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FIELD SCALE EVALUATION OF BIOSTIMULATION FOR REMEDIATION OF URANIUM-CONTAMINATED GROUNDWATER AT FRC AREA 3

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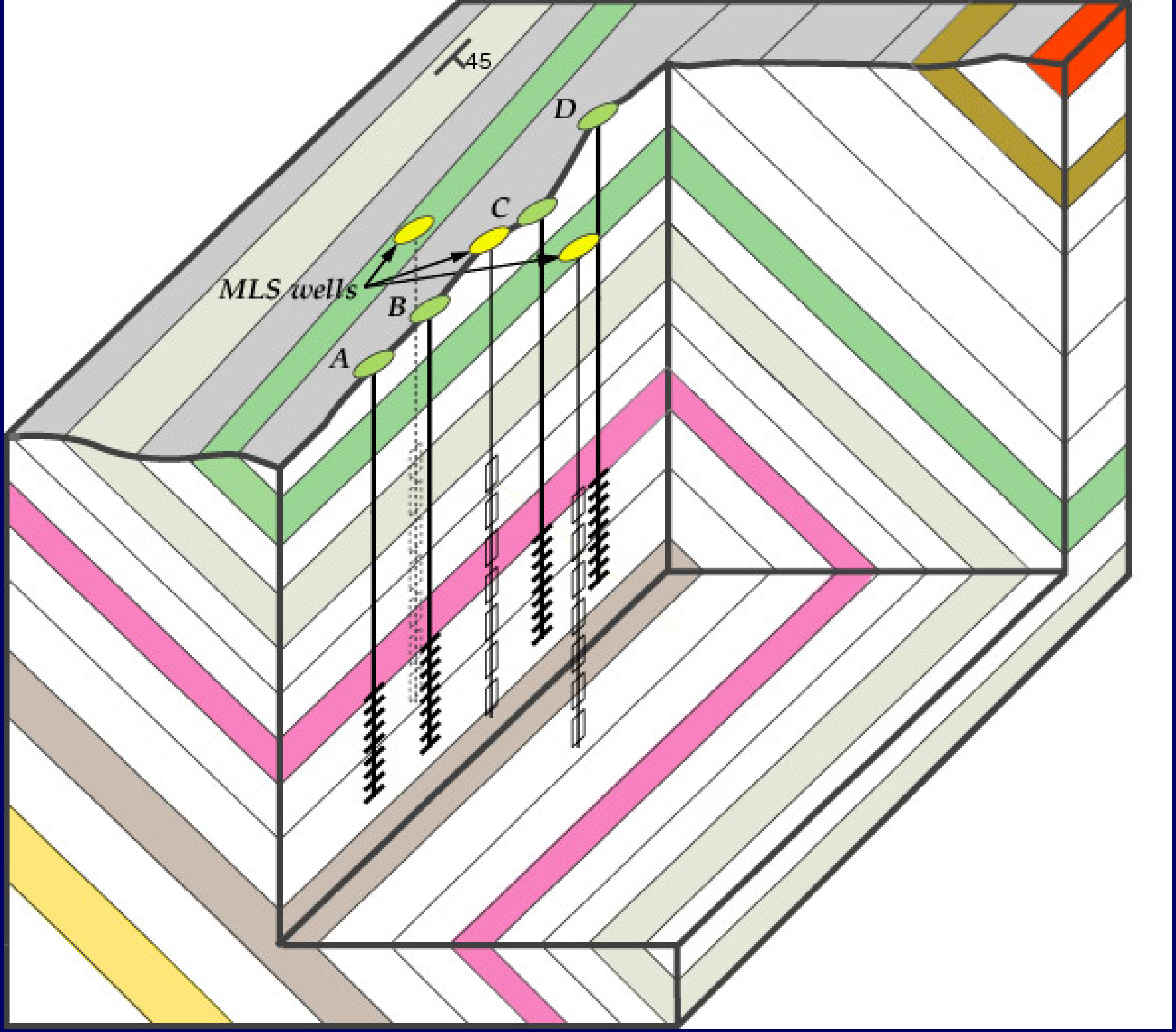
Overview

- Selection of a treatment zone
- Gaining hydraulic control
- Conditioning
- Biostimulation

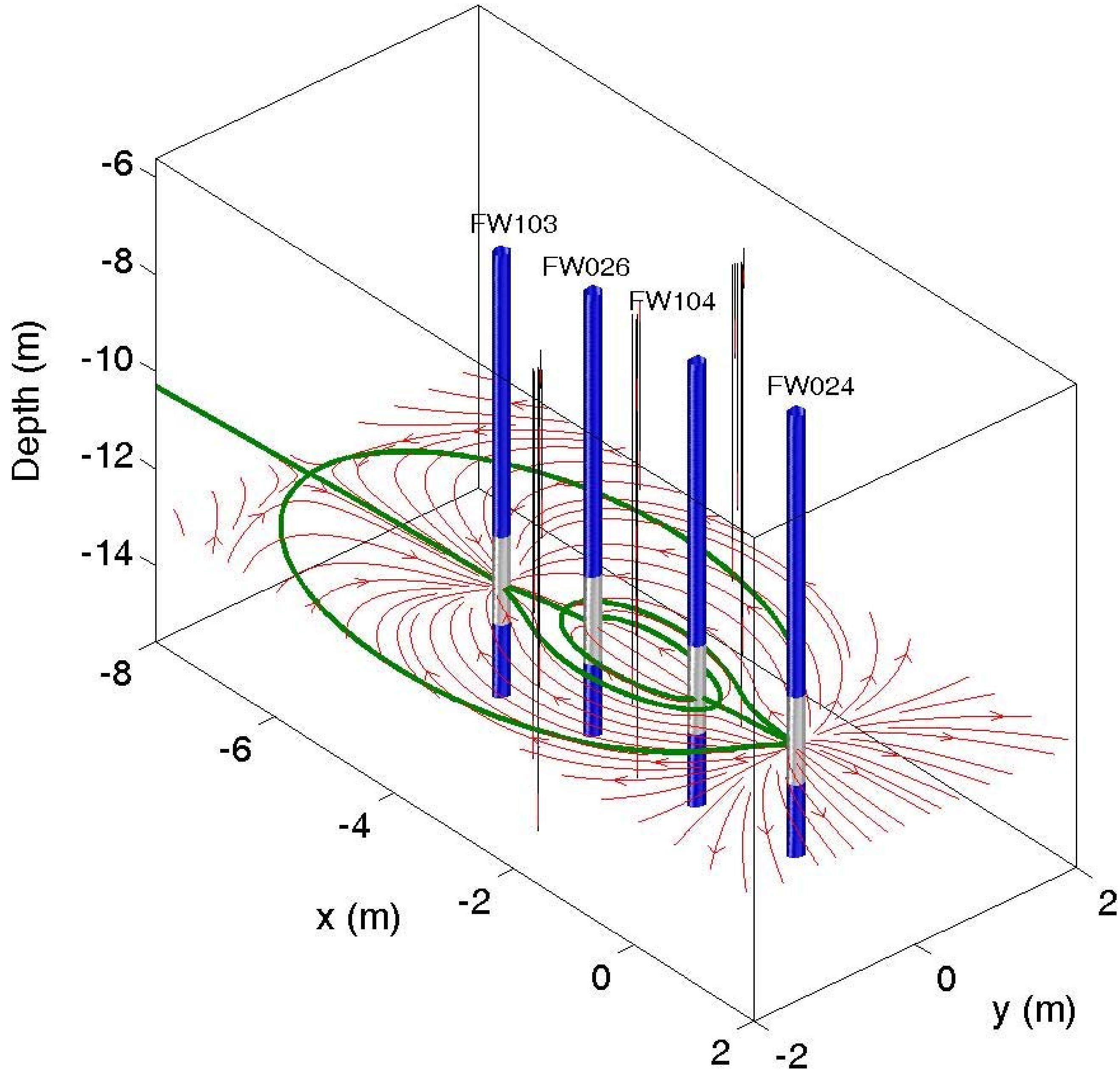
Hydraulic control in a highly contaminated aquifer:

- Nested recirculation wells
- Aboveground removal of clogging agents and inhibitors
- Clean water tracer study
- Staged remediation



Screened Interval = 38-45'

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



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

2
D

QuickTime™ and a
Cinepak decompressor
are needed to see this picture.

3D - nonuniform flow field

QuickTime™ and a
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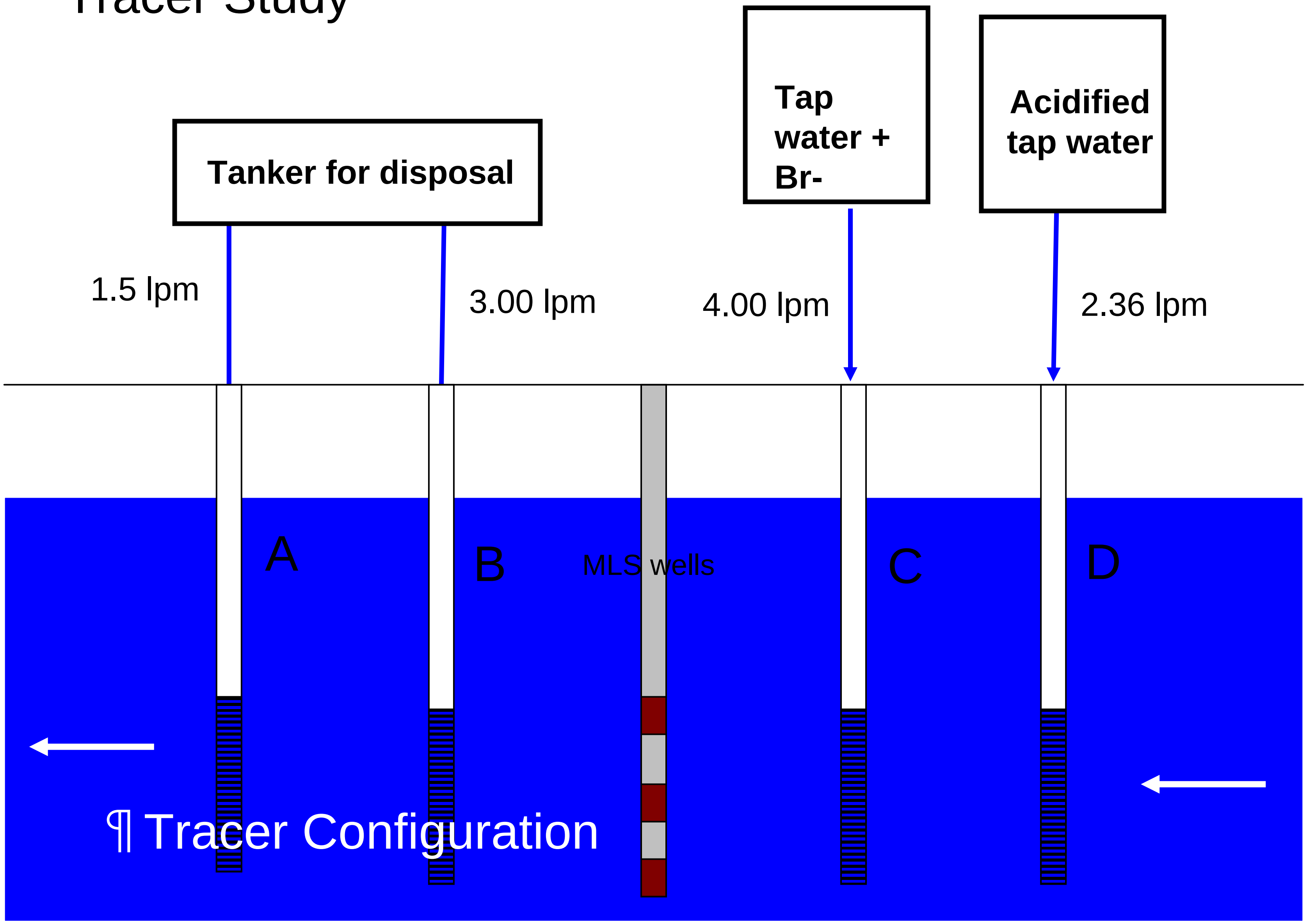
Tracer Study



MLS wells

Well B

Well C

QuickTime™ and a
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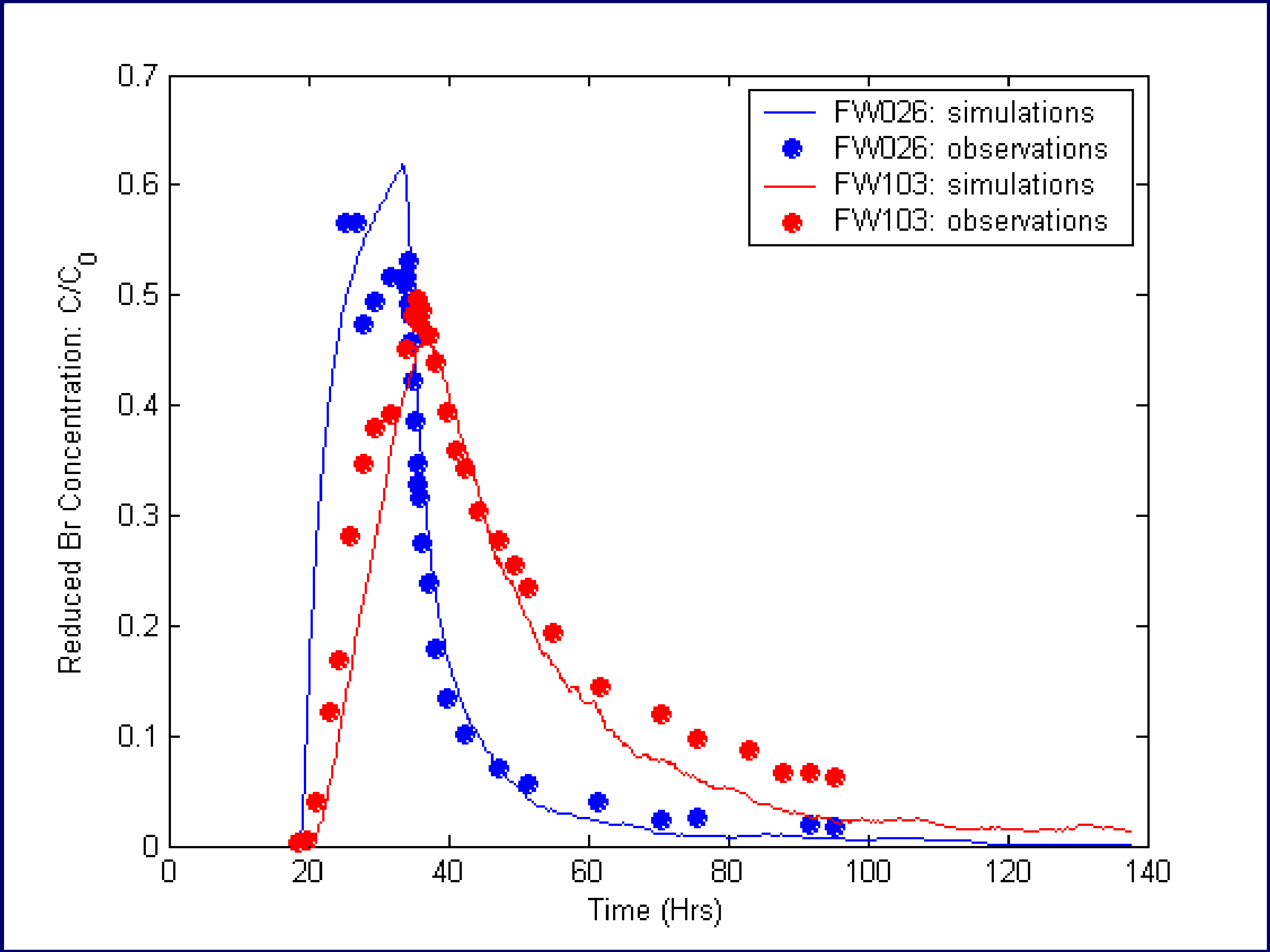
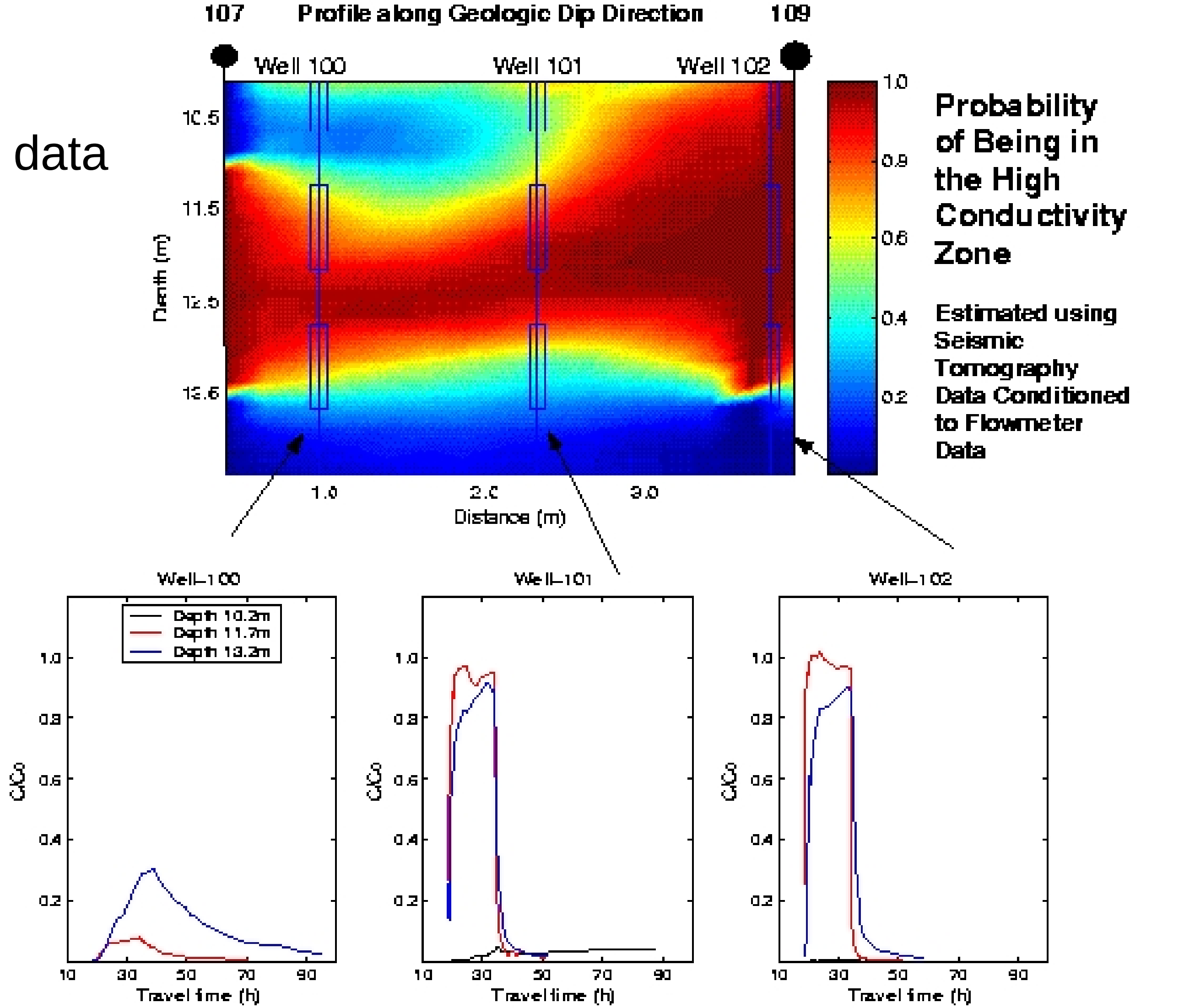
Tracer study simulations



Seismic tomography data complements tracer measurements.

