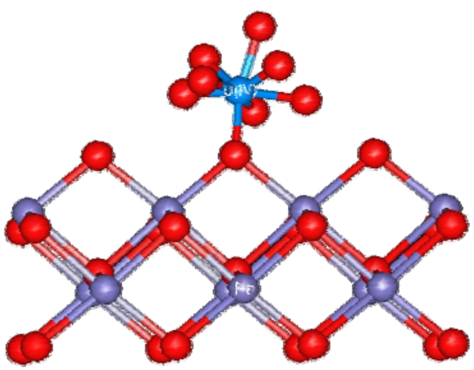
Bioremediation of Atomic Bomb Wastes:

Developing a Strategy for Long-term Immobilization of Uranium Under Field Conditions



Federal Remediation Technologies Roundtable
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C. Criddle
Stanford University

Contributing research teams

Stanford University

Craig Criddle
Scott Fendorf
Michael Fienen
Margaret E. Gentile
Matthew A. Ginder-Vogel

Peter Kitanidis
Jian Luo
Jennifer Nyman
Wei-Min Wu

Oak Ridge National Laboratory

Scott Brooks
Sue Caroll
Jack Carley
Terry Gentry

Philip Jardine
Tonia Mehlhorn
Hui Yan
Baohua Gu

Miami University

Matthew Fields
Chaichi Hwang

ERSP Field Research Center

David Watson
Kenneth Lowe

George Houser
