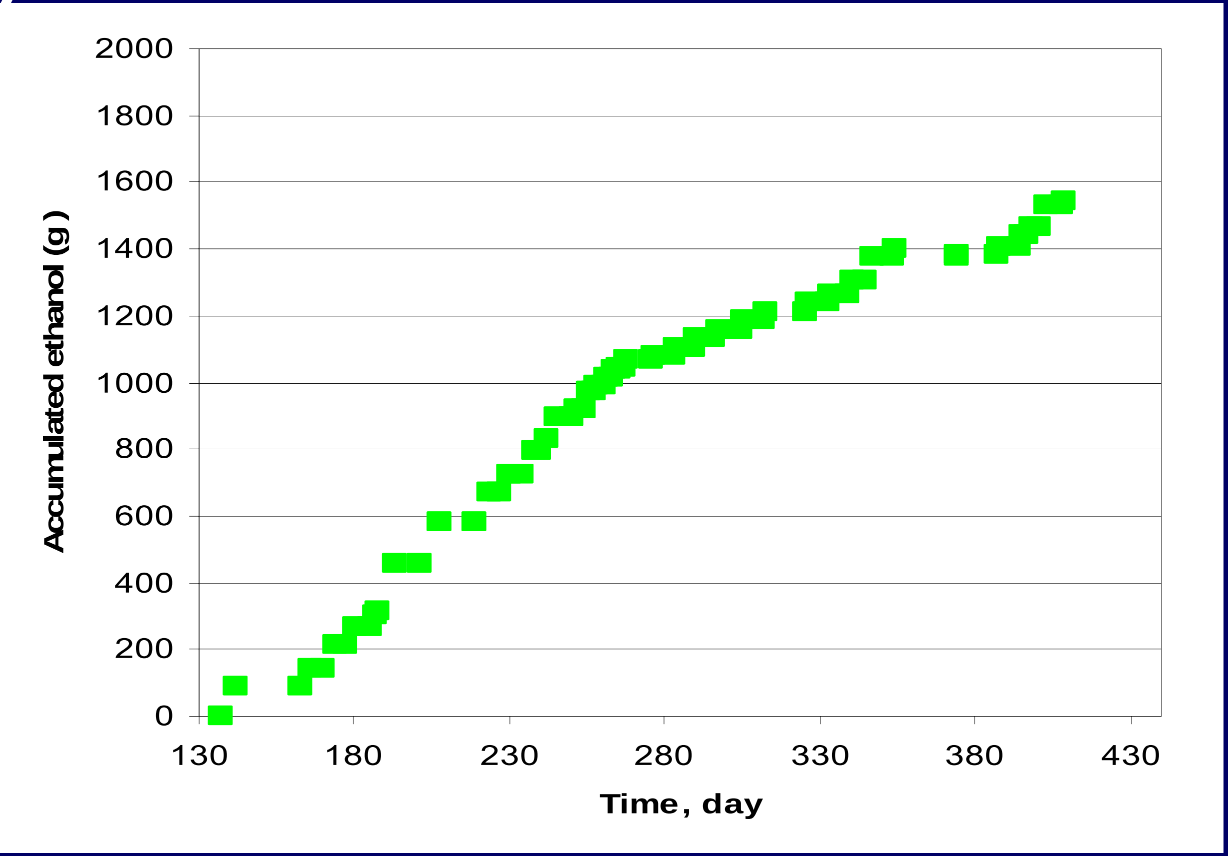
1. Perform a tracer study to determine connectivity of wells and residence time distribution. Obtain desorption rates from the rebound.

2. Flush outer and inner cell with clean water at pH 4 to remove Al, Ca, and most of the nitrate. Follow with flush at pH 5-6 to prepare for denitrification.

3. Stimulate denitrification *in-situ* and vacuum strip N_2 to remove residual nitrate.

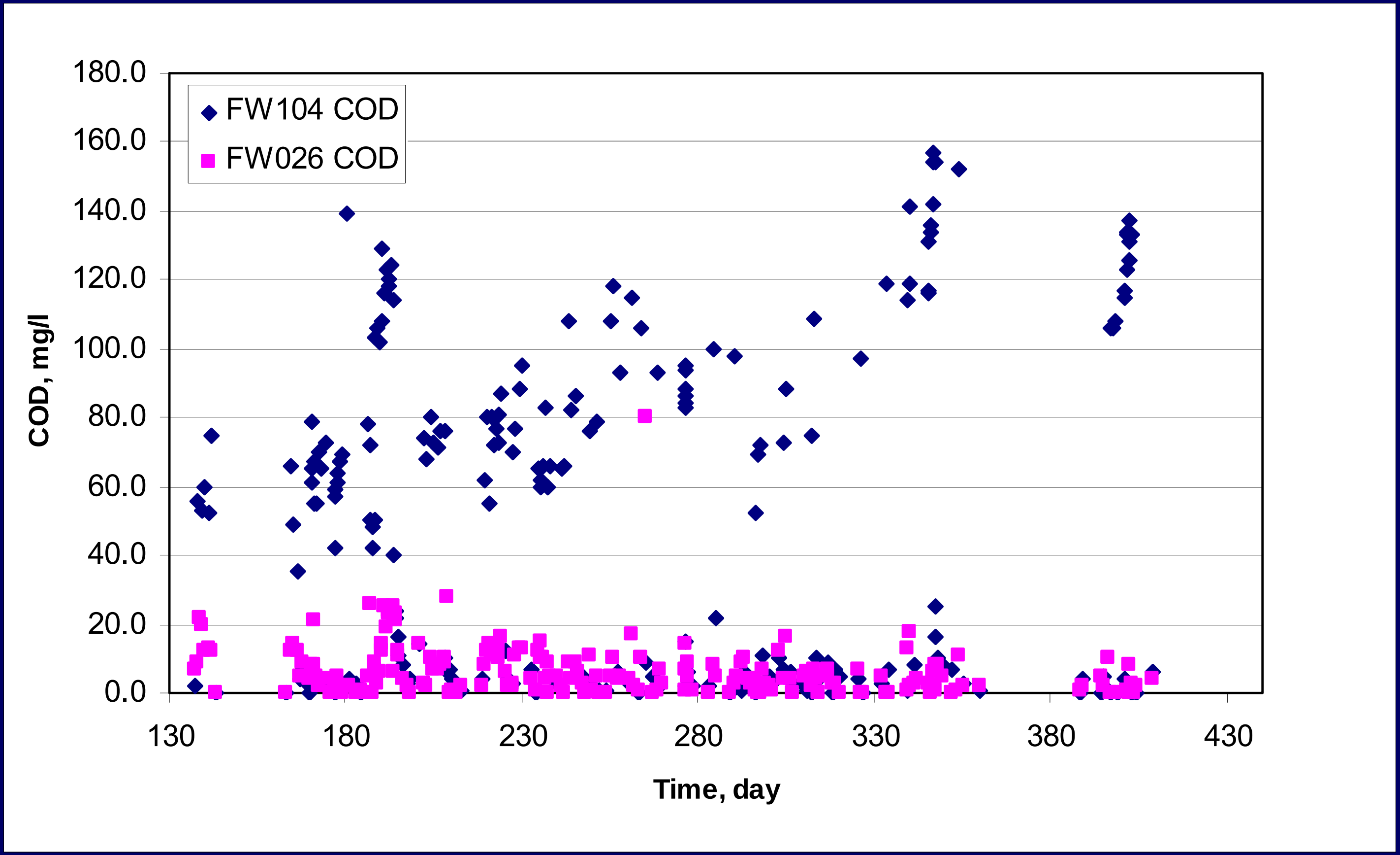
4. Increase pH of inner cell to mobilize U(VI)

Cumulative ethanol injected (Jan.7 to Oct. 5, 2004)

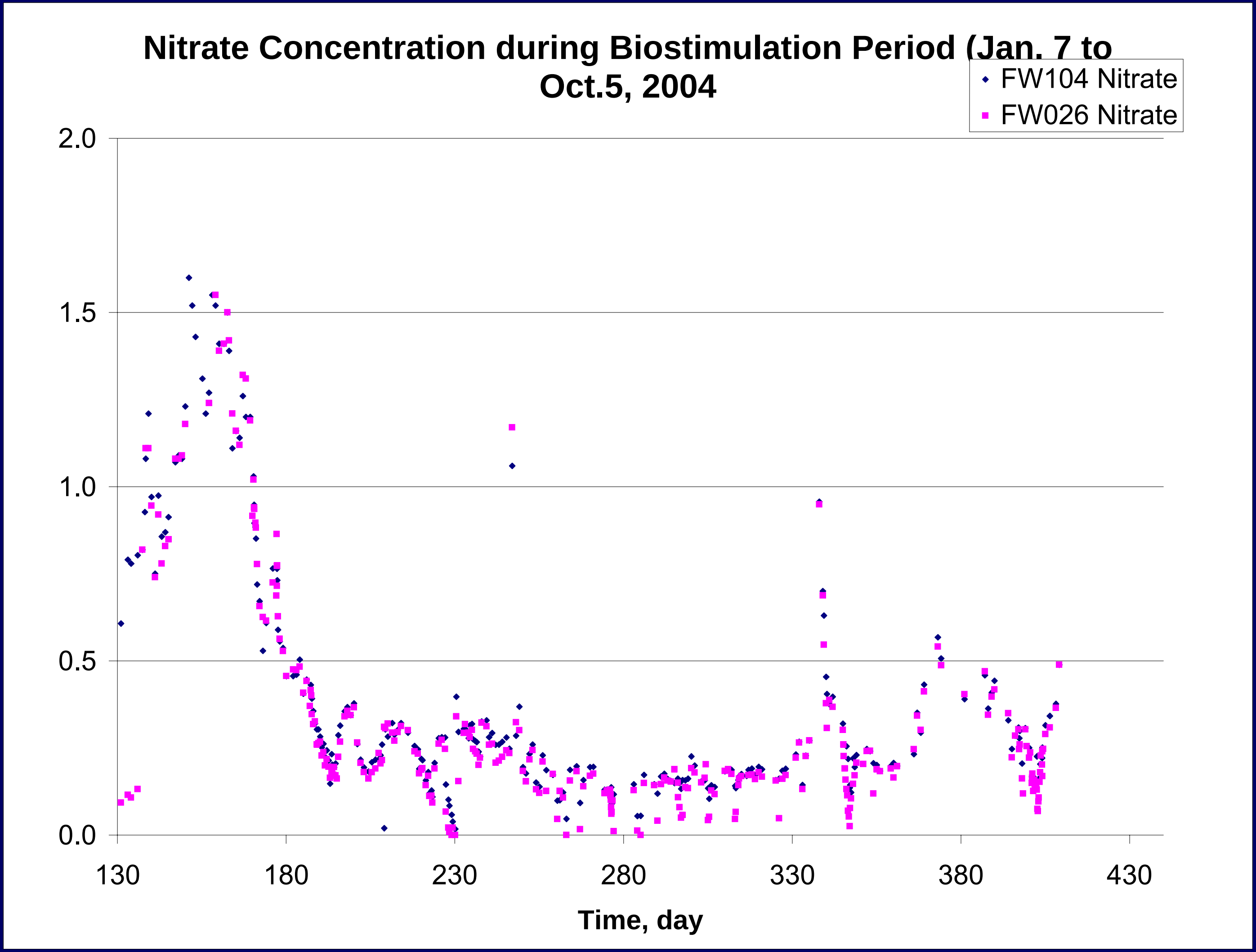


Ethanol was added 34 times. To date, a total of 1.54 kg was injected.