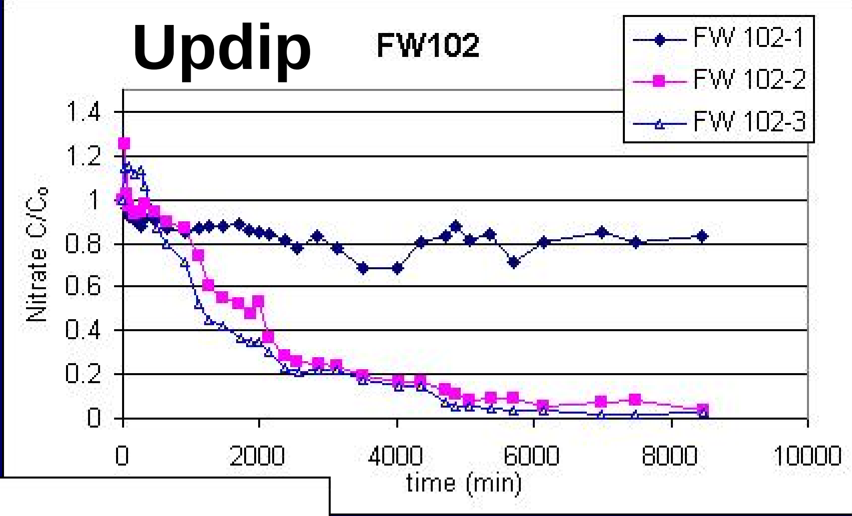


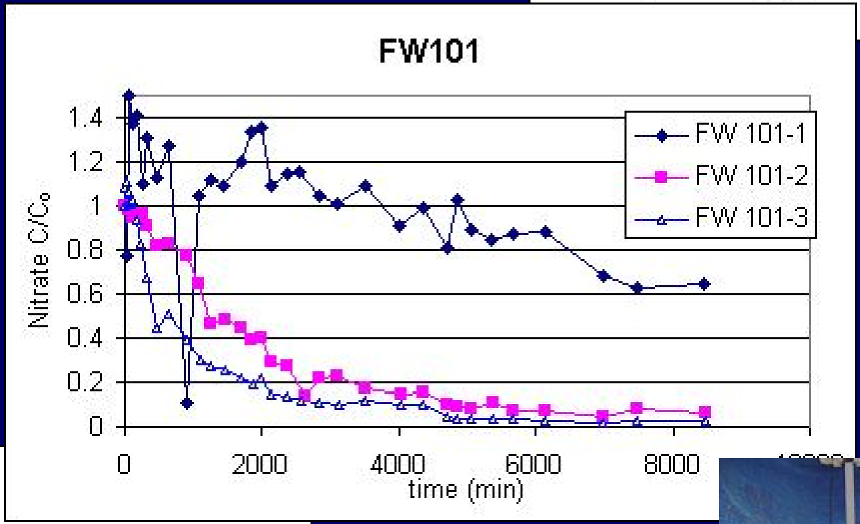
Tracer Breakthrough at 3 Multi-Level Samplers along Geologic Dip Direction

Hubbard et al., 2003

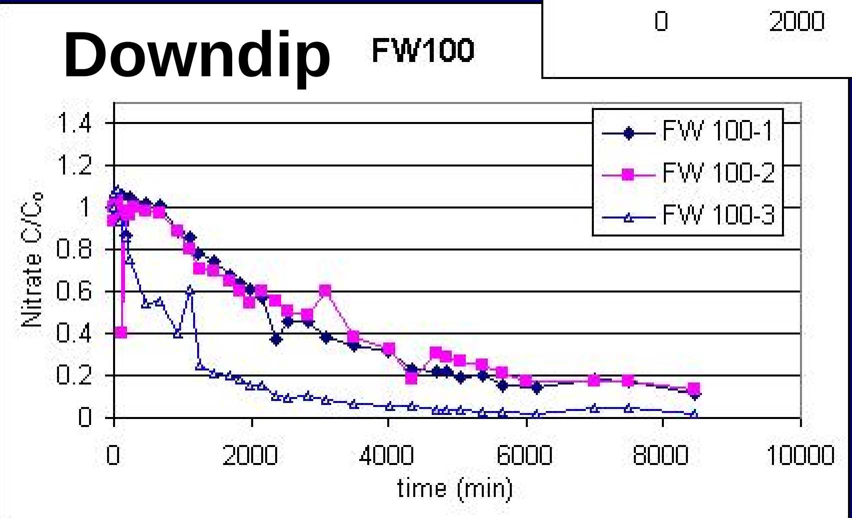
Mehlhorn et al., 2003

Effect of tracer clean water flush on nitrate in MLS wells

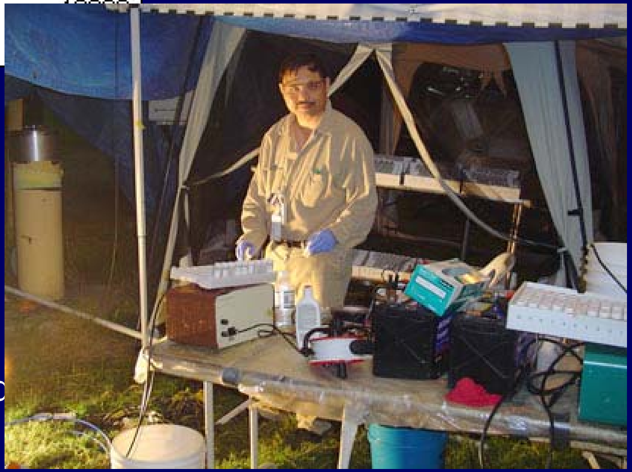




Mid-depths were flushed well
Bottom depth was poorly flushed



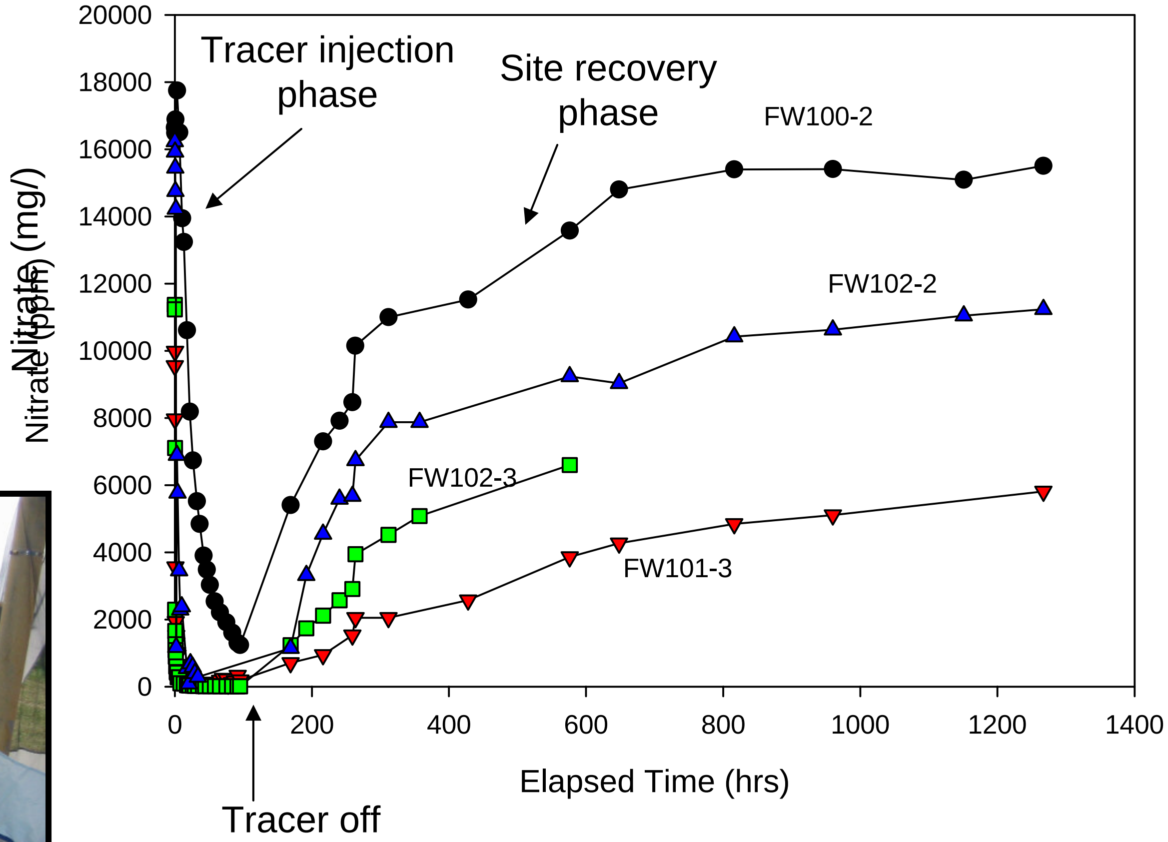
All depths were flushed

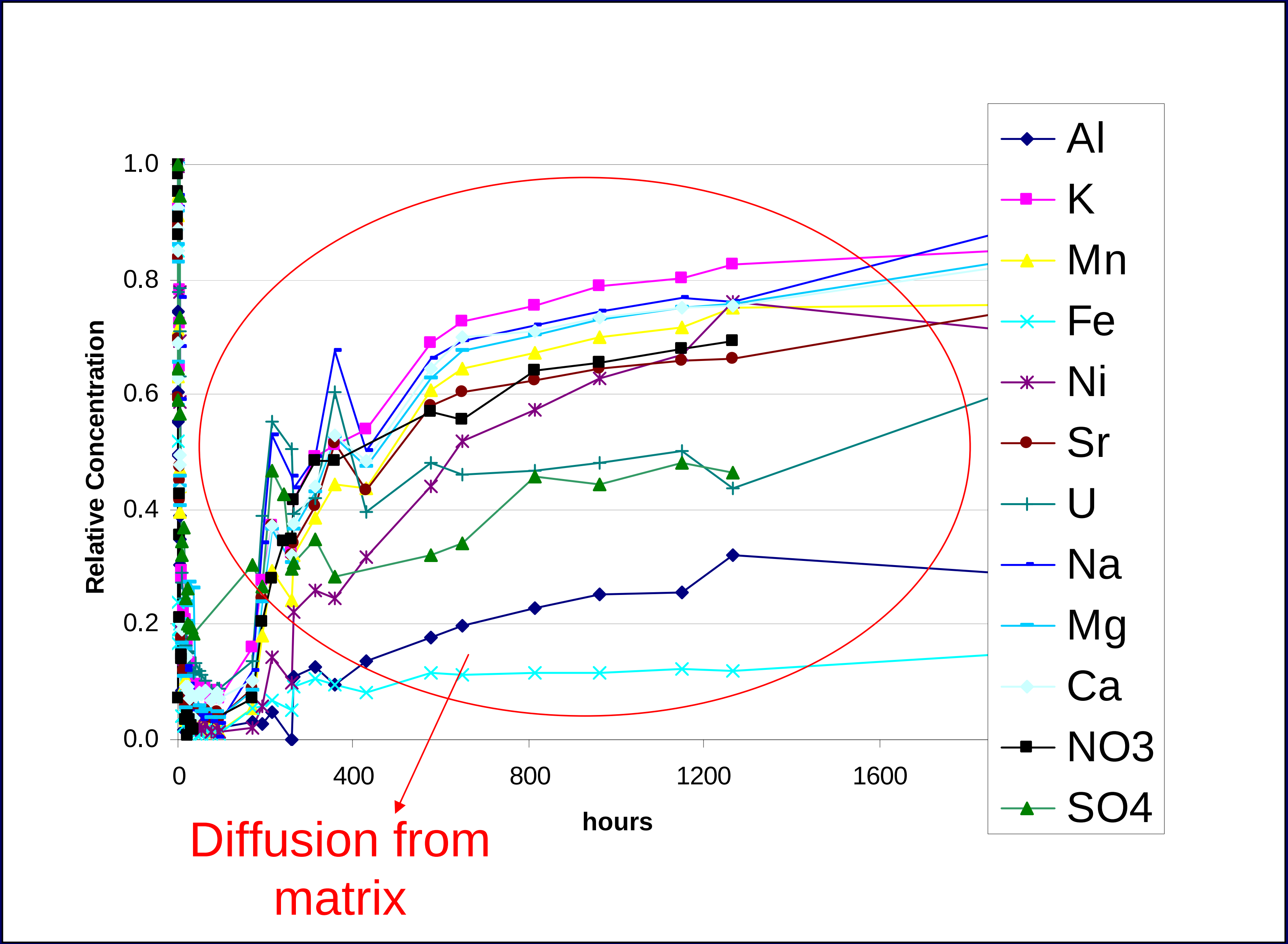


Natural gradient site recovery solute breakthrough

Natural gradient contaminant transport monitored during site recovery.

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



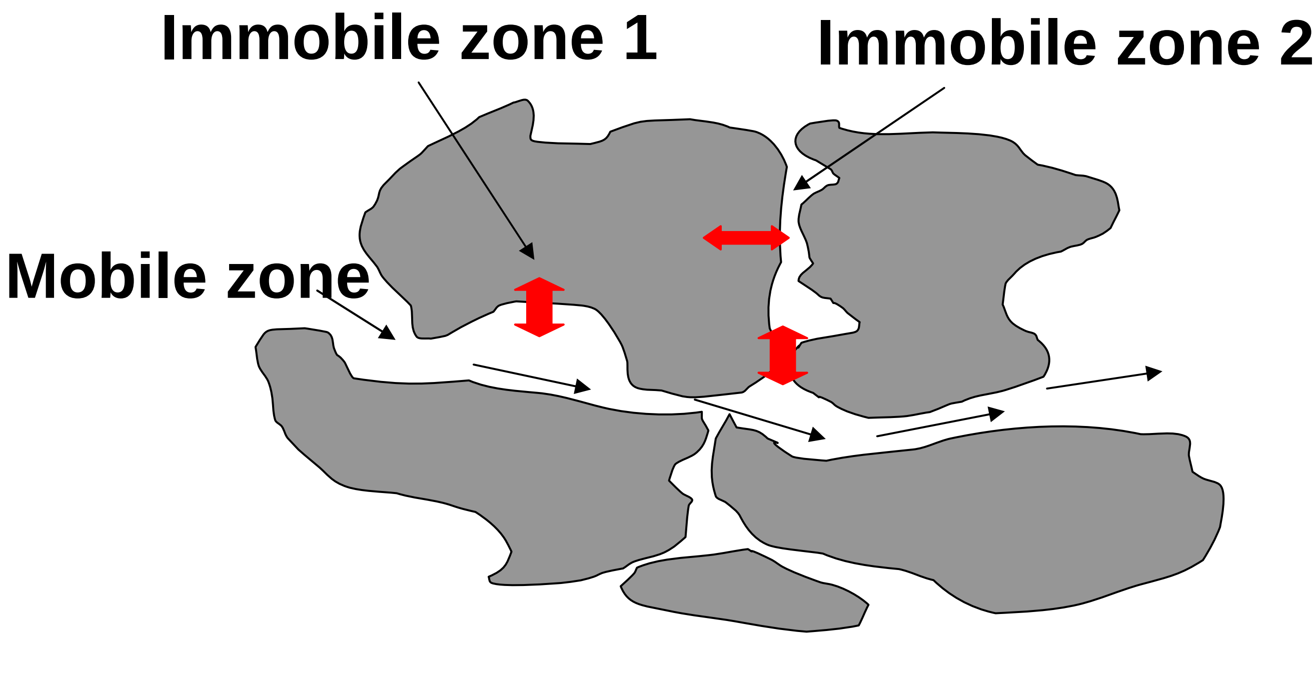


Relative Concentration
1.0
0.8
0.6
0.4
0.2
0.0
0
400
800
1200
1600
hours
Al
K
Mn
Fe
Ni
Sr
U
Na
Mg
Ca
NO3
SO4
Diffusion from matrix

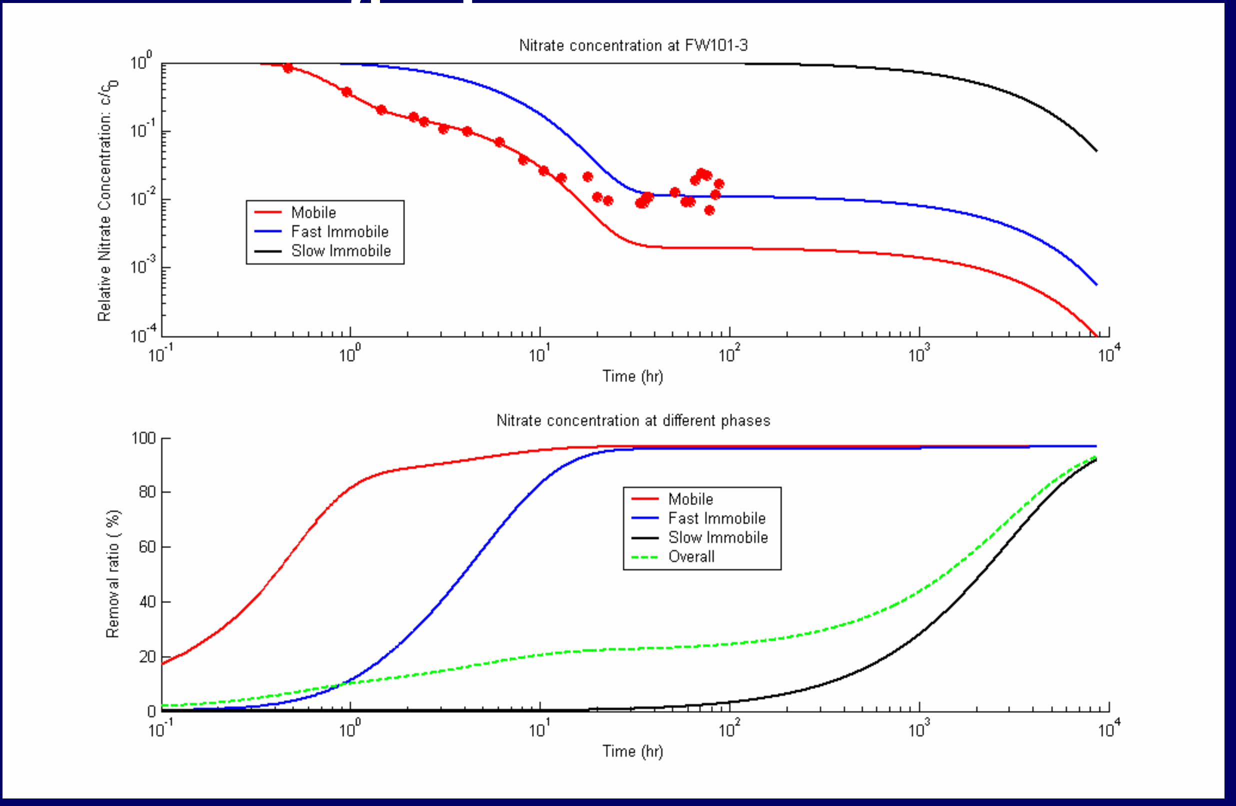
Mass transfer during the flush

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.