Kirk Hyder

University of Oklahoma

Jizhong Zhou
Liyou Wu

Michigan State University

Mary Beth Leigh
Eric Cardenas
Terrence Marsh
James Tiedje

Retec

Robert Hickey
Raj Rajan
Daniel Wagner

Argonne National Laboratory

Shelly Kelly
Kenneth Kemner

The Oak Ridge S3 ponds

1951-1984 : wastes stored in unlined ponds

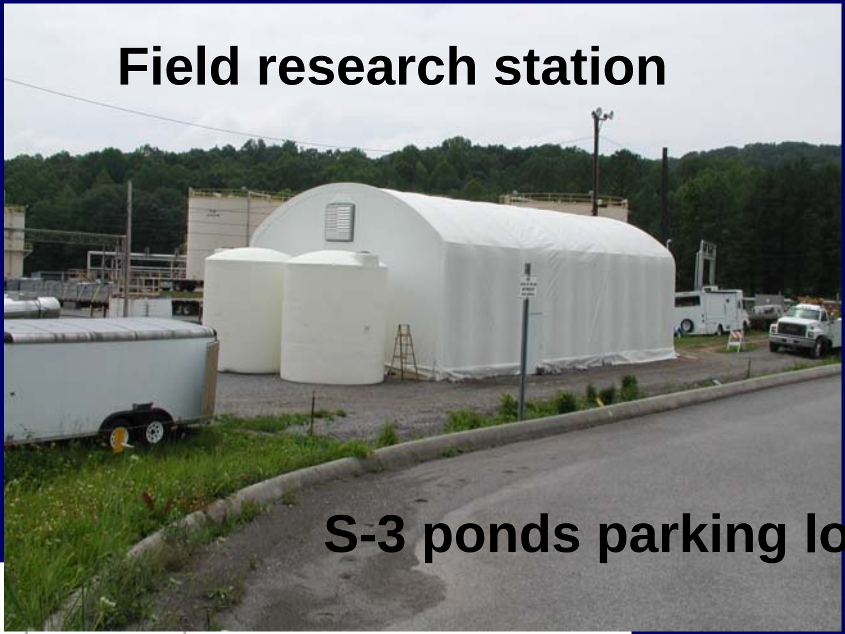
Major groundwater contaminants

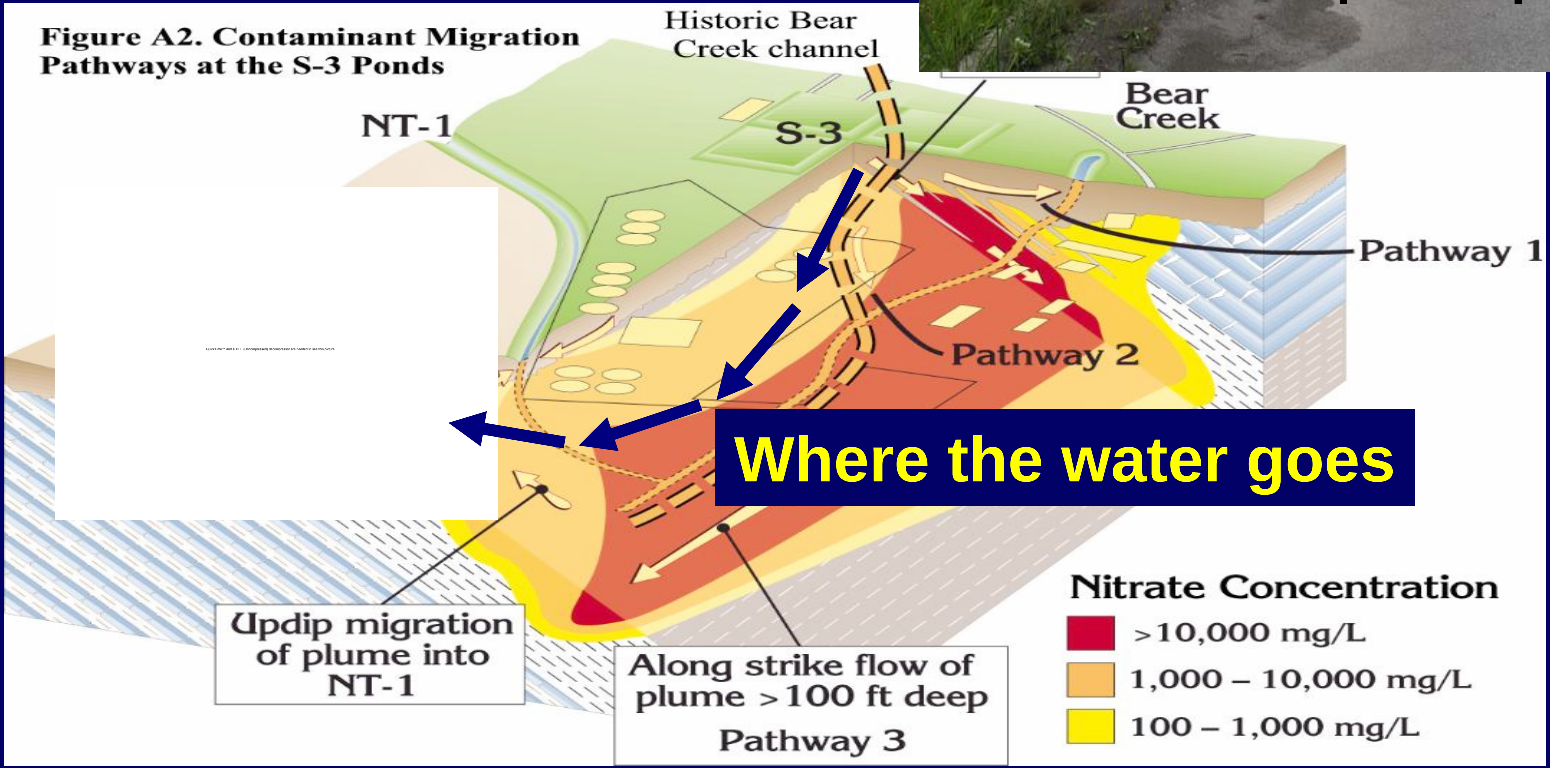
Depleted uranium: 40-50 mg/L
(EPA standard 30 µg/L)

Strong acids: pH 3.4-3.6, 8-10 g/L nitrate, 1 g/L sulfate

Chlorinated solvents: 2-3 mg/L PCE, 1 mg/L cDCE

Metals: 540 mg/L Al, 930 mg/L Ca, 11-14 mg/L Ni





Where the water goes

Geology

• Highly interconnected fracture network with 100-200 fractures/m.