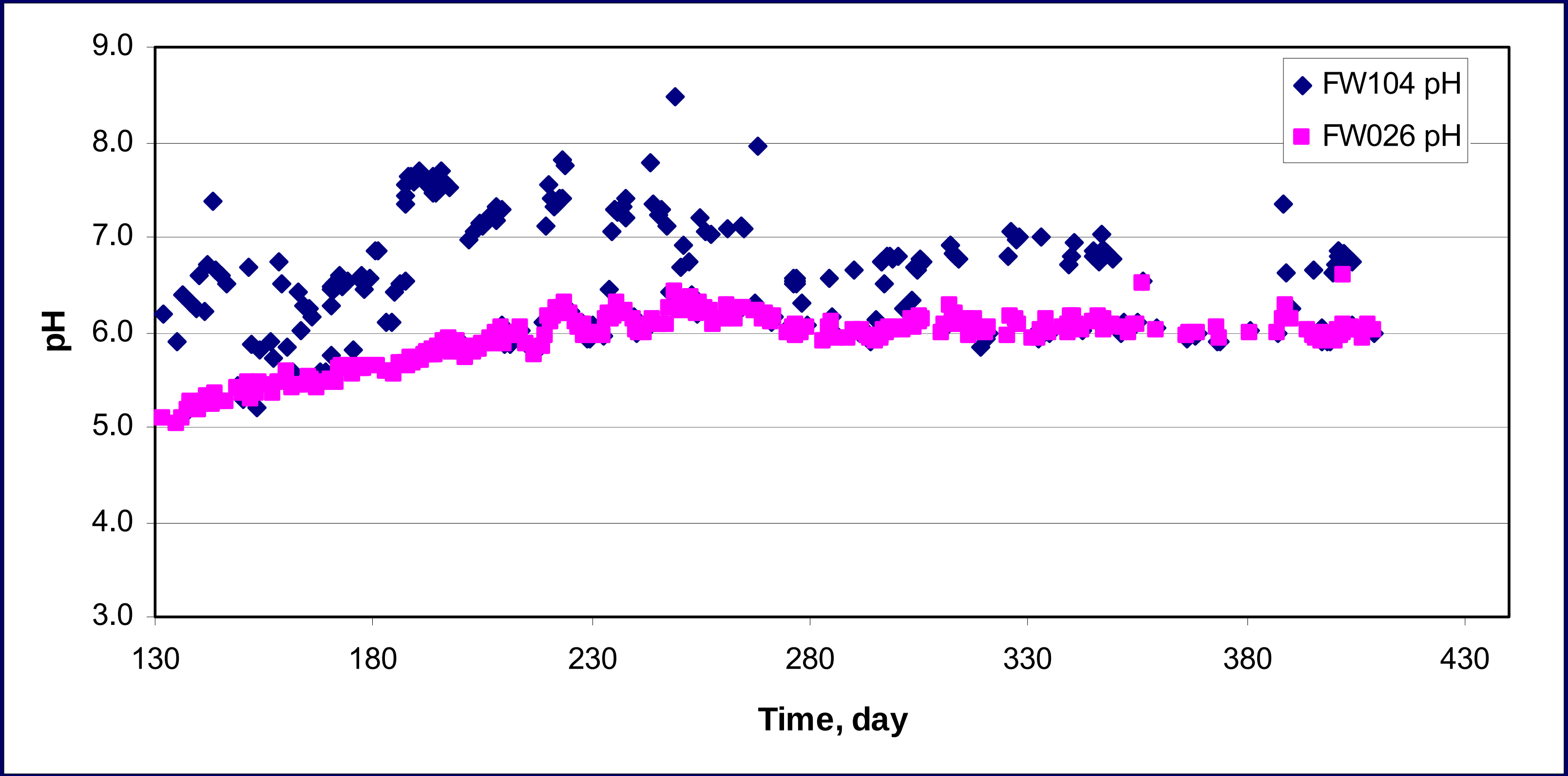
COD in inner loop Injection and extraction wells



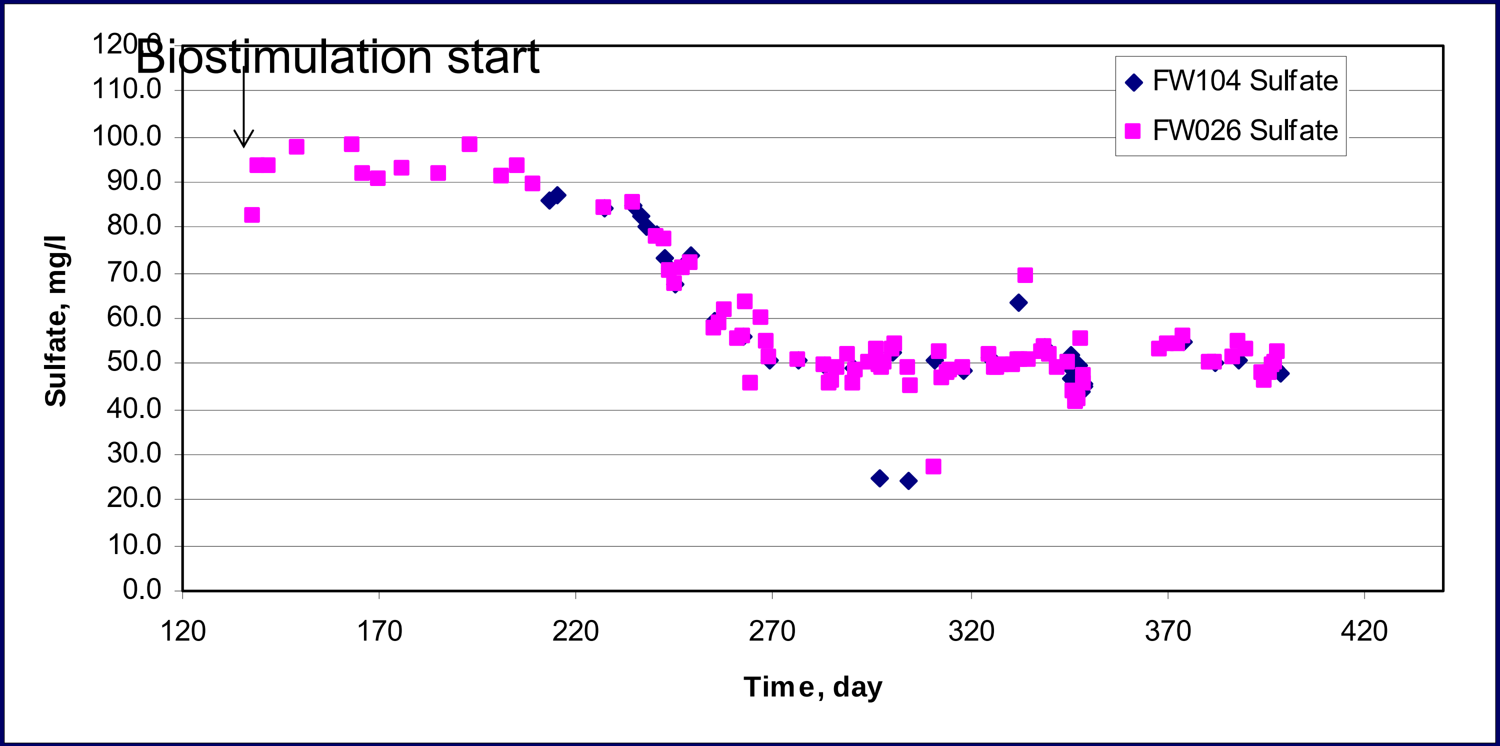
Nitrate in inner loop injection and extraction wells