Overview

- Selection of the treatment zone
- Gaining hydraulic control
- Conditioning
- Biostimulation

Conditioning - removal of clogging agents, inhibitors, adjustment of pH

1. Recirculate and flush at pH 4-4.5

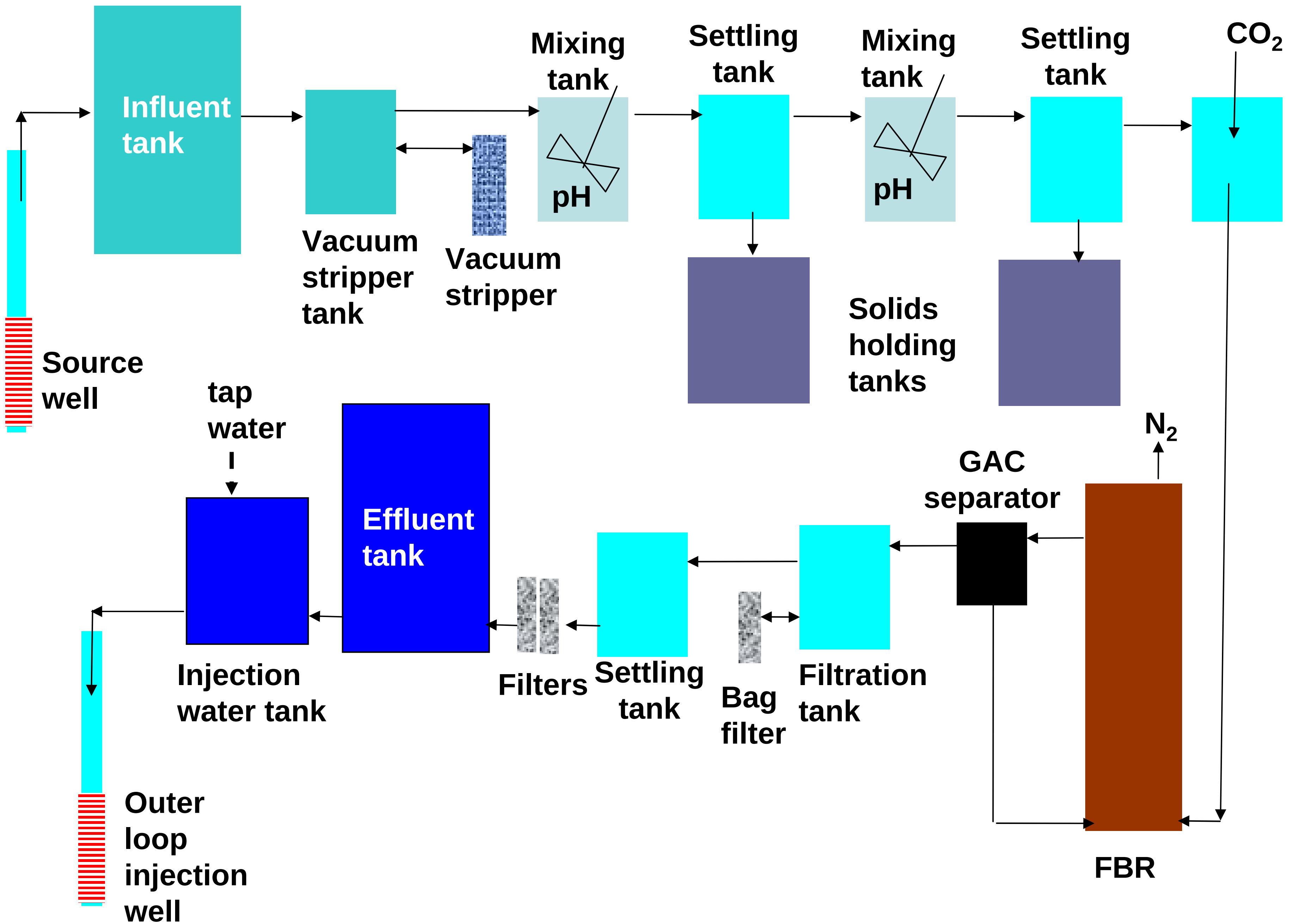
   Precipitate Al and Ca *ex-situ*

   Remove NO_3^- by denitrification in FBR

   Vacuum strip to remove VOCs and N_2

2. Recirculate and flush at pH 6-6.3

ABOVEGROUND PROCRESS TRAIN



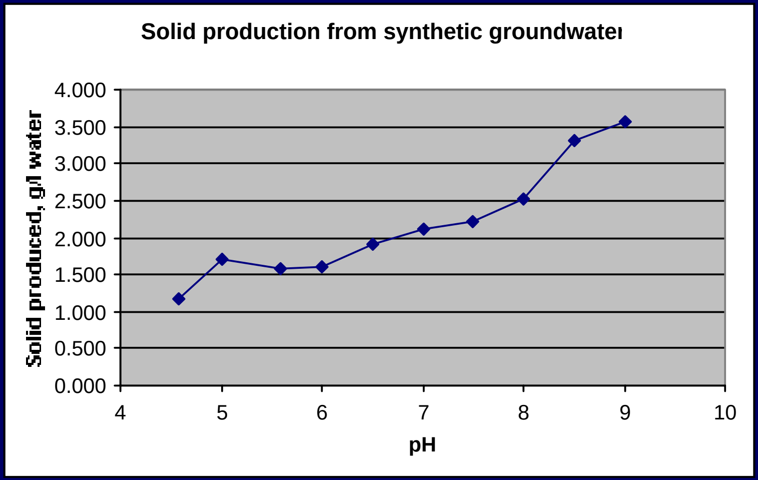
Clogging agents

- 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

Tanker for chemical sludge disposal

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

Bag filters for disposal of biomass

Inside the Big Top

The aboveground treatment train

Vacuum stripper

Two-step
chemical precipitation

Fluidized bed reactor
(FBR)

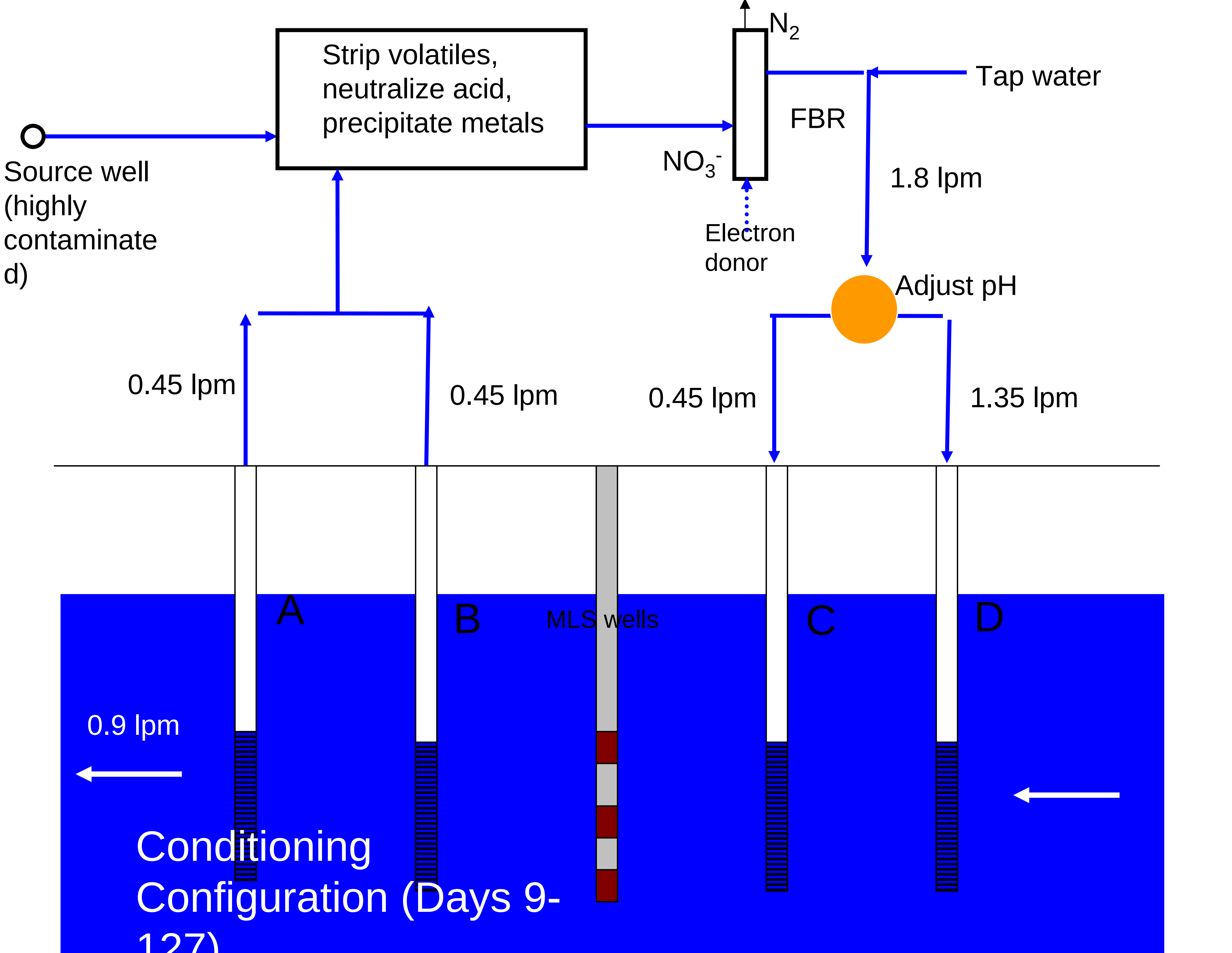
Well TPB16 enrichment

innoculum

innoculum

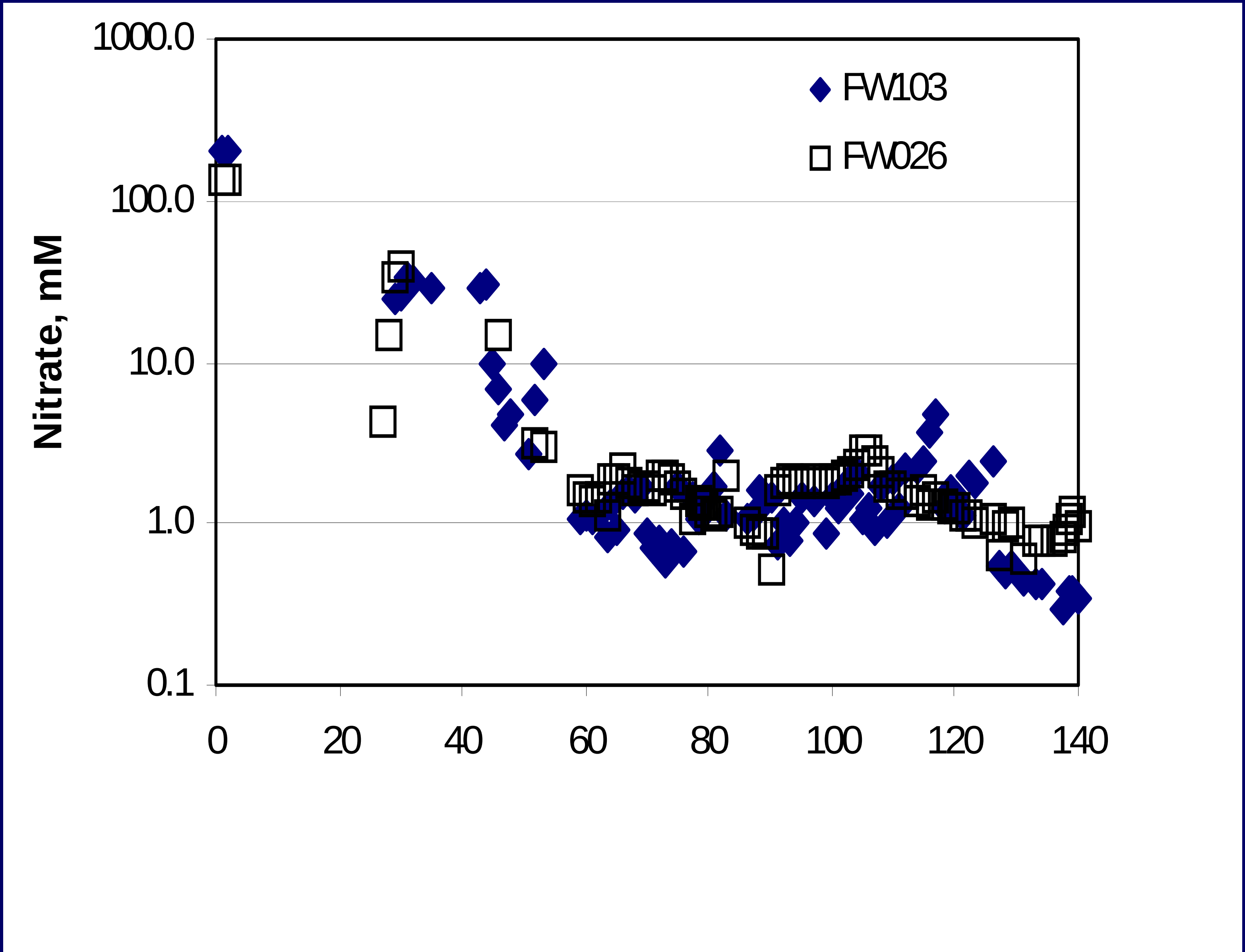
Two pilot scale FBRs

Full scale FBR

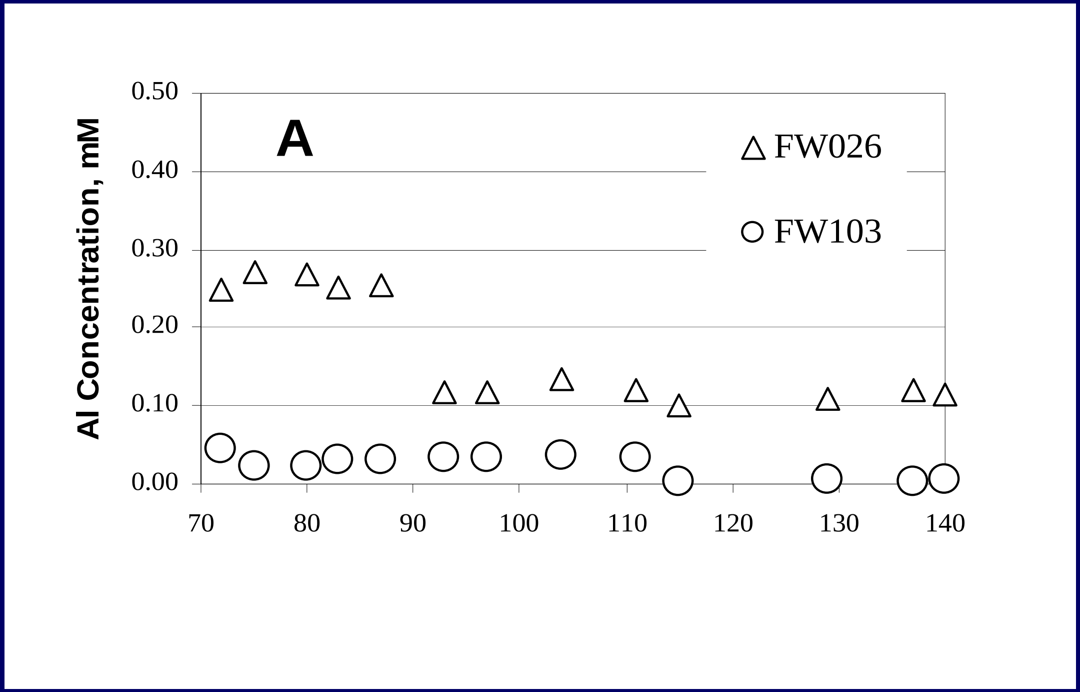


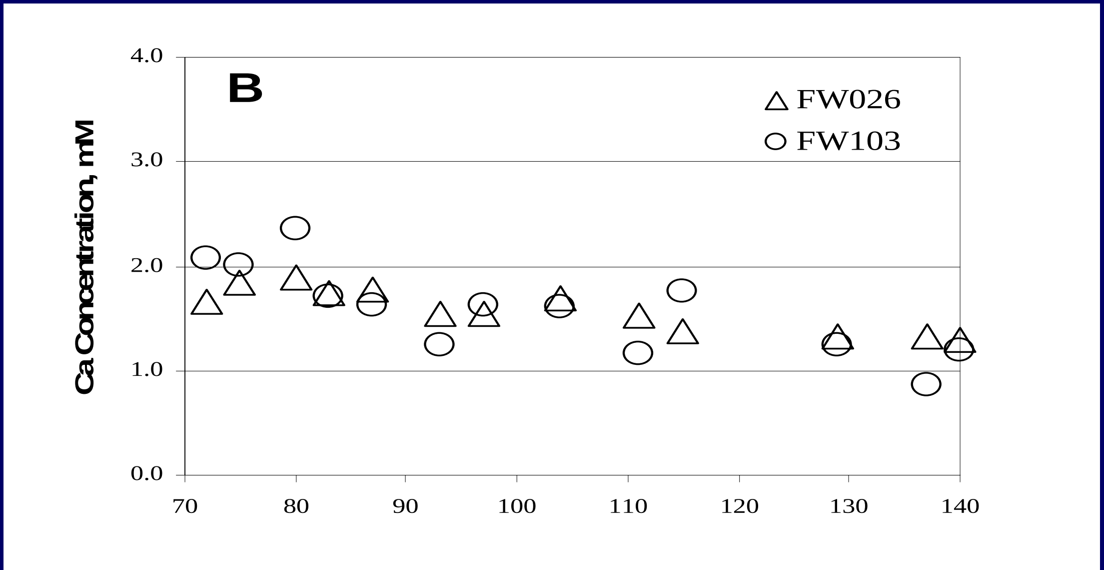
Strip volatiles, neutralize acid, precipitate metals
N_2
Tap water
FBR
NO_3^-
Source well (highly contaminated)
1.8 lpm
Electron donor
Adjust pH
0.45 lpm
0.45 lpm
0.45 lpm
1.35 lpm
A
B
MLS wells
C
D
0.9 lpm
Conditioning Configuration (Days 9-127)