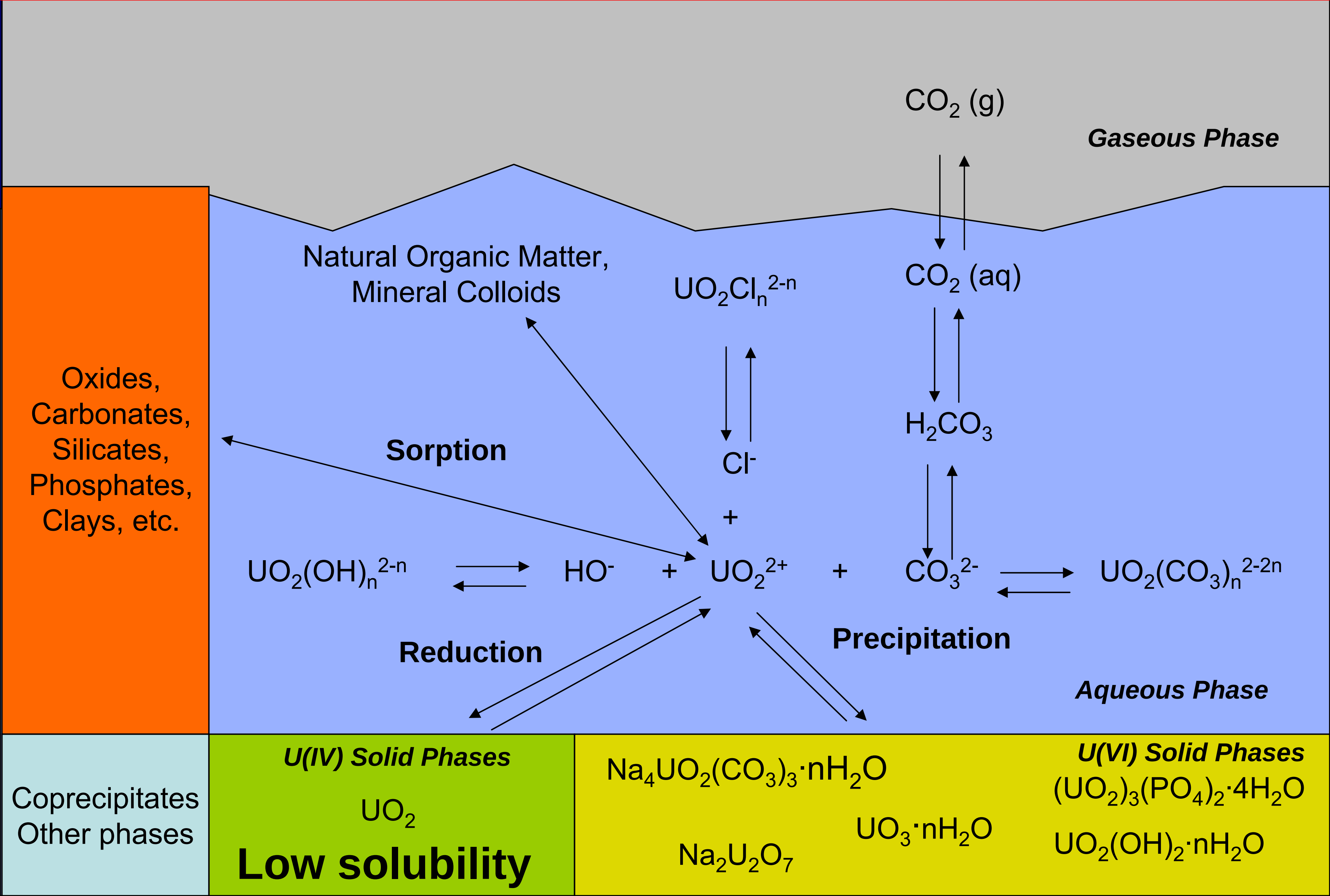
• Fractures are < 5-10% of the total porosity, but carry >95% of the flow.

• Fractures are surrounded by a high porosity, low permeability matrix that is a source and sink for contaminants.