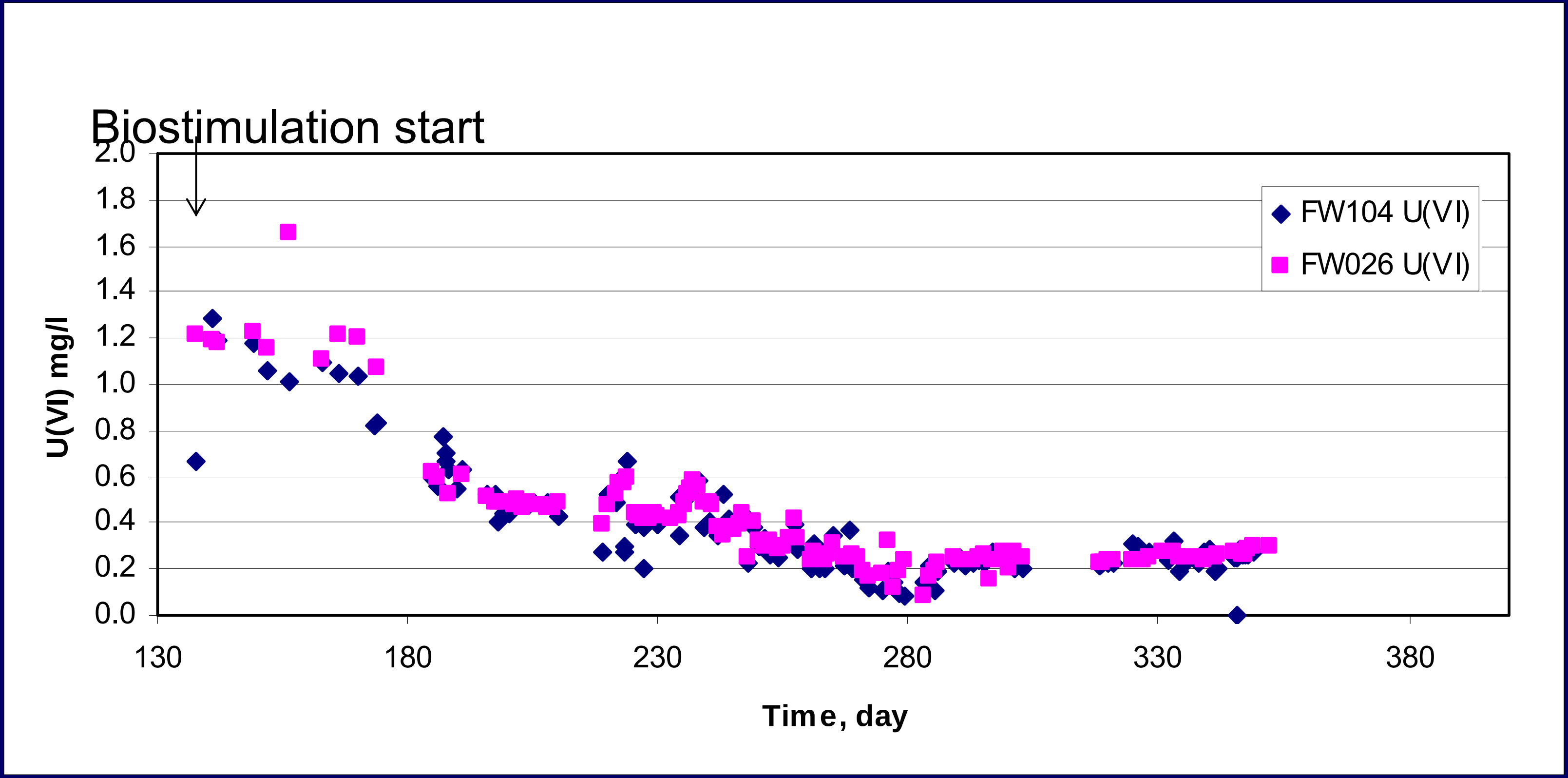
pH in inner loop injection and extraction wells



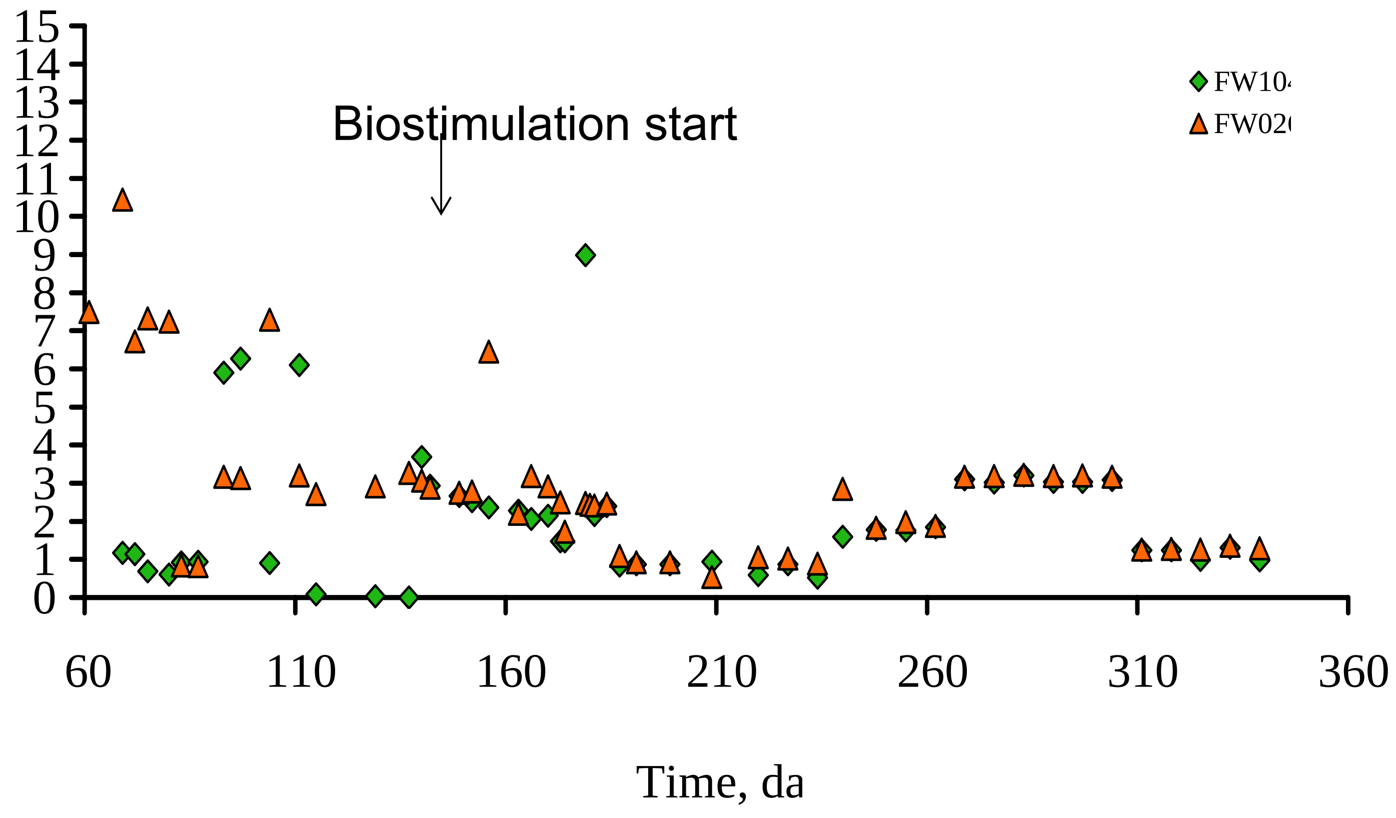
Sulfate in inner loop injection and extraction wells



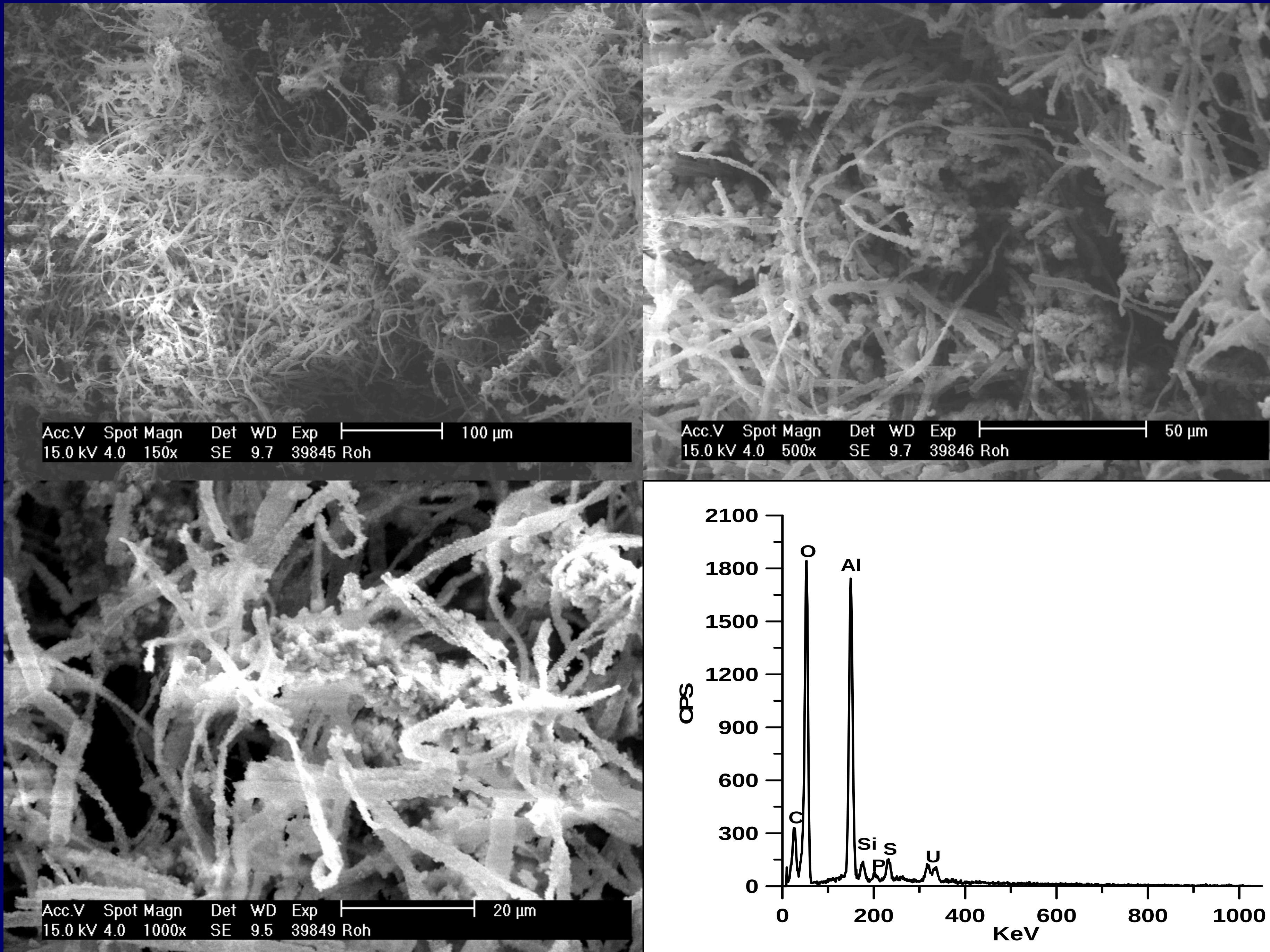
U(VI) in inner loop injection and extraction wells