Nitrate removal at injection extraction wells during condit



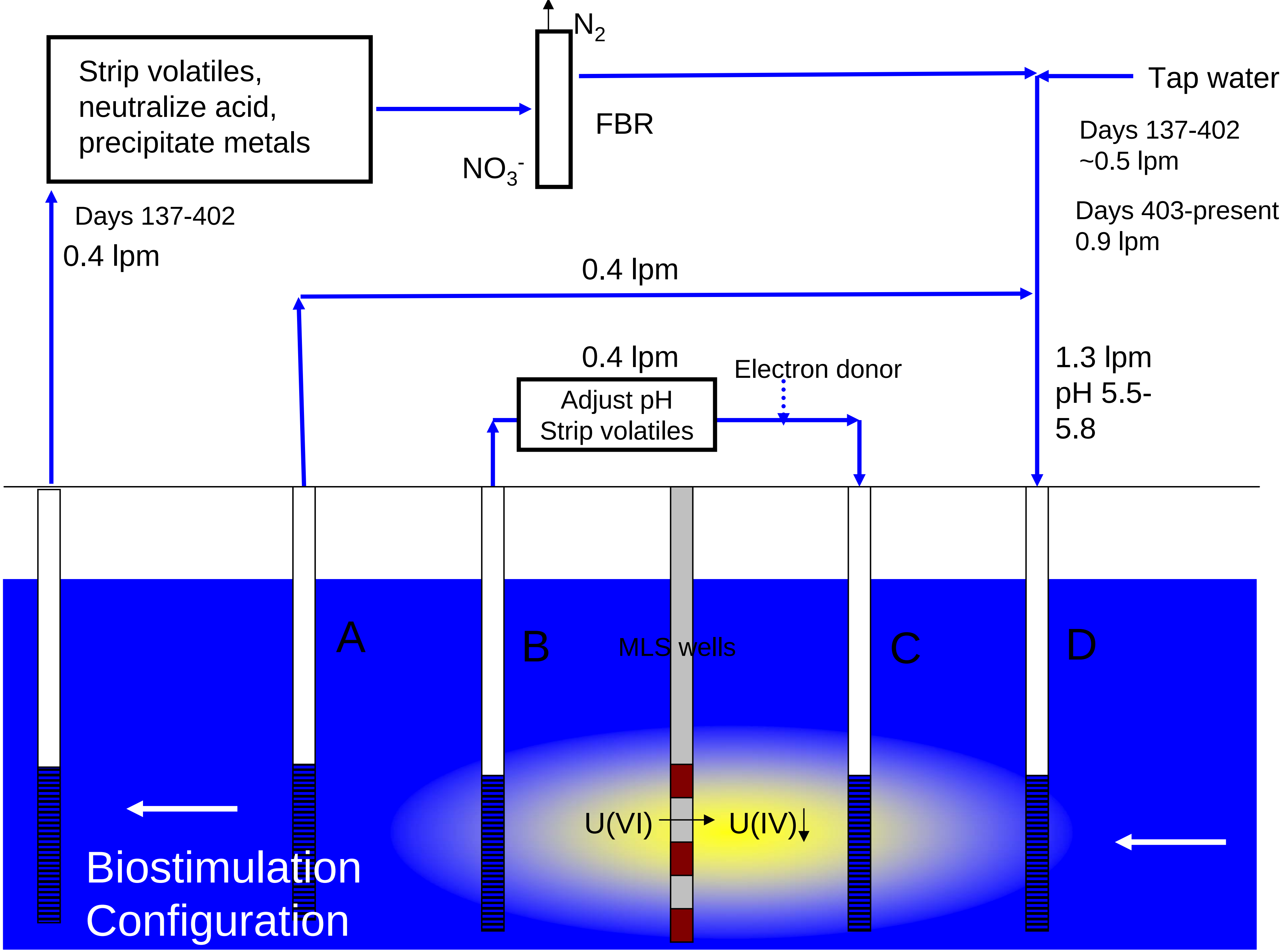
Al and Ca removal at injection extraction wells during cond





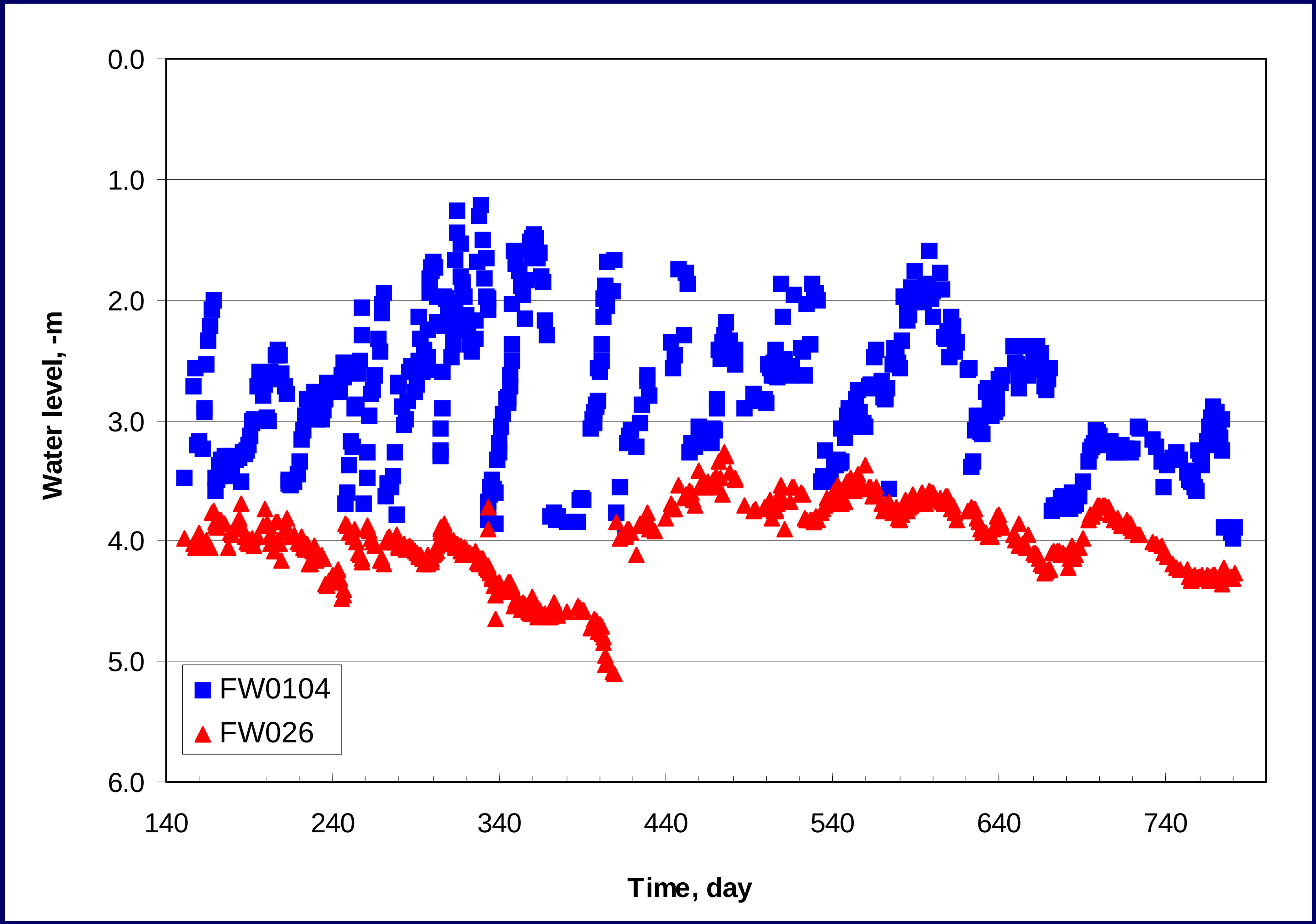
Overview

- Selection of the treatment zone
- Gaining hydraulic control
- Conditioning
- Biostimulation



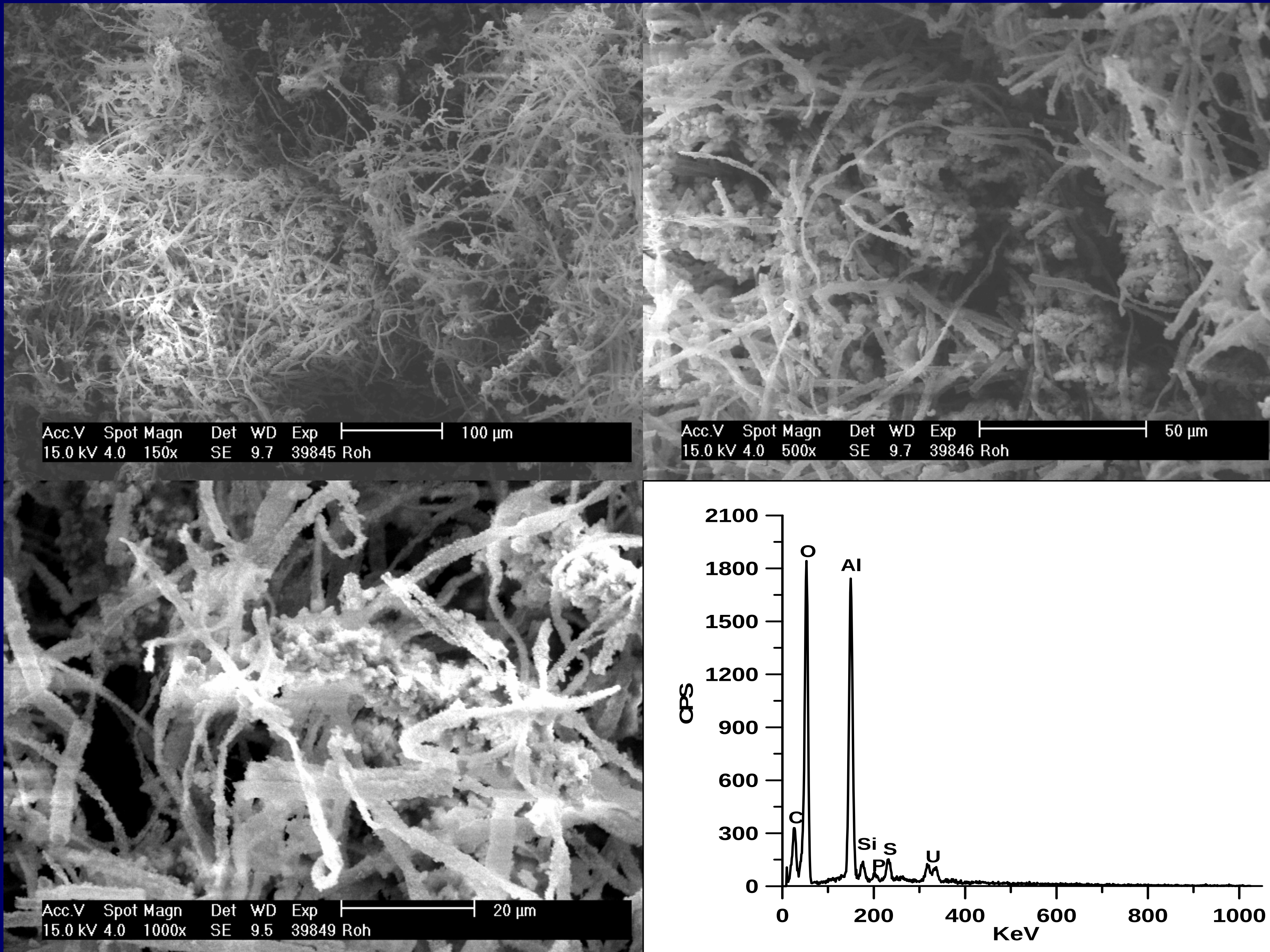
Strip volatiles, neutralize acid, precipitate metals
N2
FBR
NO3-
Tap water
Days 137-402
~0.5 lpm
Days 403-present
0.9 lpm
Days 137-402
0.4 lpm
0.4 lpm
0.4 lpm
Adjust pH
Strip volatiles
Electron donor
1.3 lpm
pH 5.5-5.8
A
B
MLS wells
C
D
U(VI)
U(IV)
Biostimulation Configuration

Water level in inner loop injection and extraction wells during biostimulation

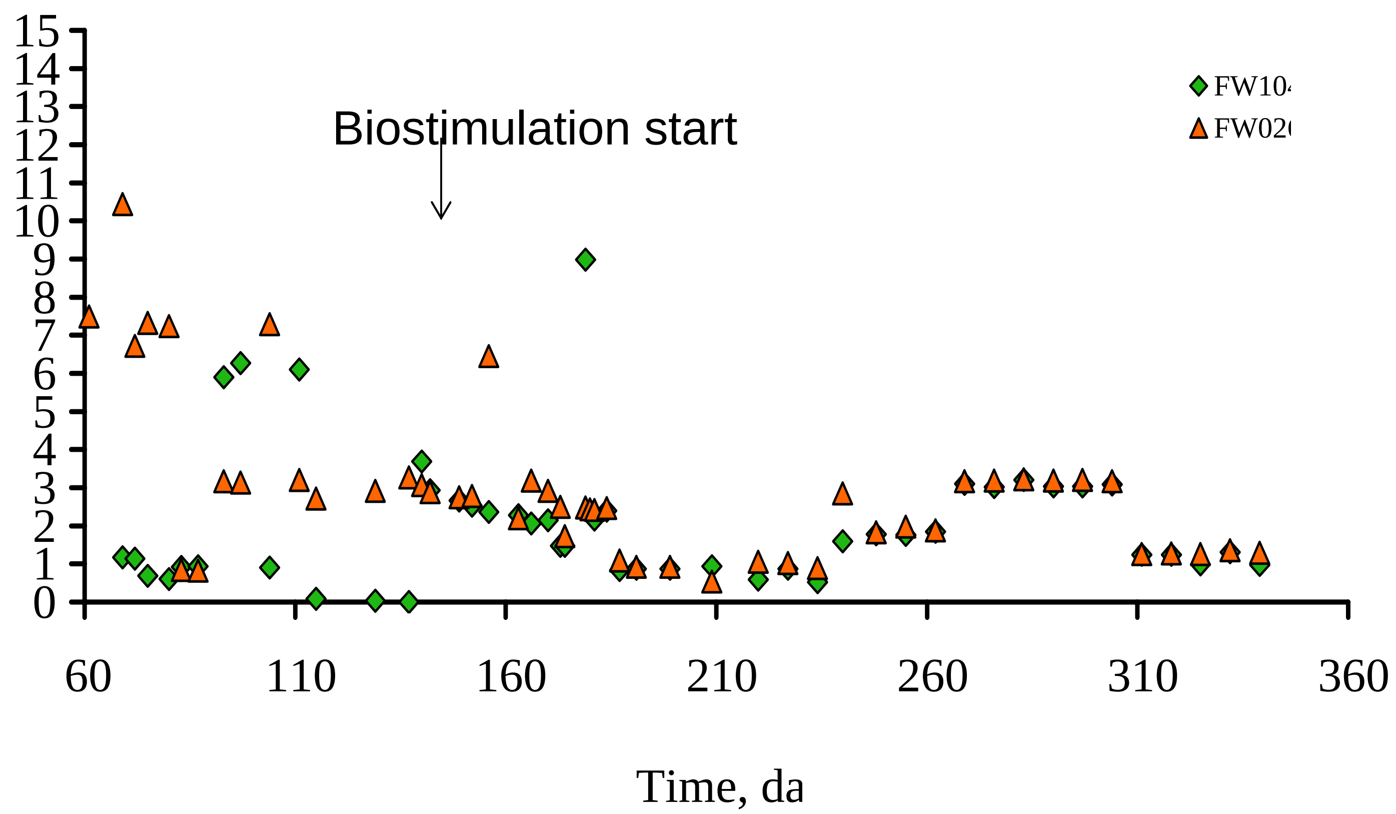


Surge block for cleaning

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
KeV
O
Al
C
Si
P
S
U
0
300
600
900
1200
1500
1800
2100
200
400
600
800
1000