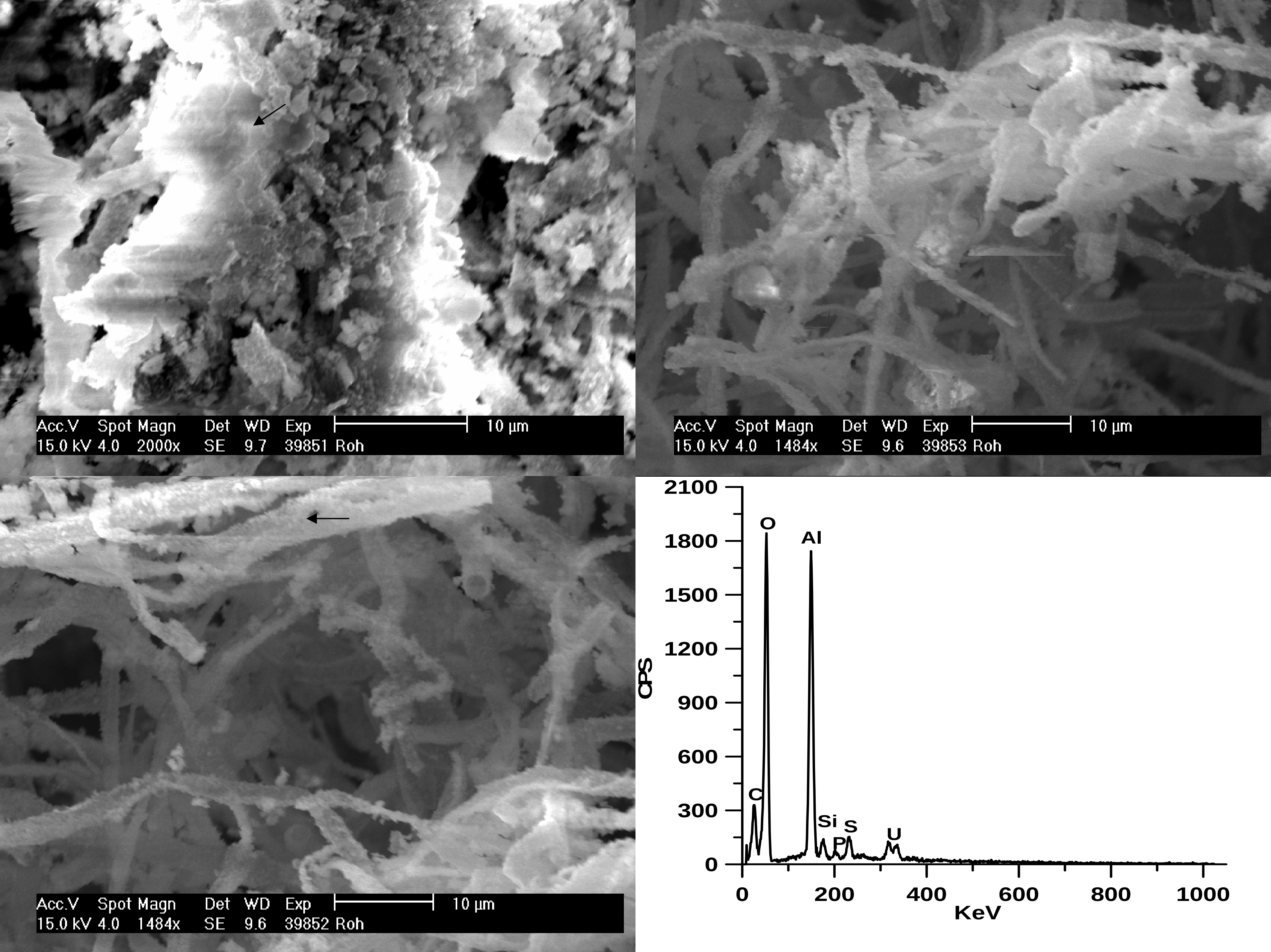


Aluminum in inner loop injection and extraction wells



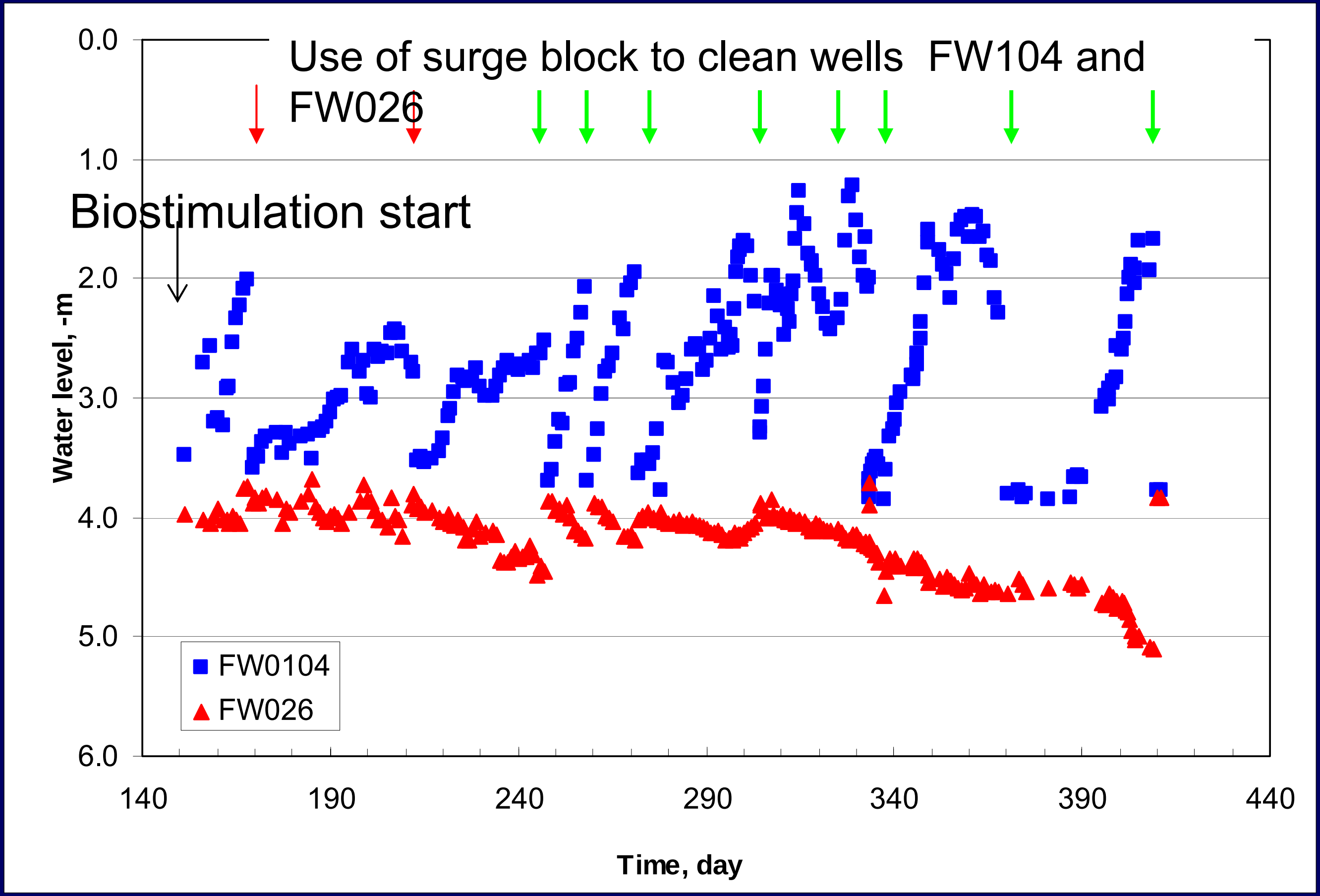
Clogged pump head screen.
The white precipitate dissolved in a 2% HCl solution after 1.5 hour.


Acc.V Spot Magn Det WD Exp 100 µm
15.0 kV 4.0 150x SE 9.7 39845 Roh
Acc.V Spot Magn Det WD Exp 50 µm
15.0 kV 4.0 500x SE 9.7 39846 Roh
Acc.V Spot Magn Det WD Exp 20 µm
15.0 kV 4.0 1000x SE 9.5 39849 Roh
CPS
2100
1800
1500
1200
900
600
300
0
C
O
Al
Si
P
S
U
0
200
400
600
800
1000
KeV


Acc.V Spot Magn Det WD Exp 10 µm
15.0 kV 4.0 2000x SE 9.7 39851 Roh
Acc.V Spot Magn Det WD Exp 10 µm
15.0 kV 4.0 1484x SE 9.6 39853 Roh
Acc.V Spot Magn Det WD Exp 10 µm
15.0 kV 4.0 1484x SE 9.6 39852 Roh
CPS
0
300
600
900
1200
1500
1800
2100
O
Al
C
Si
P
S
U
0
200
400
600
800
1000
KeV

Biofouling of pump intake on inner loop extraction well - Day 245

Water level in inner loop injection and extraction wells during biostimulation



Surge block for cleaning

Surge block allowed for sampling of sediment/biomass in wells

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

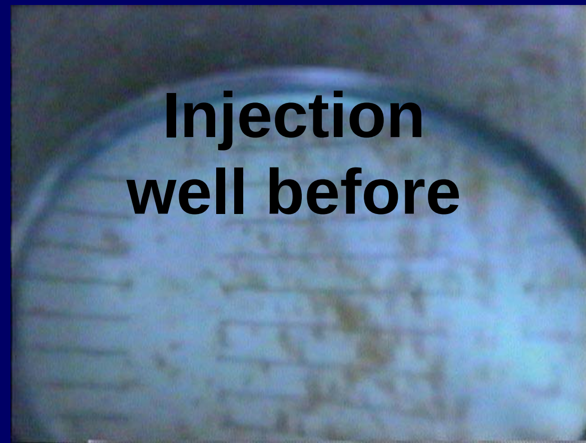
QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

Effects of surging: what a borehole camera shows

reference well

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.



after

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

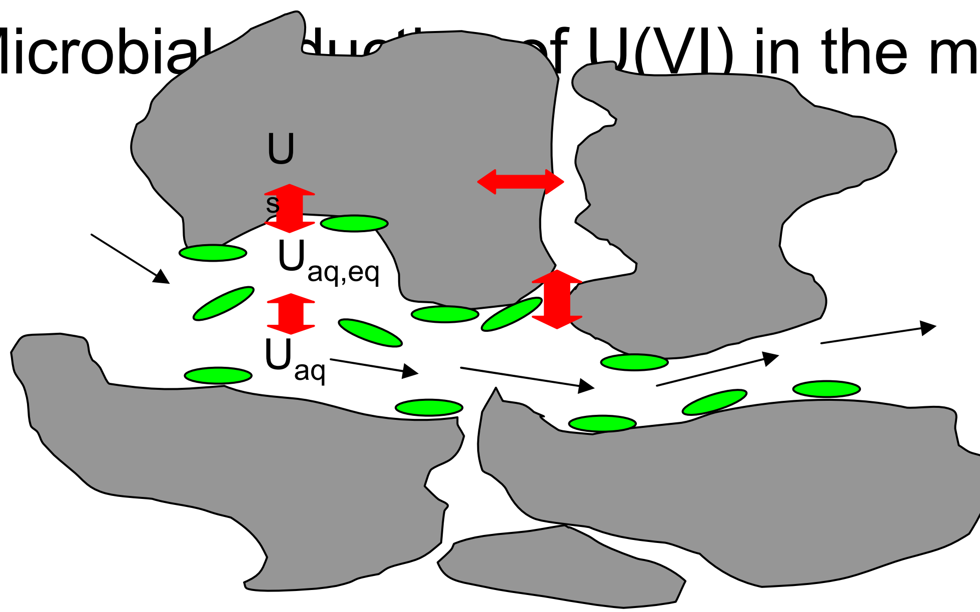
after

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

- **Model - coupled mass transfer and reaction**

  Assumptions

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



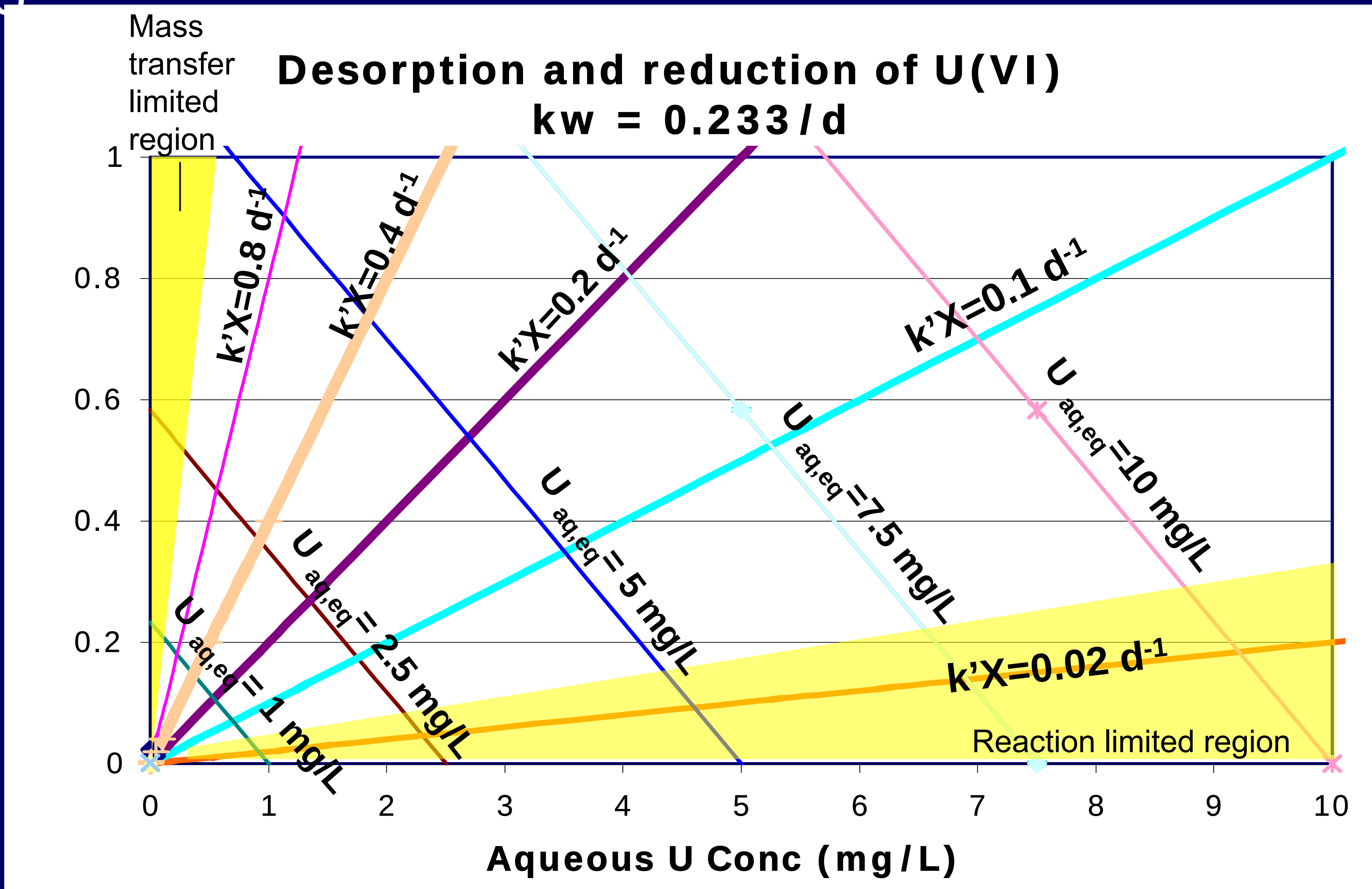
k_w is a lumped parameter accounting for mass transfer. It has units of time^{-1}. $U_{eq,aq}$ is the concentration of U in equilibrium with the solid phase concentration. It is a function of pH and TIC. X is biomass concentration, and k' is a pseudo second order rate coefficient .

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

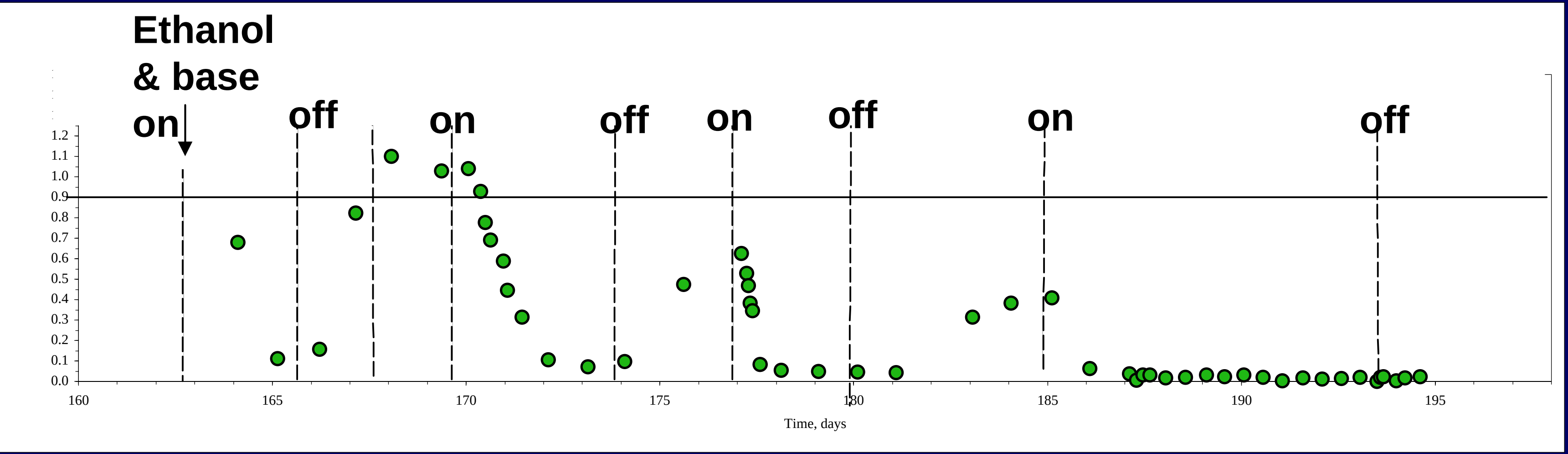


Preliminary calculations indicate that MT limitation is likely

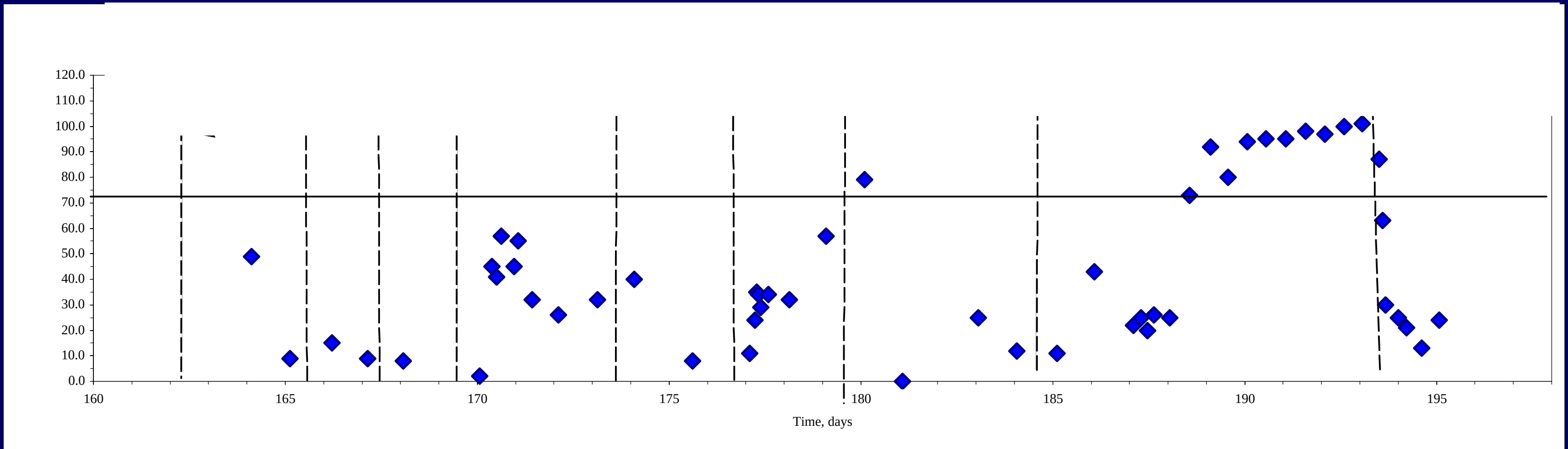
Initlal biostimulation period (Days 165-195)