Aluminum in inner loop injection and extraction wells



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

Surge block allowed for sampling of sediment/biomass in wells

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

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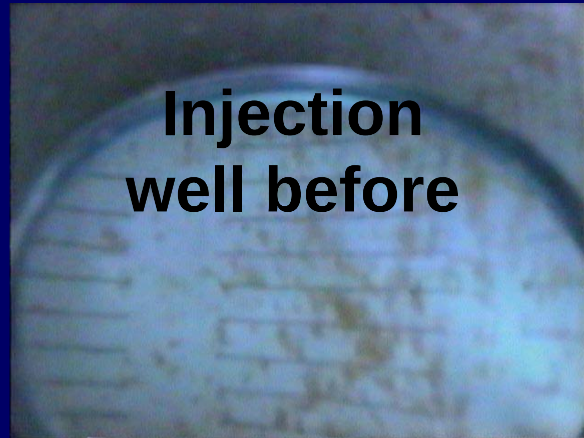
Effects of surging: what a borehole camera shows

reference well

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



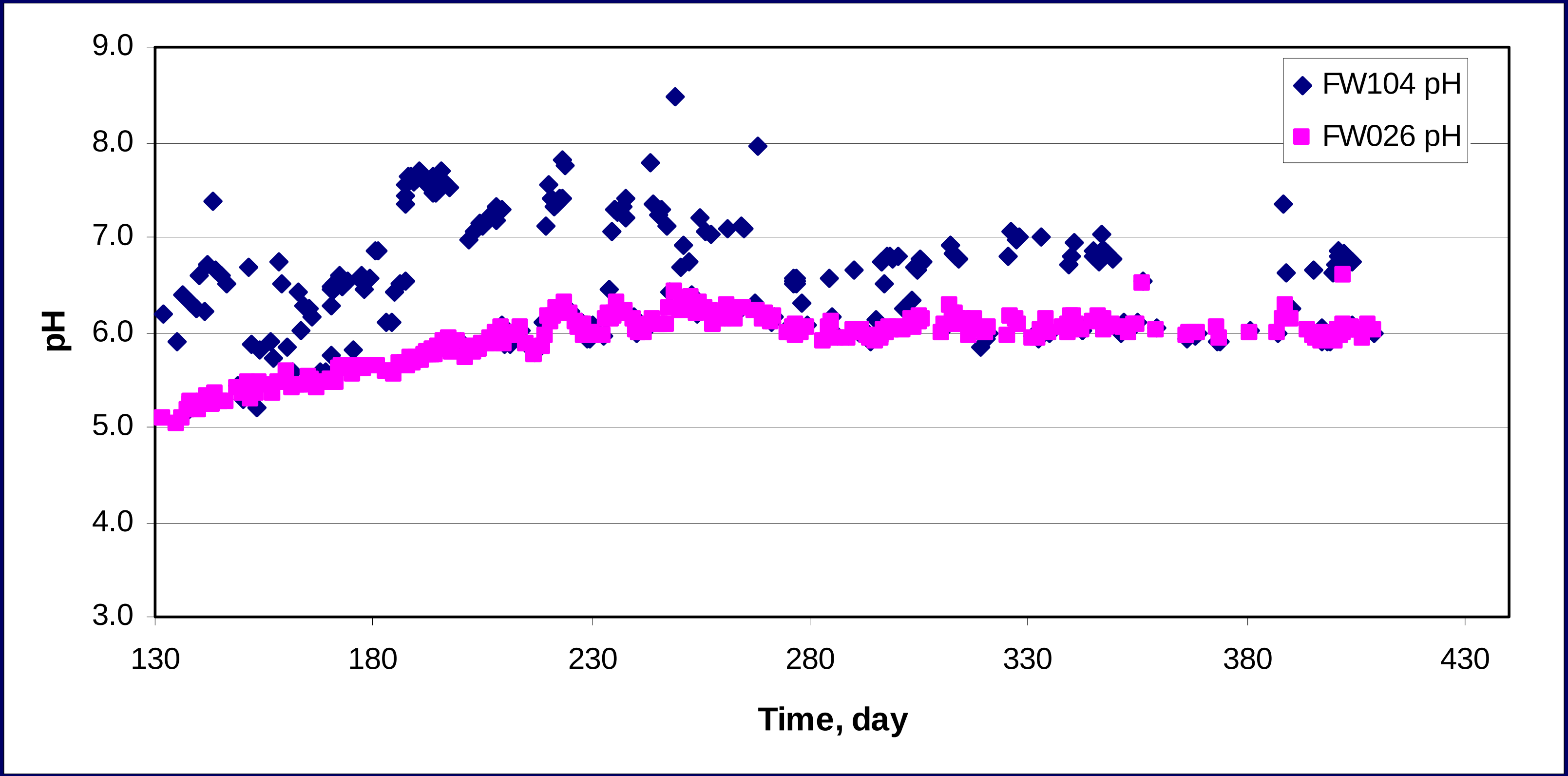
after

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

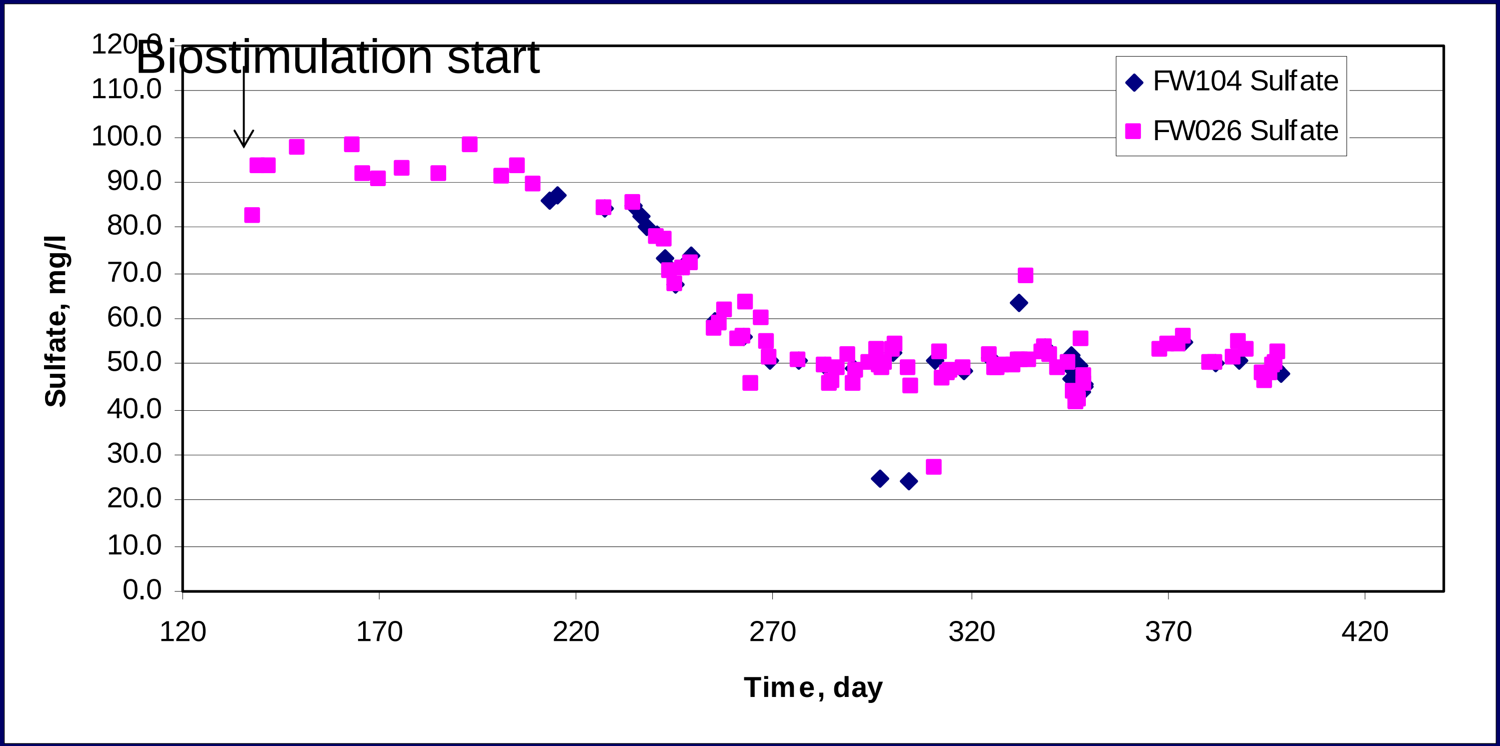
after

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

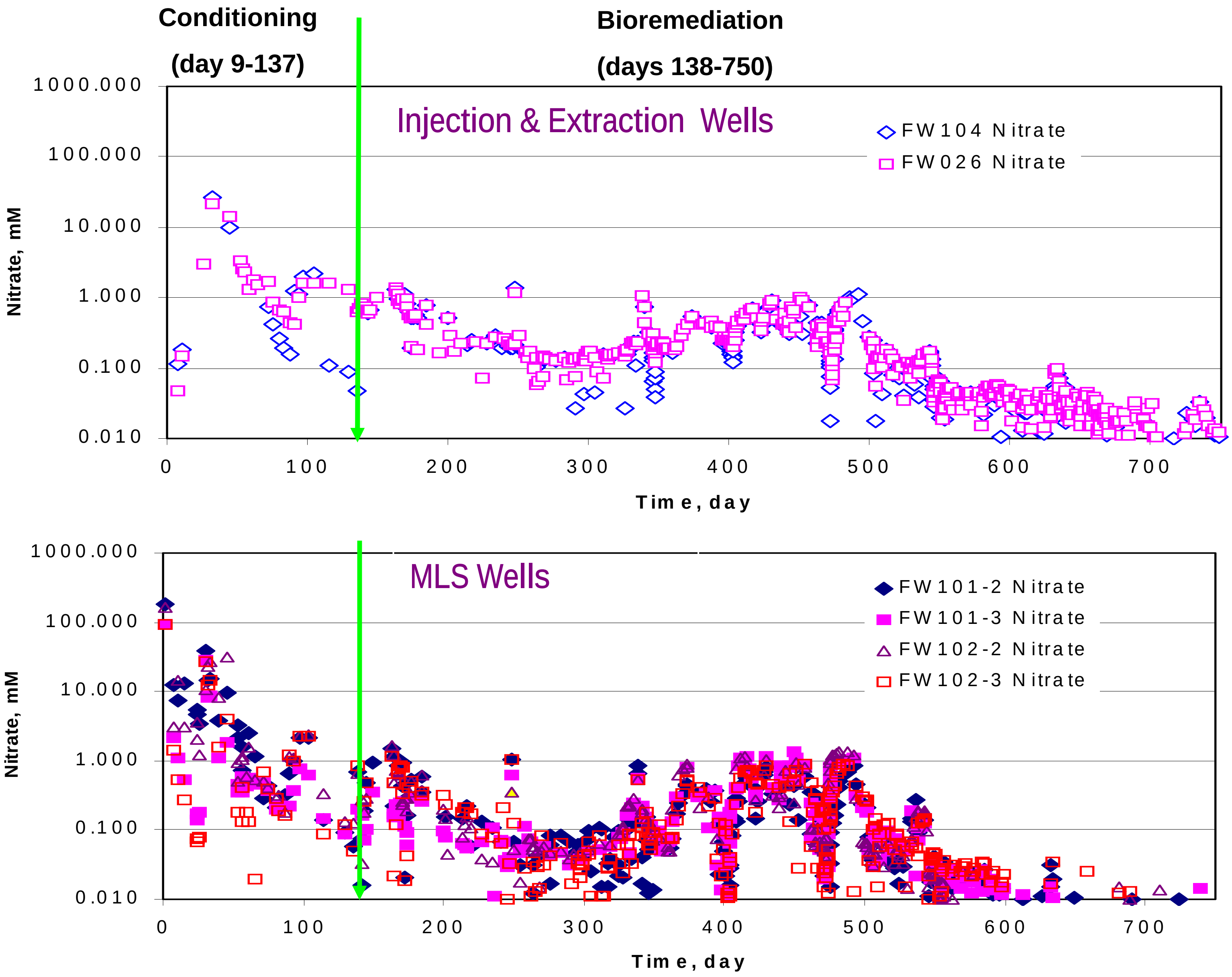
pH in inner loop injection and extraction wells during biostimulation



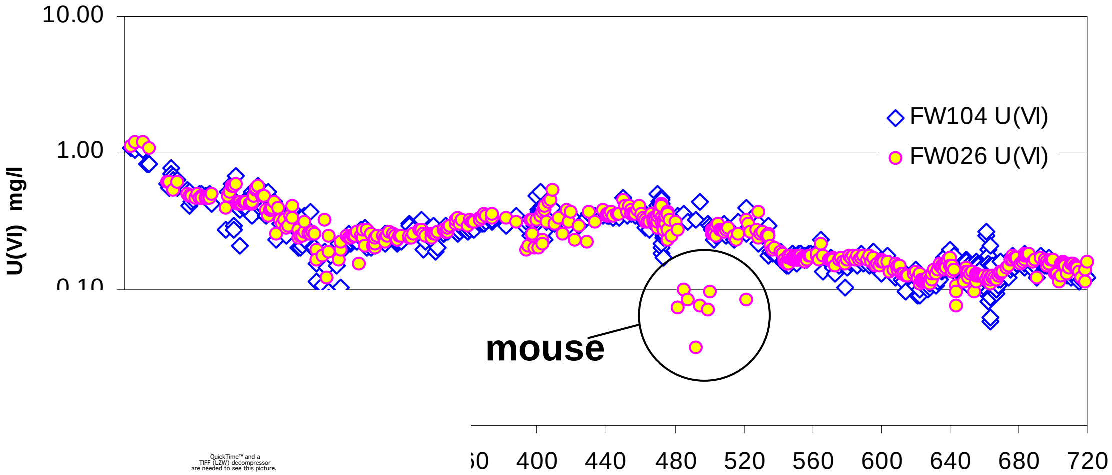
Sulfate in inner loop injection and extraction wells

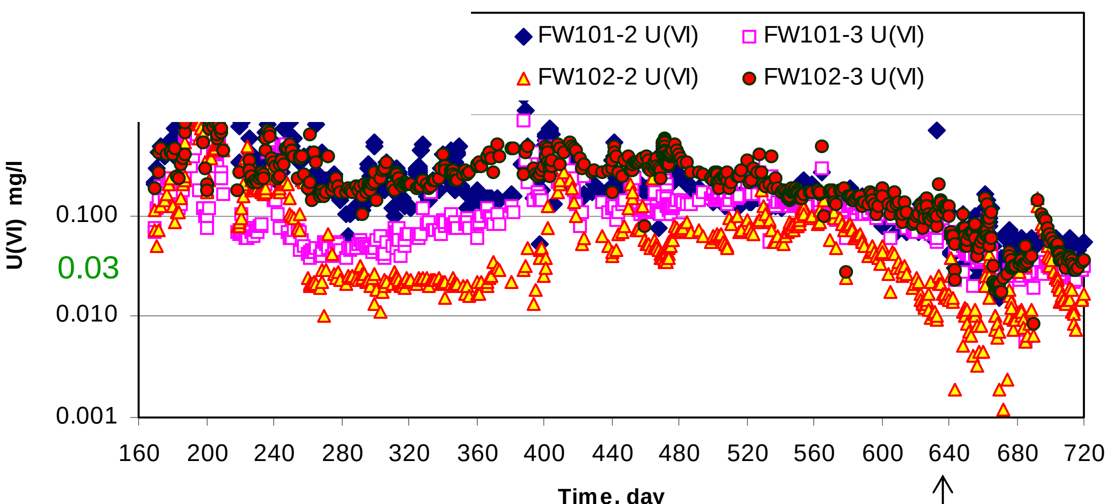


Nitrate removal during biostimulation



Dissolved U(VI) concentrations during biostimulation (Day 160-preset)





O_2 removed from outer loop

Key Findings

1. Ethanol adddition stimulated In *situ* bioreduction of U(VI).

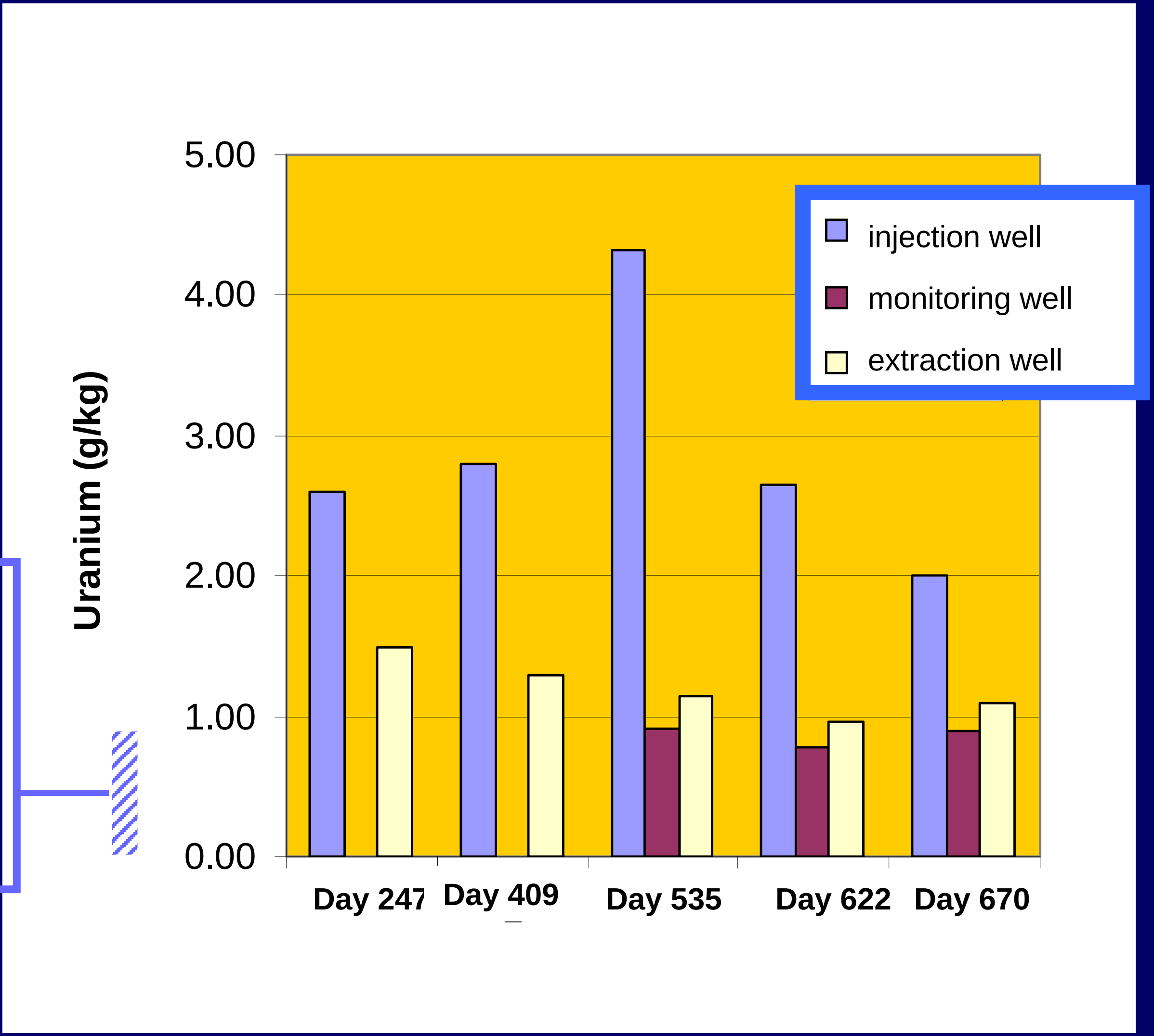
2. U(VI) concentration dropped below EPA MCL.