MLS 102-3

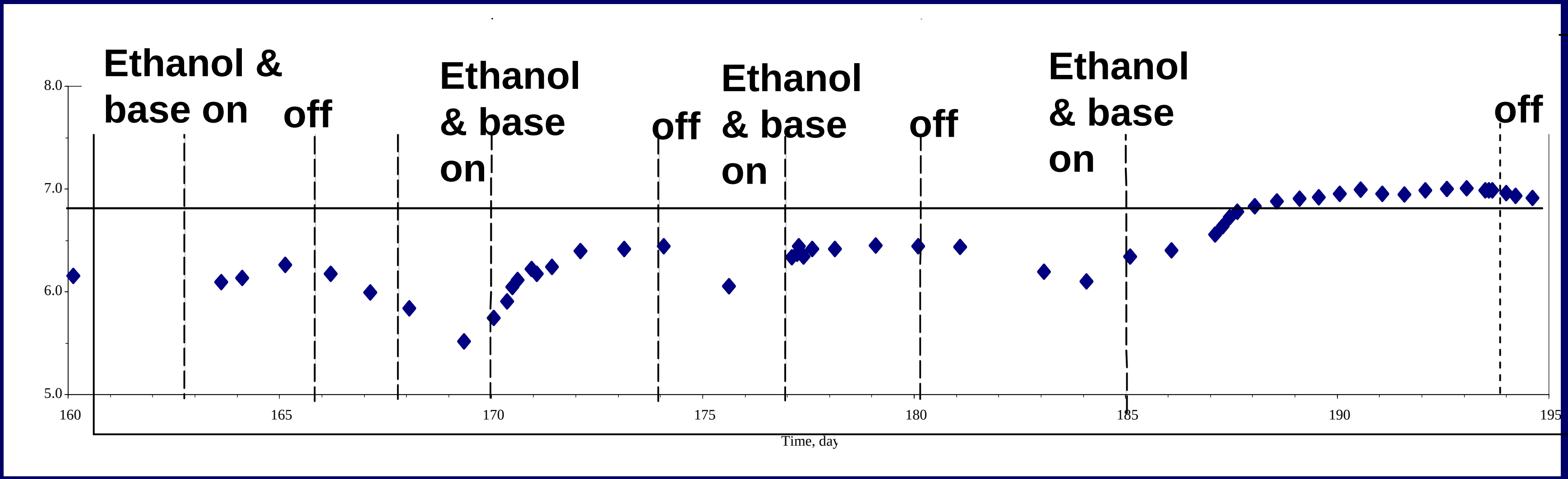
NO_3^-



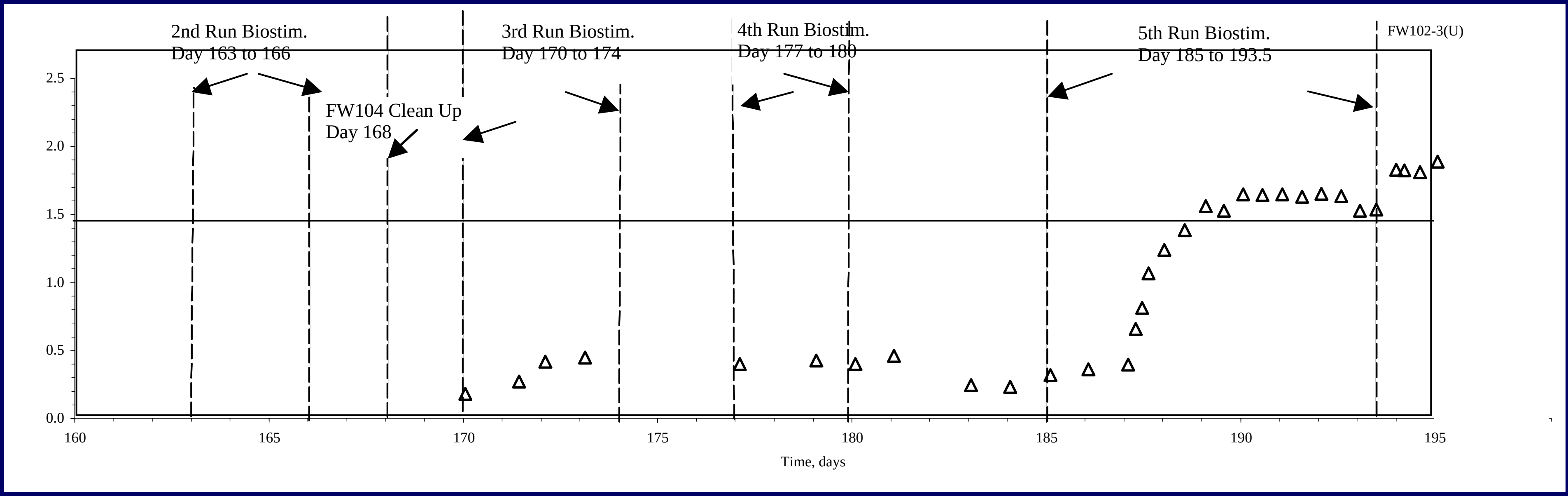
Soluble COD



MLS 102-3 (Days 165-195) pH



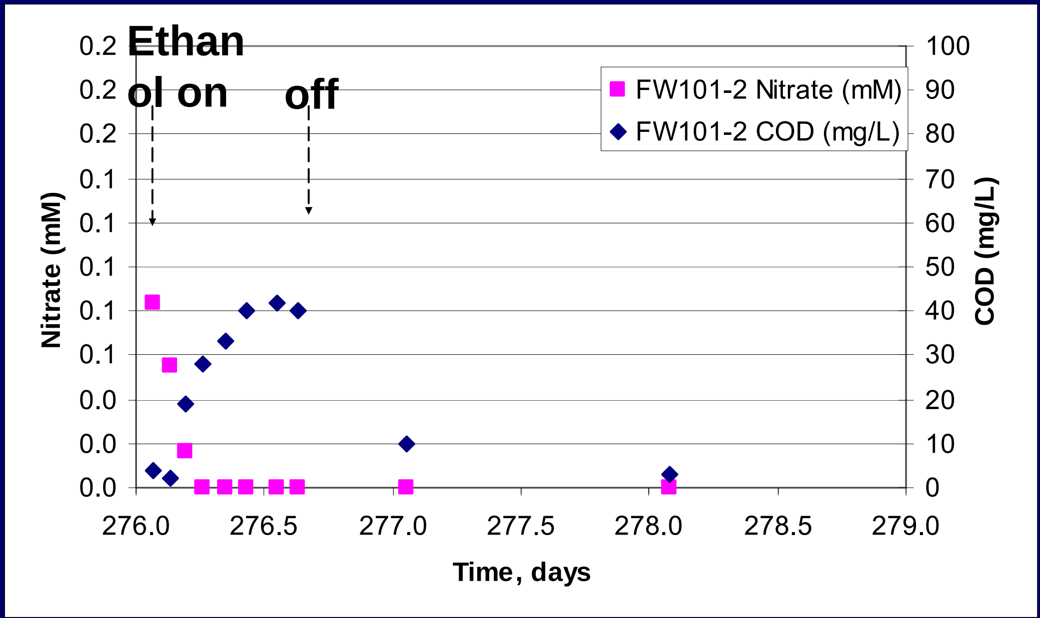
Soluble U(VI)

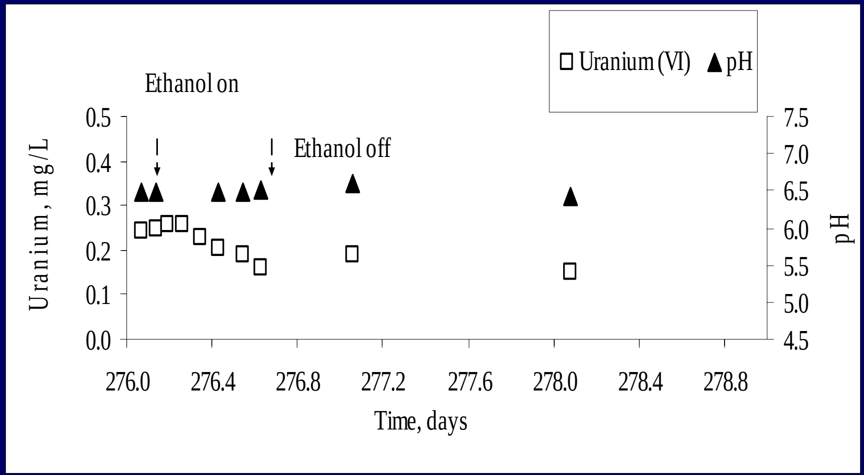


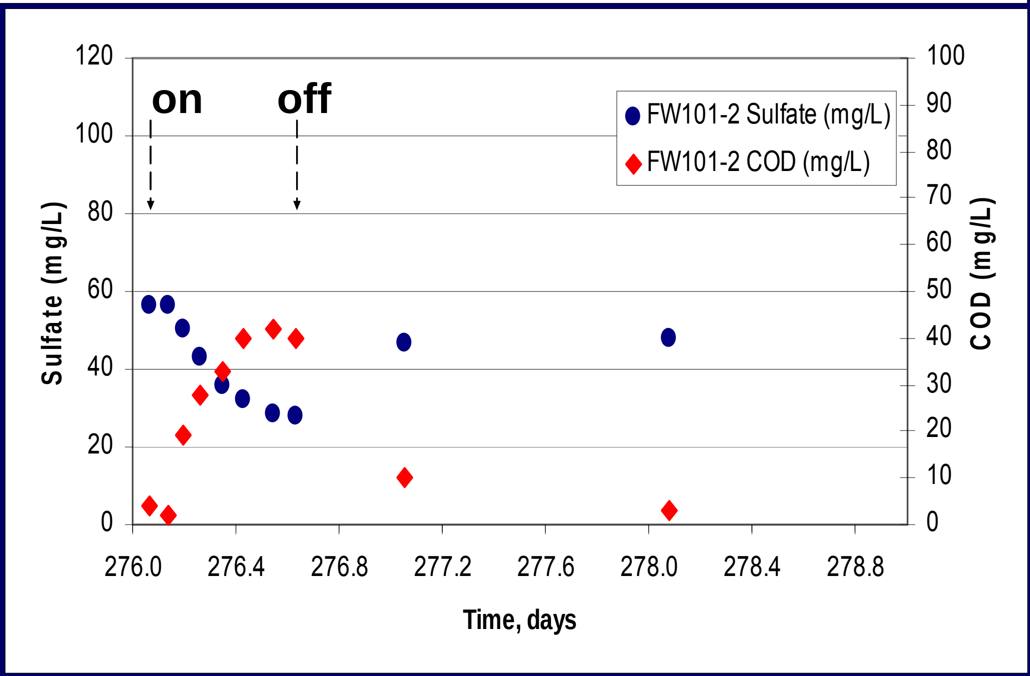
Mid-stage biostimulation (Days 277 -284)

MLS 101-2

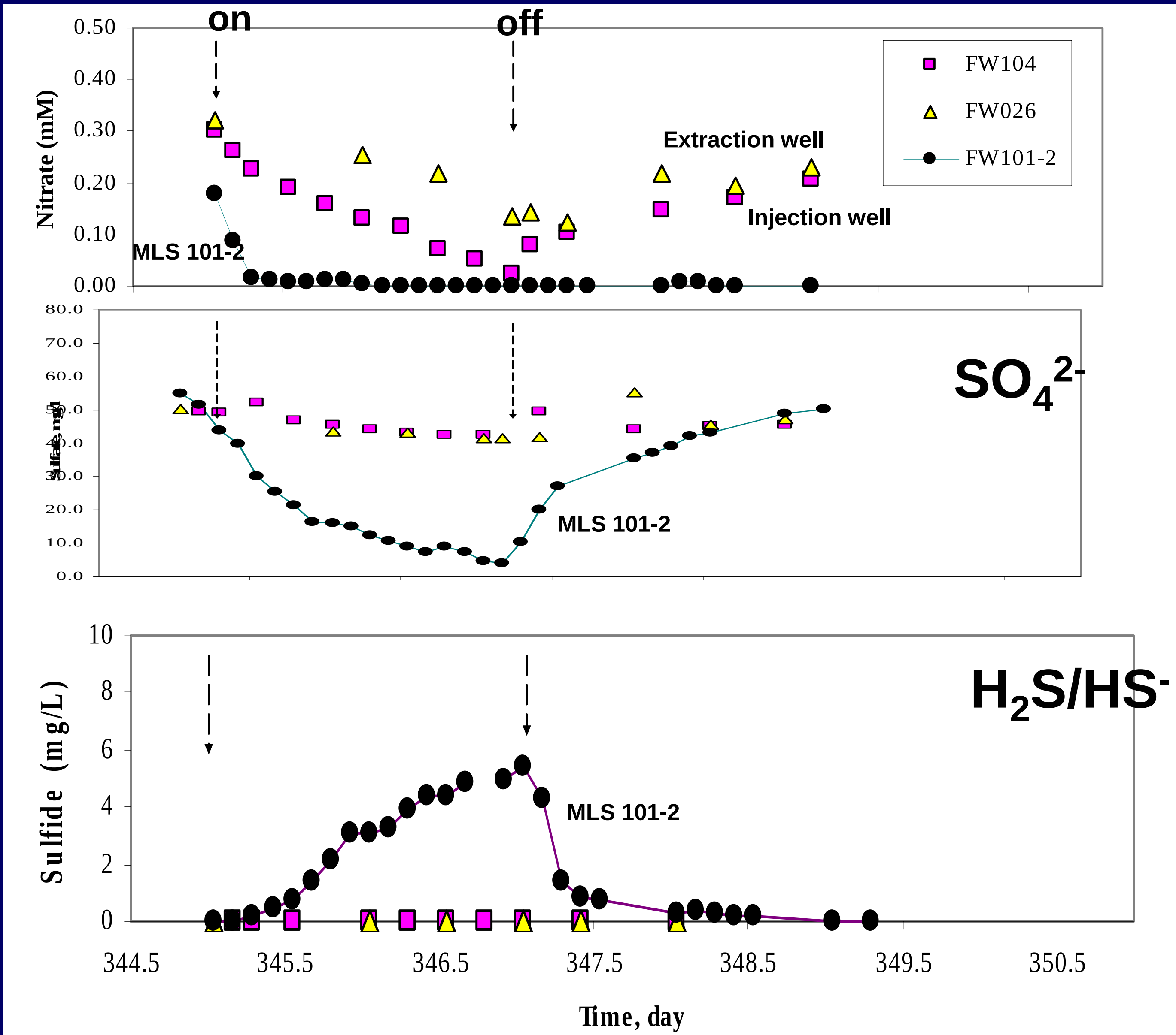
1. Nitrate decline occurs immediately after ethanol injection.
2. Sulfate decline occurs after 3 hours of of ethanol injection.
3. U(VI) decline occurs after 5 hours of ethanol injection.