3. Sulfate reduction and Fe(III) Reduction were concomitant with U(VI) reduction.

4. U(IV) was stable under controlled anaerobic conditions

Maximum concentration of uranium in drinking water of 0.03 mg/l (US EPA) is achievable.

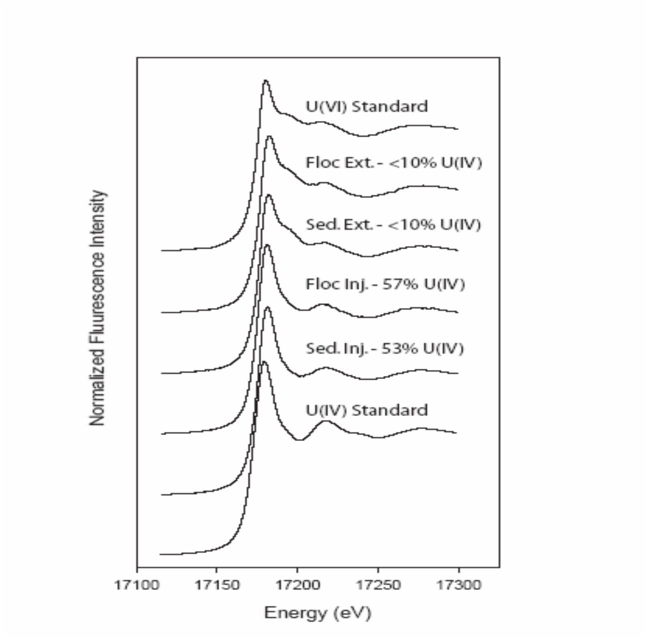
Uranium Content in Sediments from Injection, Monitoring and Extraction Wells during Bioremediation



Uranium content in core samples from FW104 was in the range of 0.03-0.8 g/kg **before bioremediation**

Variability in the content of U in the injection well sediment is likely due to variability in the removal of U during the surging operation.

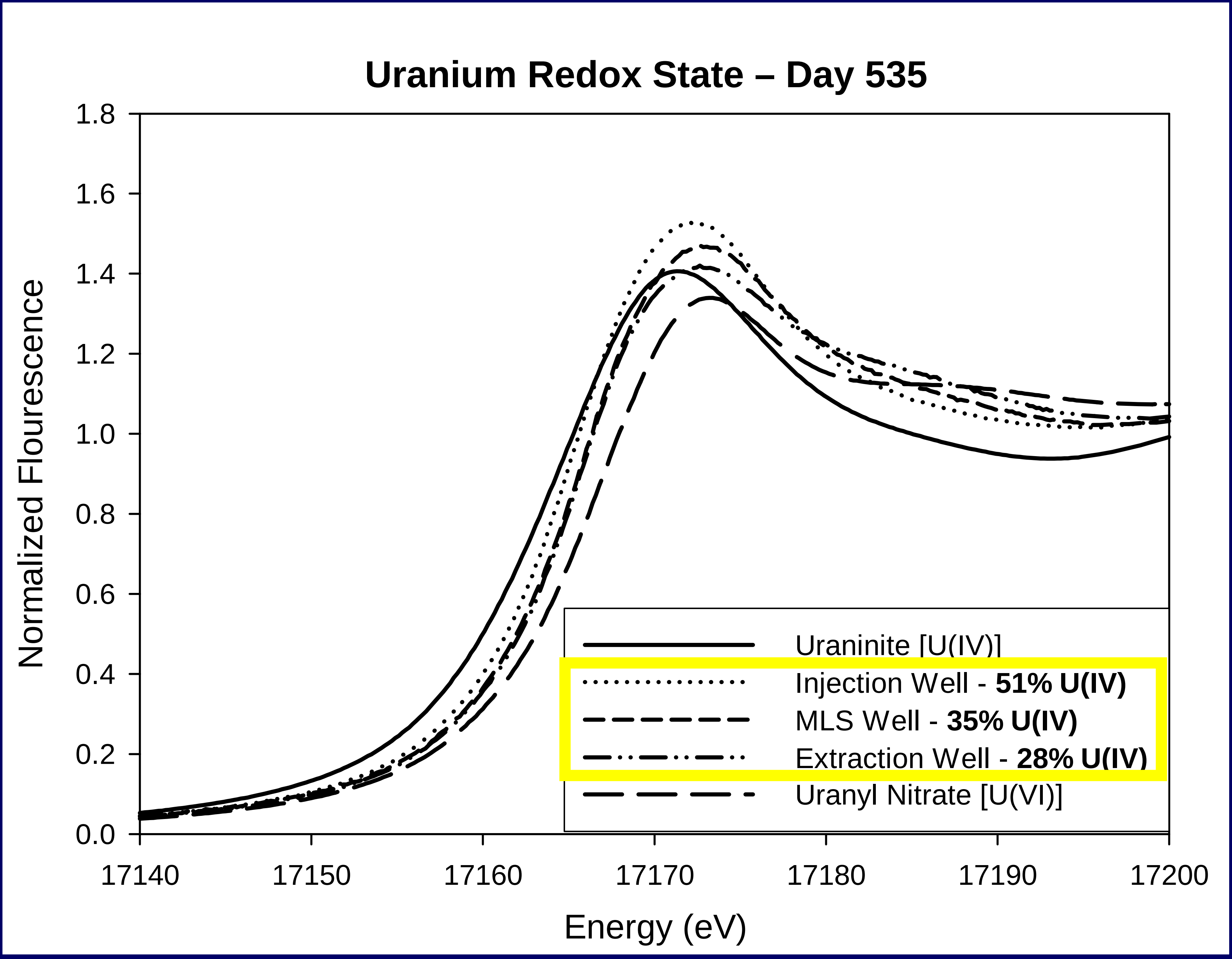
XANES analysis of sediment samples taken from inner loop injection well confirms U(VI) reduction to U(IVI)



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

Samples for day 409.

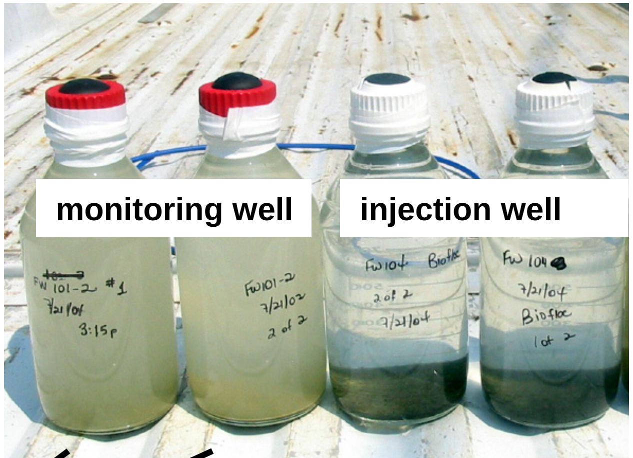
U(IV) at the injection well was more than 50% of the total U.   At the extraction well, it was less than 10%.



Uranium Redox State – Day 535
Normalized Flourescence
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
17140
17150
17160
17170
17180
17190
17200
Energy (eV)
Uraninite [U(IV)]
Injection Well - 51% U(IV)
MLS Well - 35% U(IV)
Extraction Well - 28% U(IV)
Uranyl Nitrate [U(VI)]

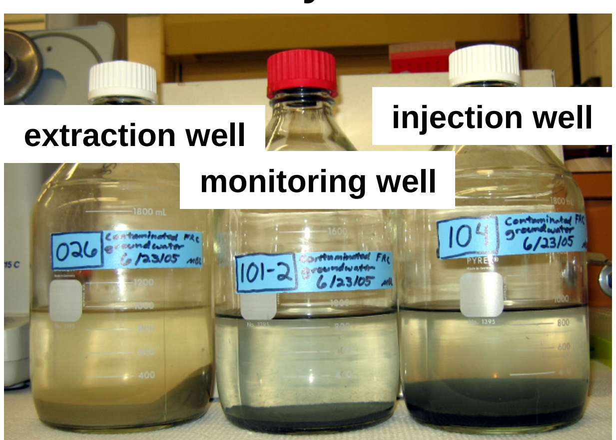
The sediment changes color as microbial reduction progresses

Day 333



brown

Day 670



Now black

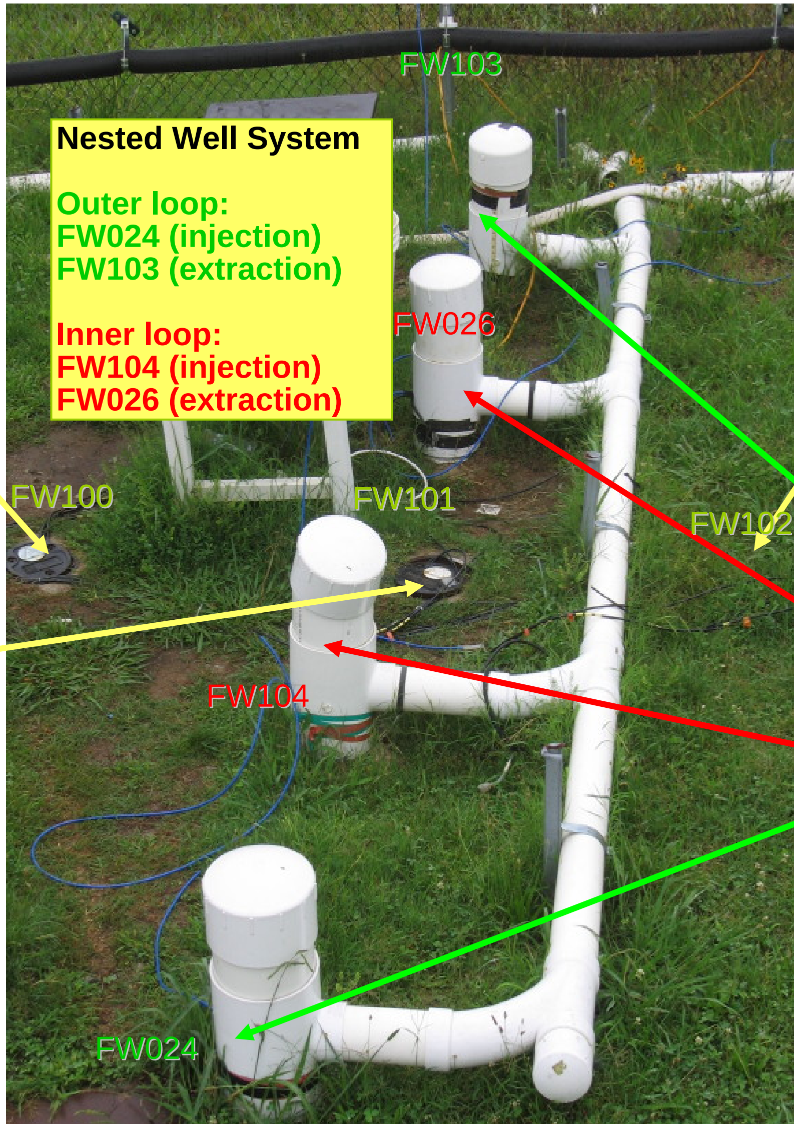
extraction well sample from day 670 incubated 3 days with no added ethanol

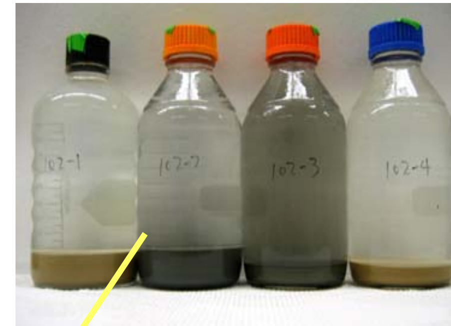
extraction well sample from day 670 incubated 3 days after adding 100 mg/L ethanol

Sediment from the treatment zone give visual evidence of reduction and expansion of the zone of reduction

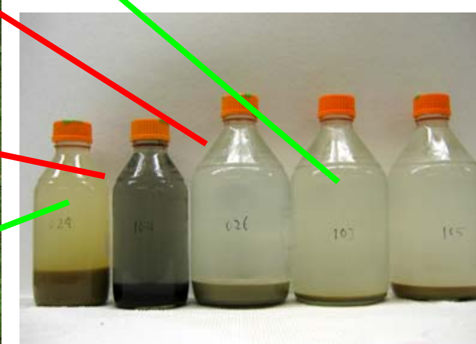
Samples from FW100 at 45ft, 40 ft, 35ft and 30ft.

Samples from FW101 at 45ft, 40 ft, 35ft and 30ft.





Samples from FW102 at 45ft, 40 ft, 35ft and 30ft.



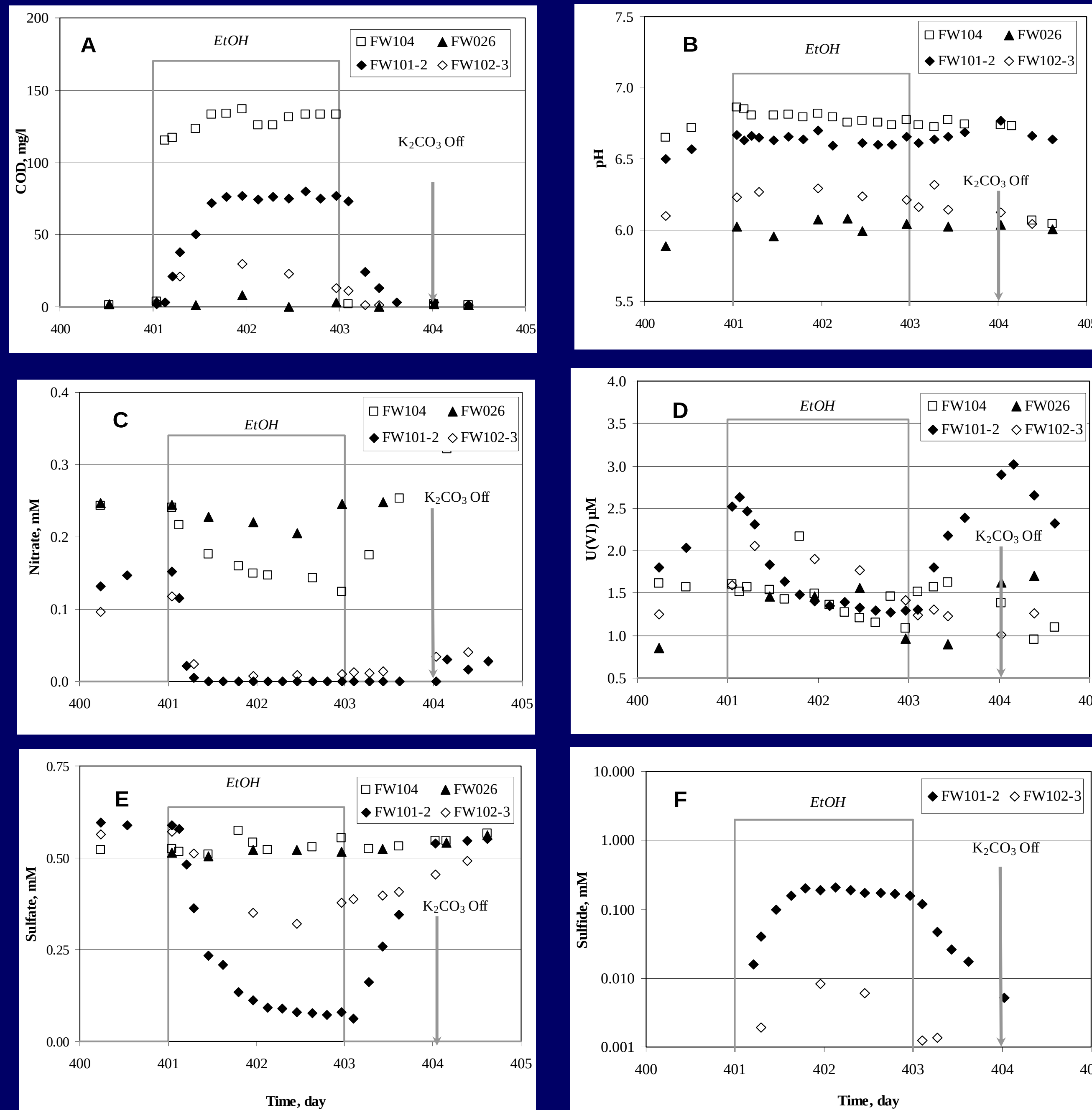
Samples from FW024, FW104, FW026, FW103 and FW105 (down gradient well).

U(VI) bioavailability experiments

See Wu poster

Days 399-409

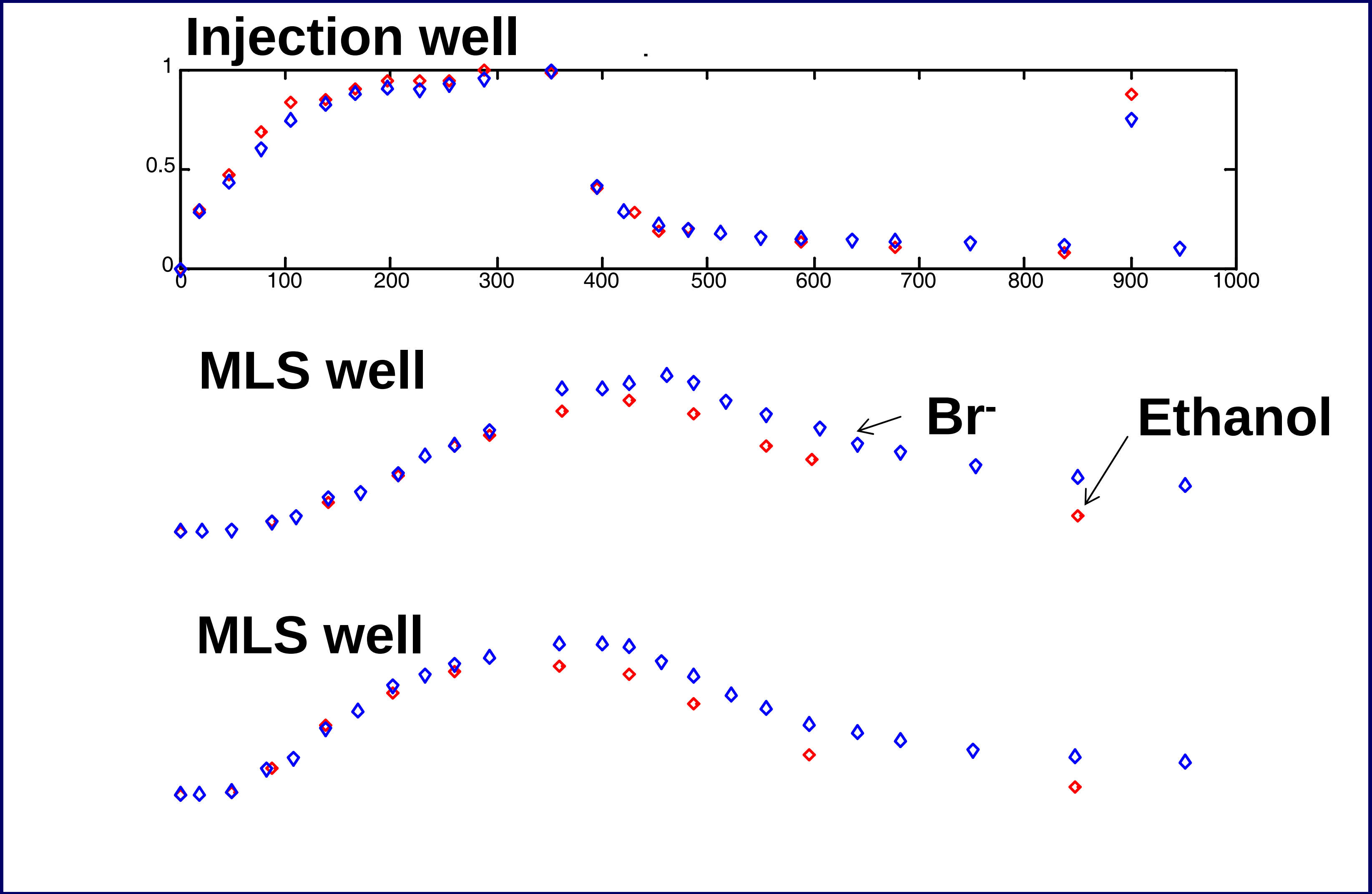
Sequence:
base on,
ethanol on,
ethanol off
base off.
(Summer)



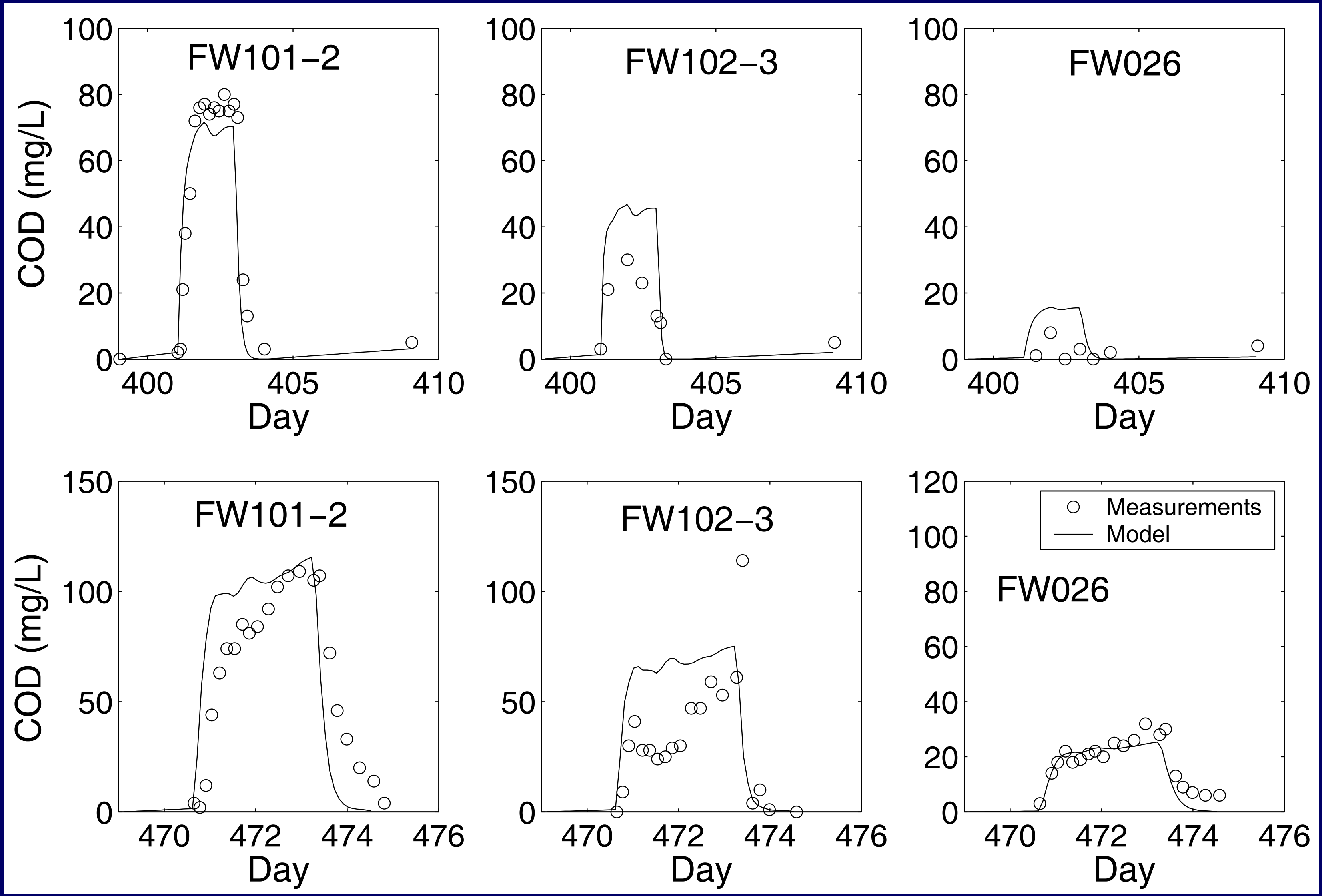
Modeling

See Jian Luo poster

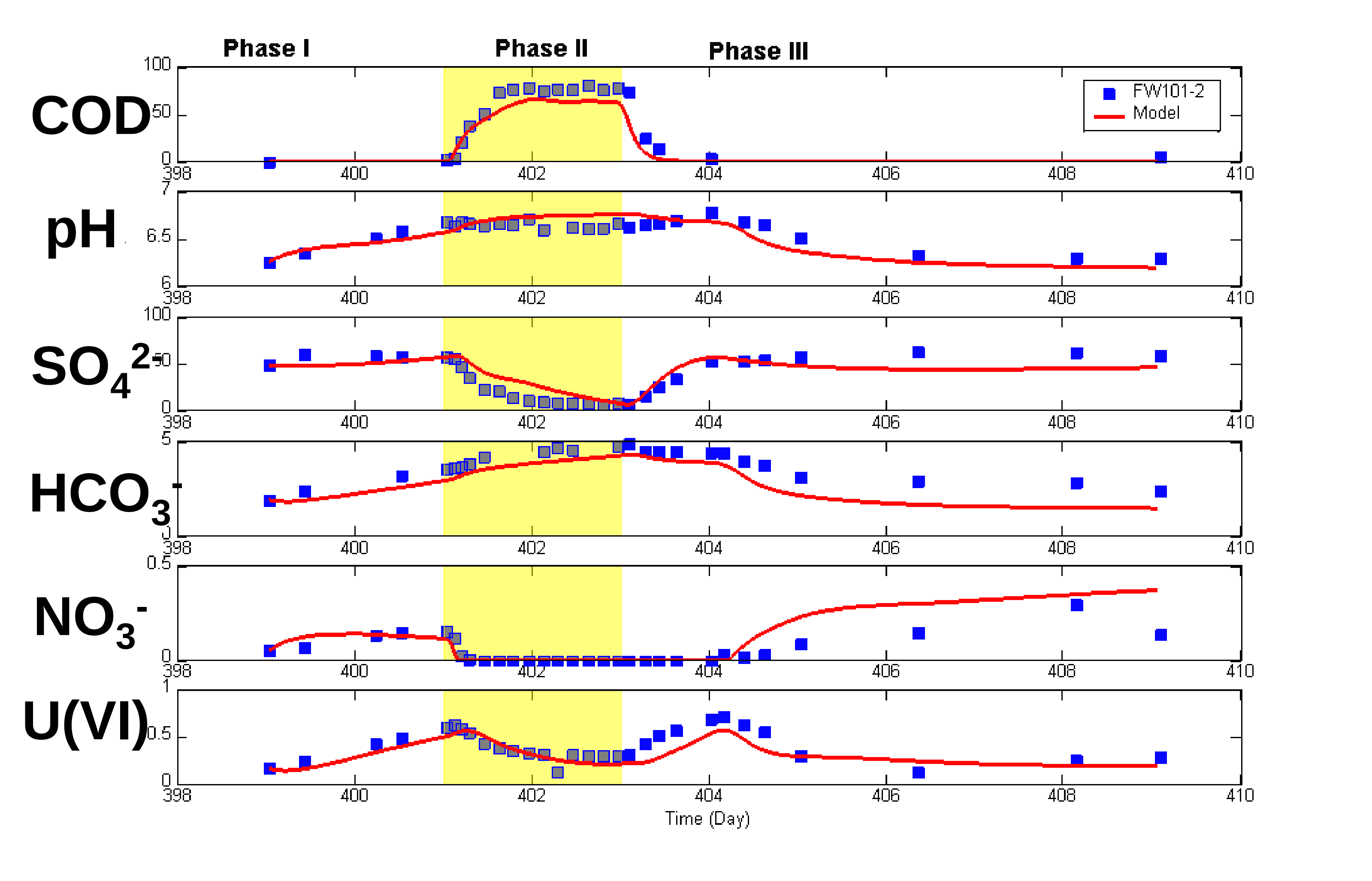
Model calibration: ethanol and bromide tracer stu



Predictions for ethanol consumption



Reactive transport simulation (Days 399-409)



Microbiology

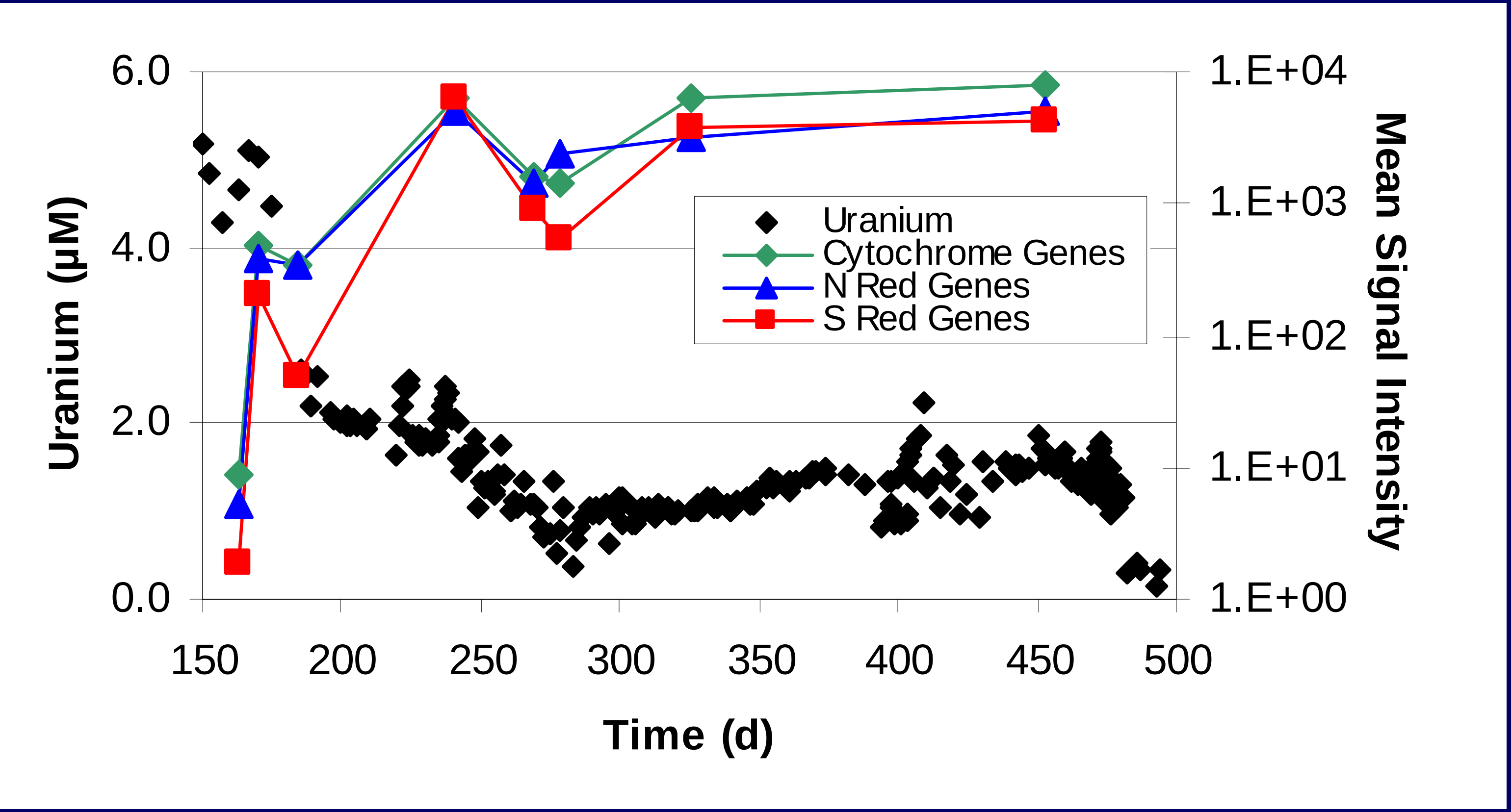
See Terry Gentry poster

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

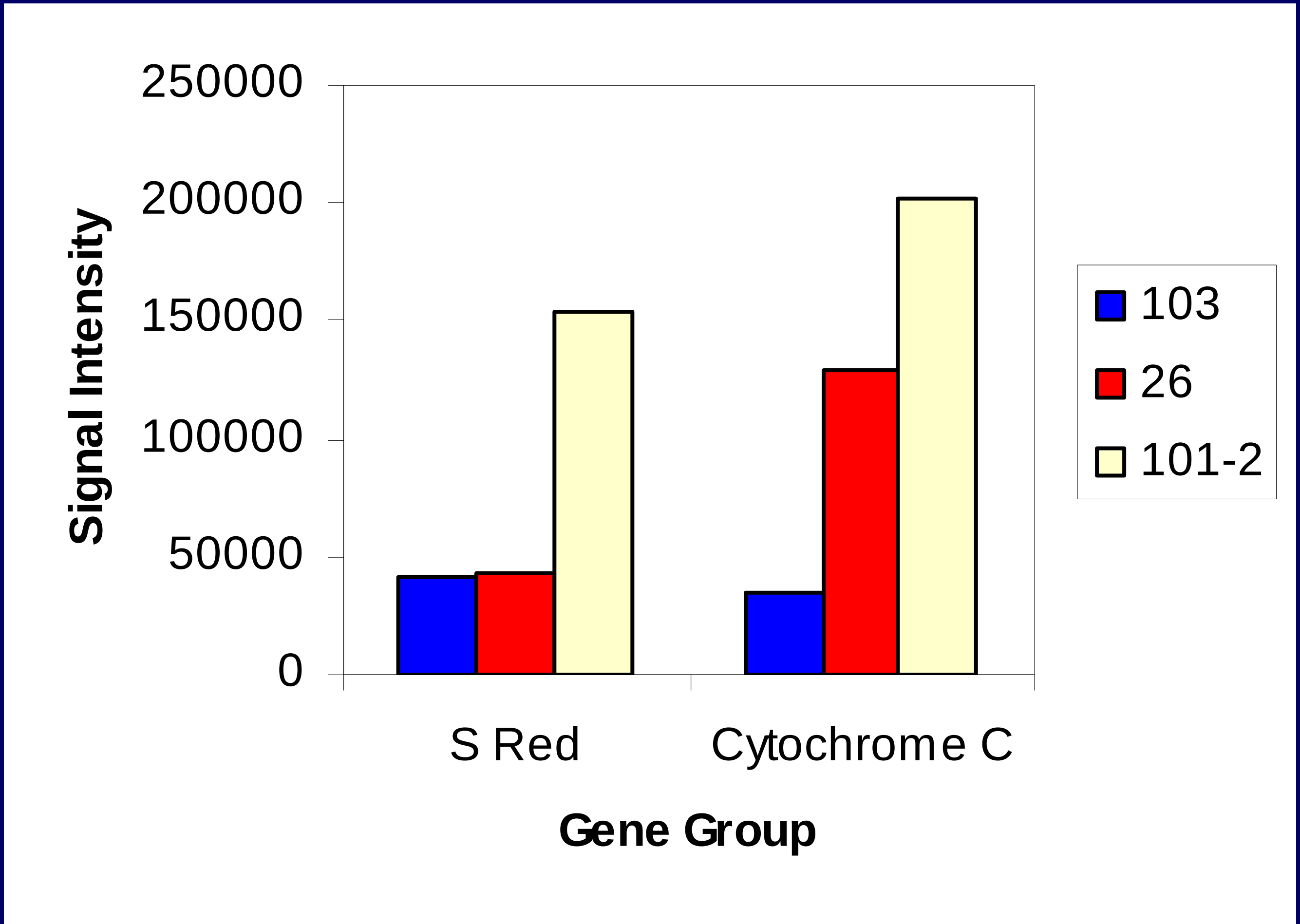
Note: MPN values for five replicates. Test wells sampled 8/20/04. Control well sampled 5/28/04.