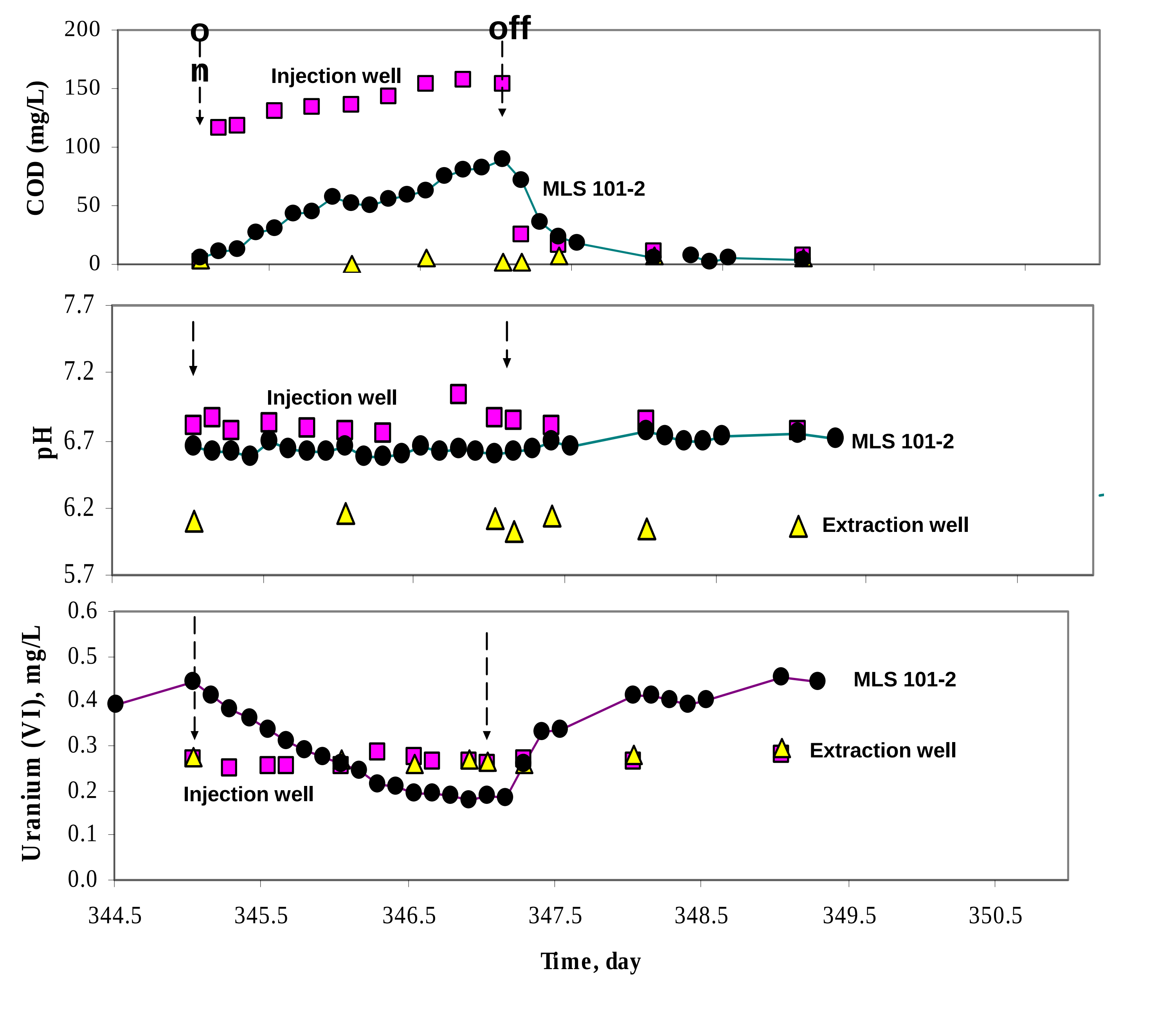


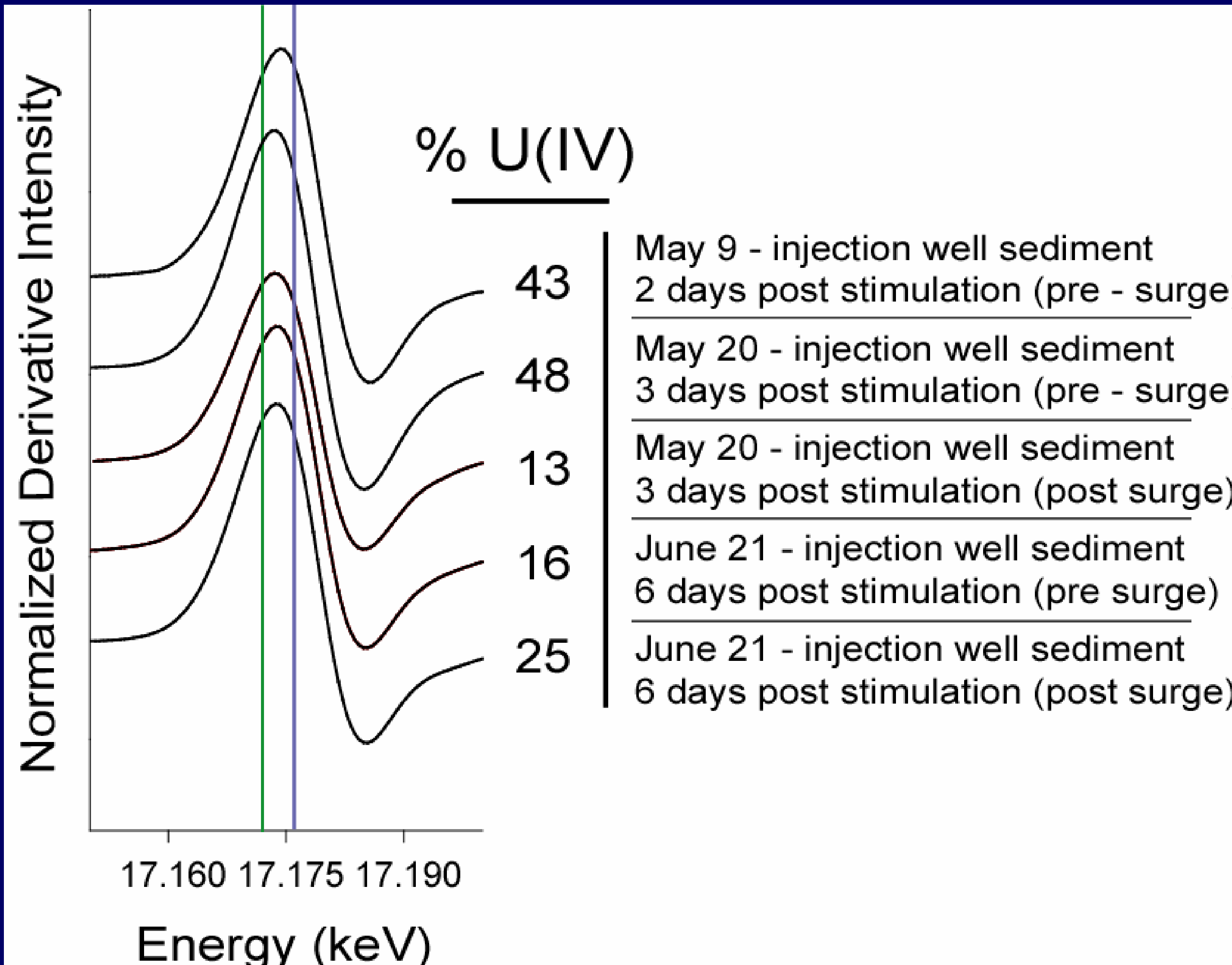


Recent biostimulation (Days 345-349)



Recent biostimulation (Days 345-349)




% U(IV)
43
48
13
16
25
May 9 - injection well sediment
2 days post stimulation (pre - surge)
May 20 - injection well sediment
3 days post stimulation (pre - surge)
May 20 - injection well sediment
3 days post stimulation (post surge)
June 21 - injection well sediment
6 days post stimulation (pre surge)
June 21 - injection well sediment
6 days post stimulation (post surge)
Normalized Derivative Intensity
17.160 17.175 17.190
Energy (keV)


QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

MPN values for different trophic groups (number/mL)

Well	Denitrifiers	Sulfate Reducers	Iron Reducers
Inner loop extraction	3.5×10^5	1.6×10^5	2.0×10^3
MLS 101-2	5.6×10^2	1.4×10^5	2.4×10^3
MLS102-2	5.4×10^5	0.92×10^4	2.8×10^2
MLS102-3	2.1×10^6	2.4×10^5	3.2×10^3
106 Control well	5.4 x 10	0	0

Note: MPN values for five replicates. Test wells sampled 8/20/04. Control well sampled 5/28/04.

Key points

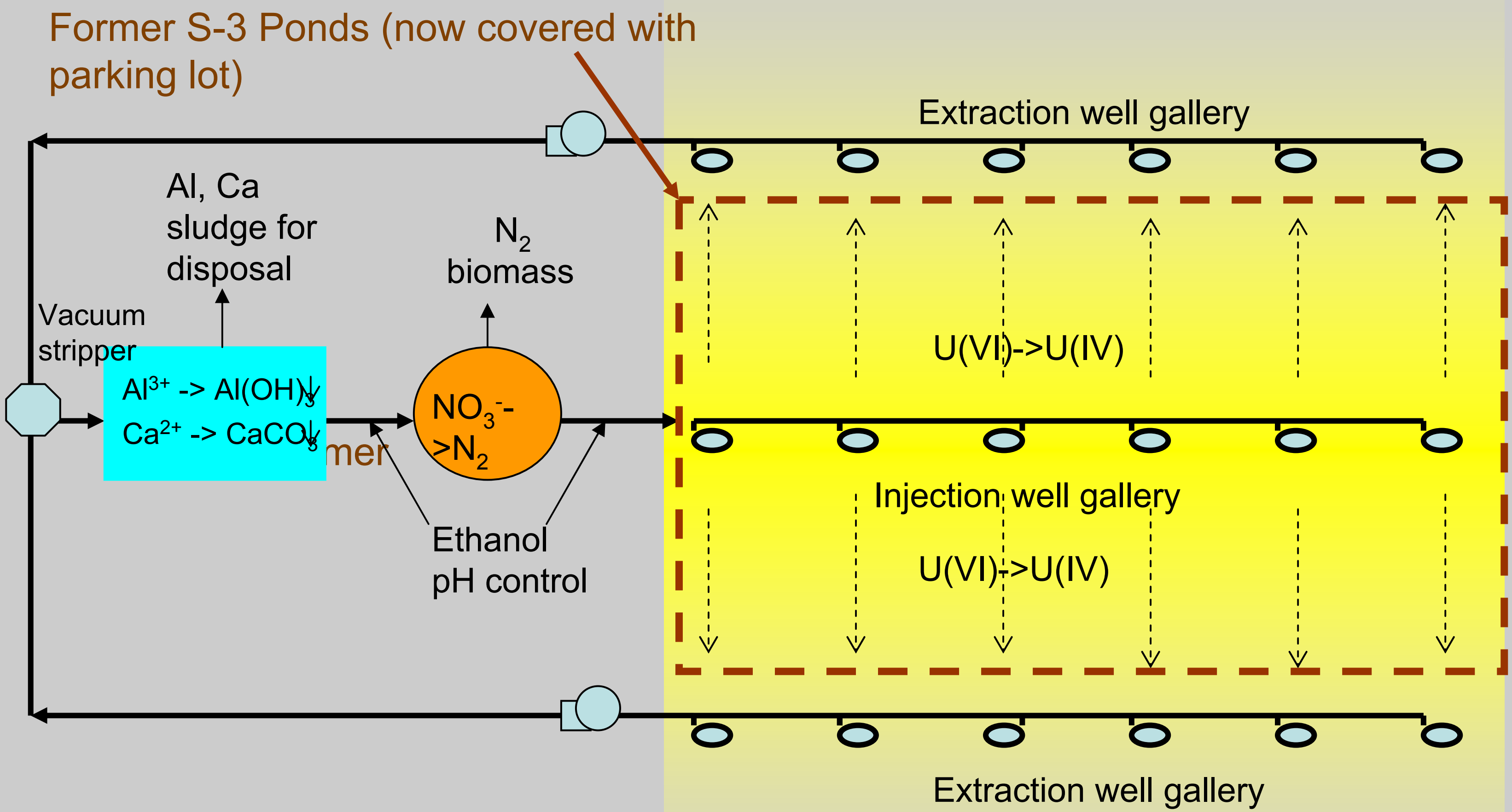
- Aluminum buffers the system at low pH and precipitates when the pH is increased. It can be removed *ex-situ*.

- Nitrate inhibits U(VI) reduction. Bulk nitrate can be removed *ex-situ,* and residual nitrate can be removed *in-situ.*

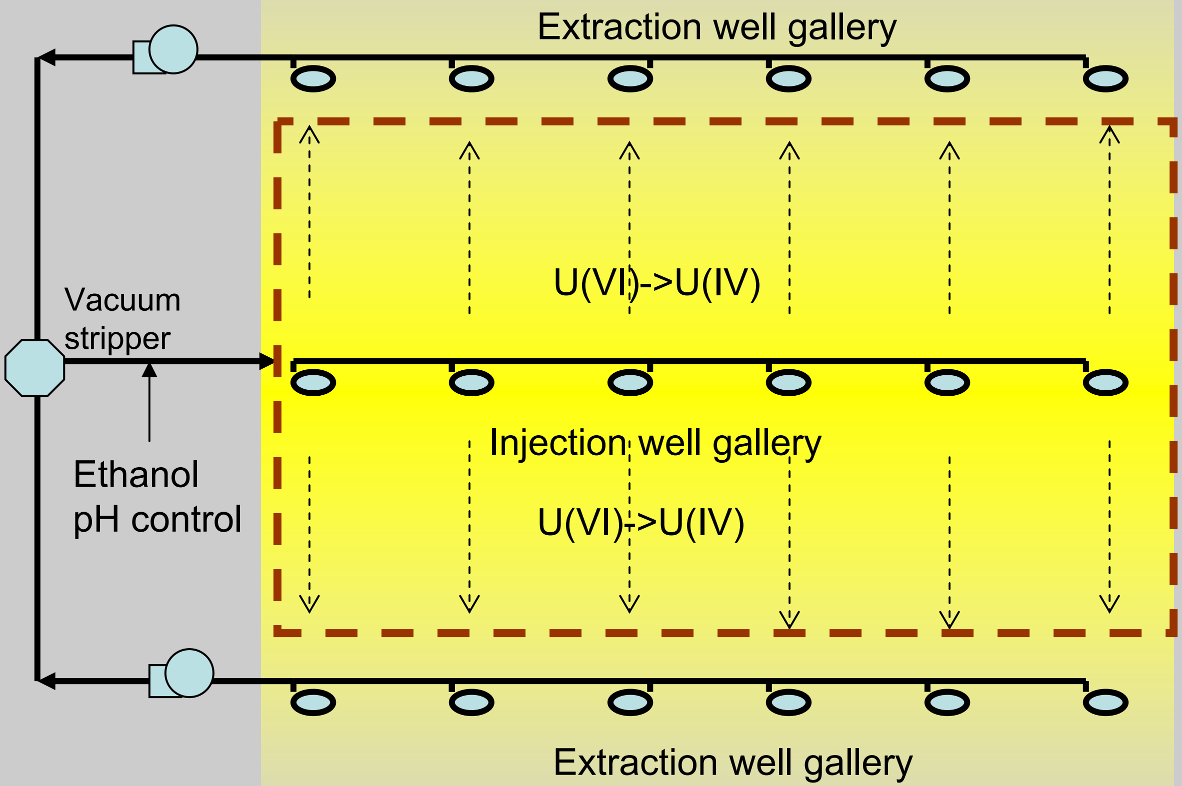
- A nested recirculation scheme appears to protect the treatment zone from aluminum, nitrate, and acidity.

- We have evidence of in-situ microbial U reduction.

Stage 1 -removal of aluminum, calcium, nitrate



Stage 2 - conversion of U(VI) to U(IV)



Next up

Single pass experiments:

- Br^-/He + ethanol
- Tracer + ethanol + U
- Tracer + ethanol + oxidants