FW101-2 Denitrification, Sulfate Reduction & Cytochrome C Genes



- Increased levels of cytochrome C genes correlated with lower uranium levels

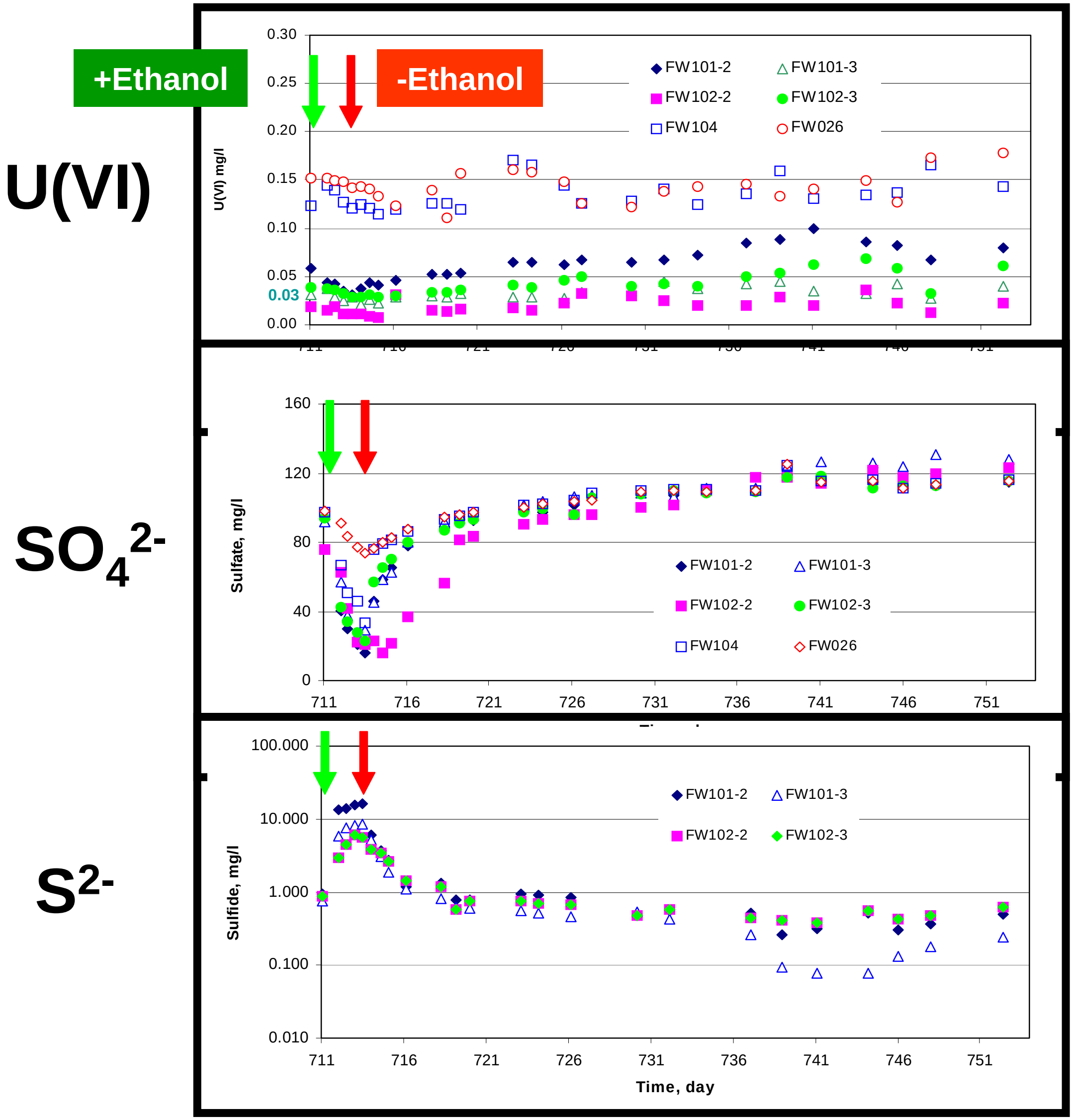
Sediment Sulfate Reduction and Cytochrome C Genes – 535 d



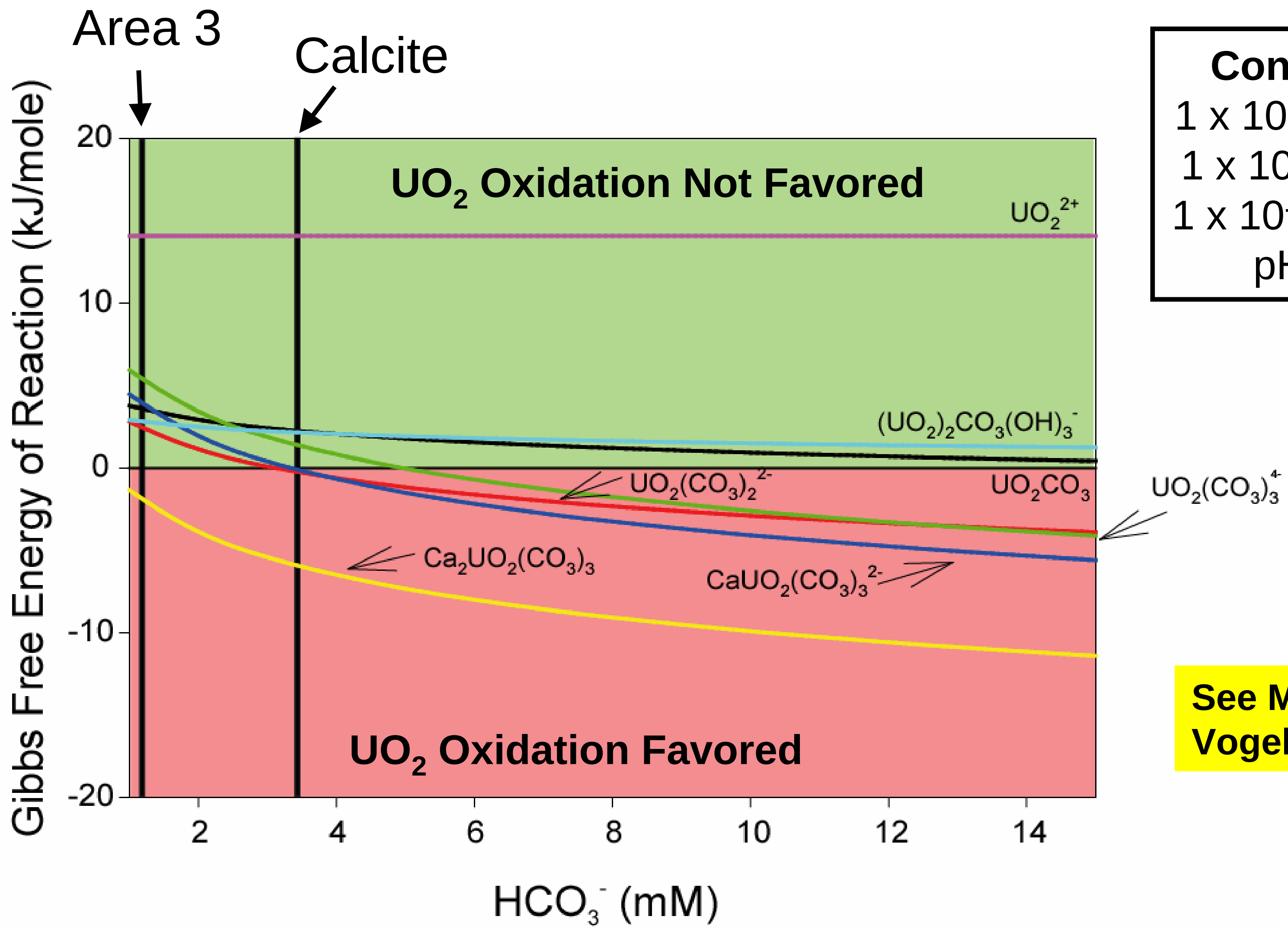
- Both sulfate reduction and cytochrome C genes were elevated in biostimulated sediment

Stability experiments ± O_2

System stability during a 41-day starvation period (days 713-754) - No O_2 in system



$UO_{2(Biogenic)}$ Oxidation by Ferrihydrite



Conditions
1×10^{-6} M U(VI)
1×10^{-3} M Ca^{2+}
1×10^{-5} M Fe(II)
pH = 7

See Matt Ginder-Vogel poster

High bicarbonate concentration results in UO_2 oxidation becoming more energetically favorable

Conclusions: strategies for highly contaminated sites

- Aboveground removal of inhibitors and clogging agents.

- Use of clean water flush to determine mass transfer rates and to condition a treatment zone.

- Staged treatment with soil conditioning before biostimulation.

- A nested recirculation scheme can protect a treatment zone from clogging agents and inhibitors.

- Mass transfer considerations may enable manipulation of contaminant bioavailability.

Future Work

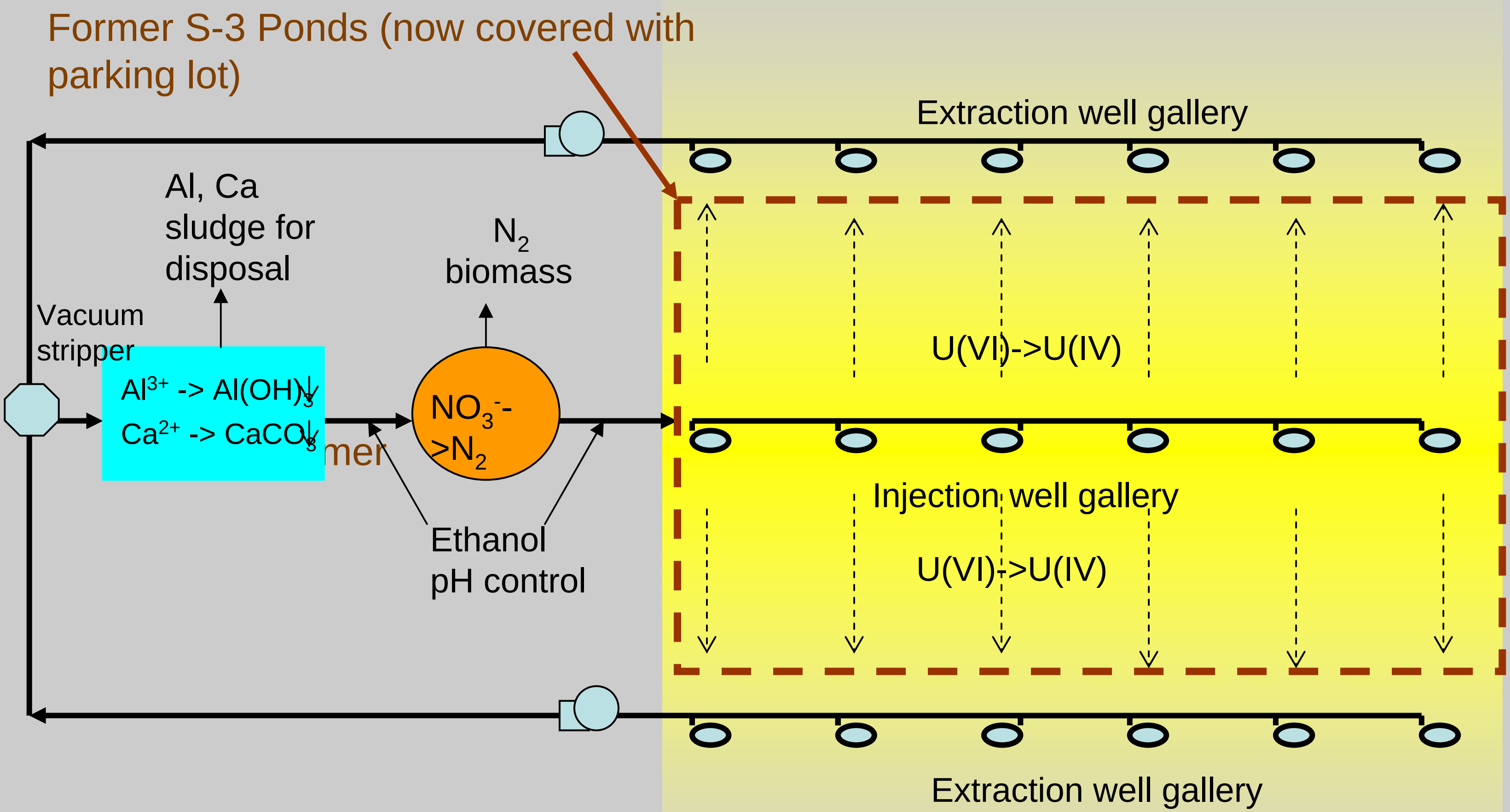
- Effects of oxygen on dissolved U(VI) levels.

- Evaluation of the extent of reduction required for stability.

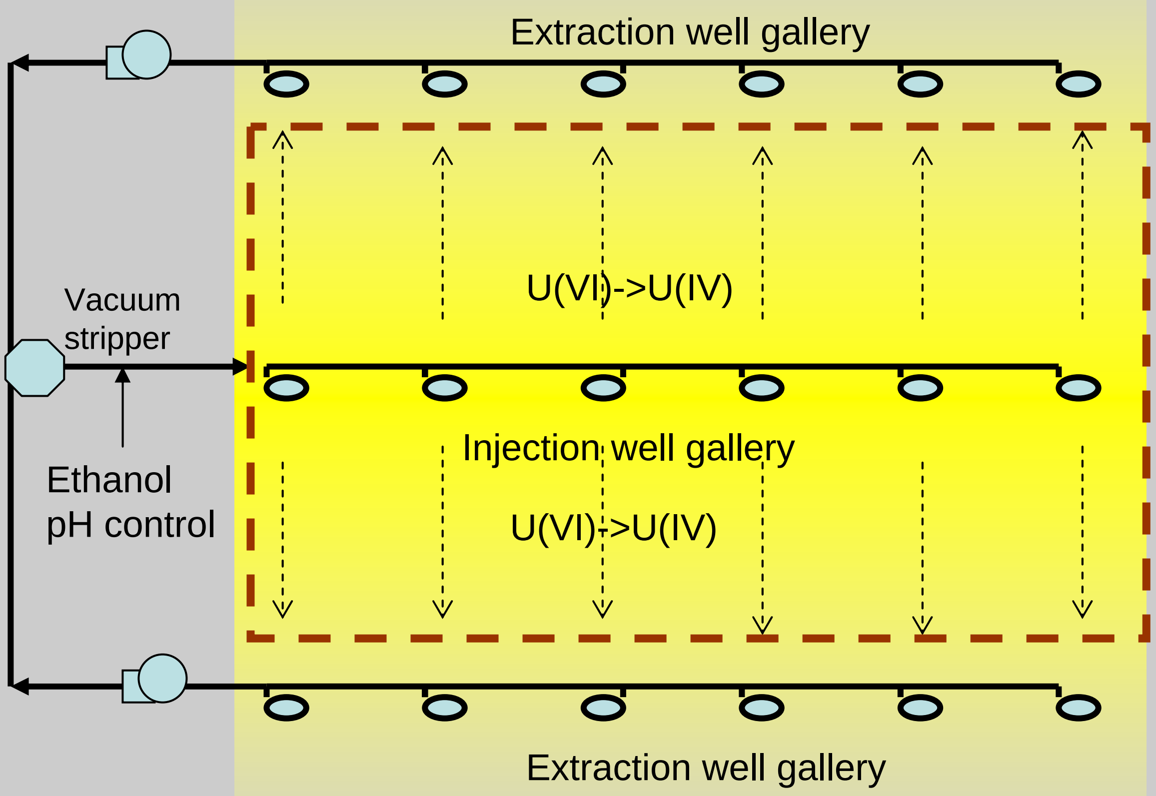
- Microbial succession during stable and unstable operation

- Modeling of dissolved U flux from a reduced zone under different operational scenarios.

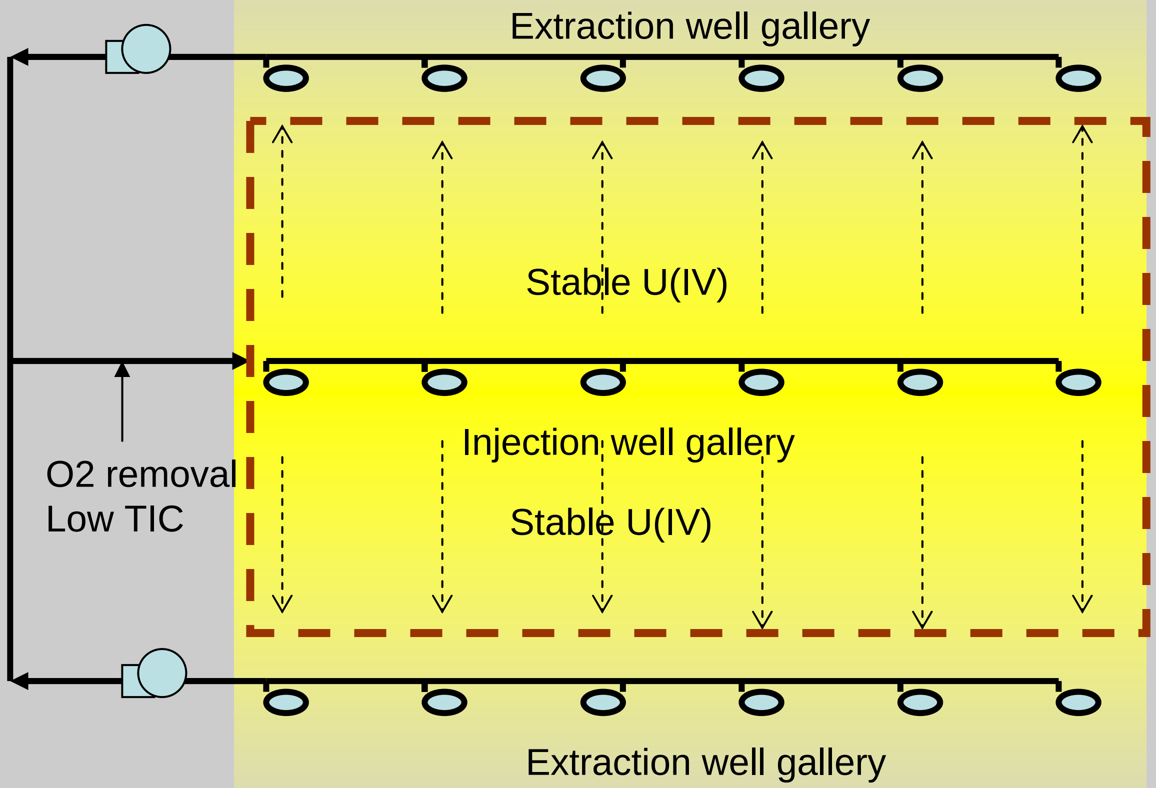
Stage 1 -removal of aluminum, calcium, nitrate



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



Stage 3 - Long-term maintenance of stable U(IV)



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