Overlying Saprolites

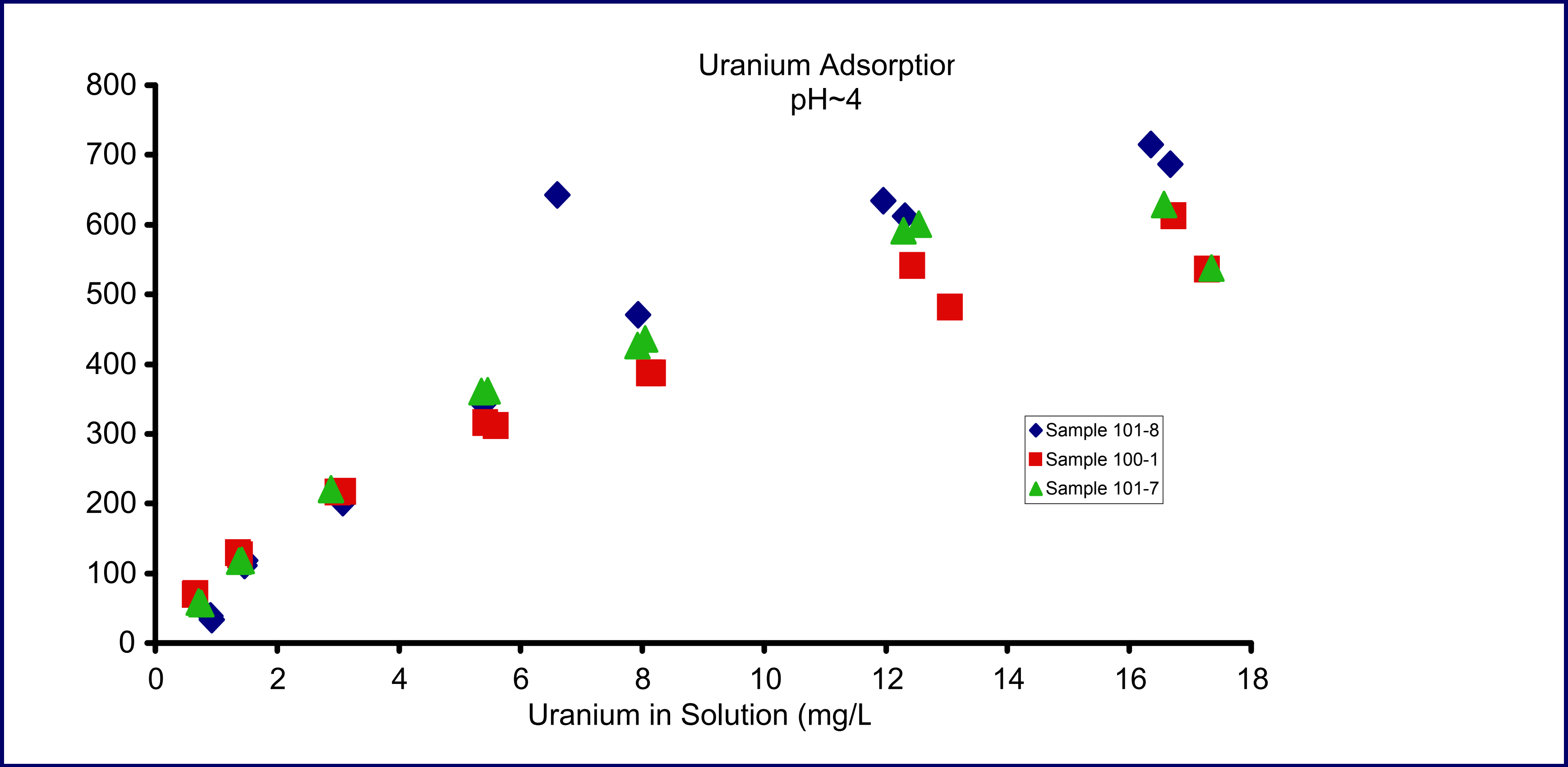
Underlying Bedrock

Uranium Geochemistry



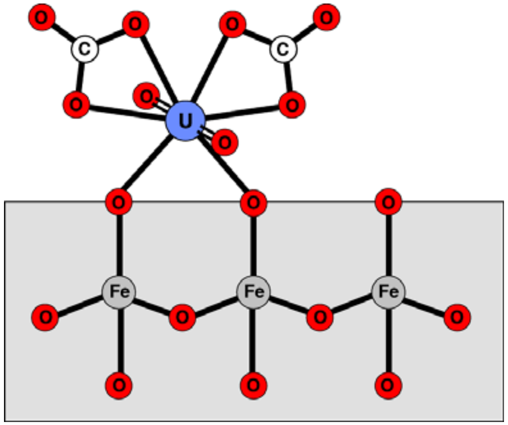
At the S3 ponds, the solid phase is a long-term source of U (VI).

The aqueous phase U concentrations exceed the U.S. EPA drinking water standard by over 1000 times. But most of the U is still on the soil, as illustrated by the sorption isotherm at pH 4.

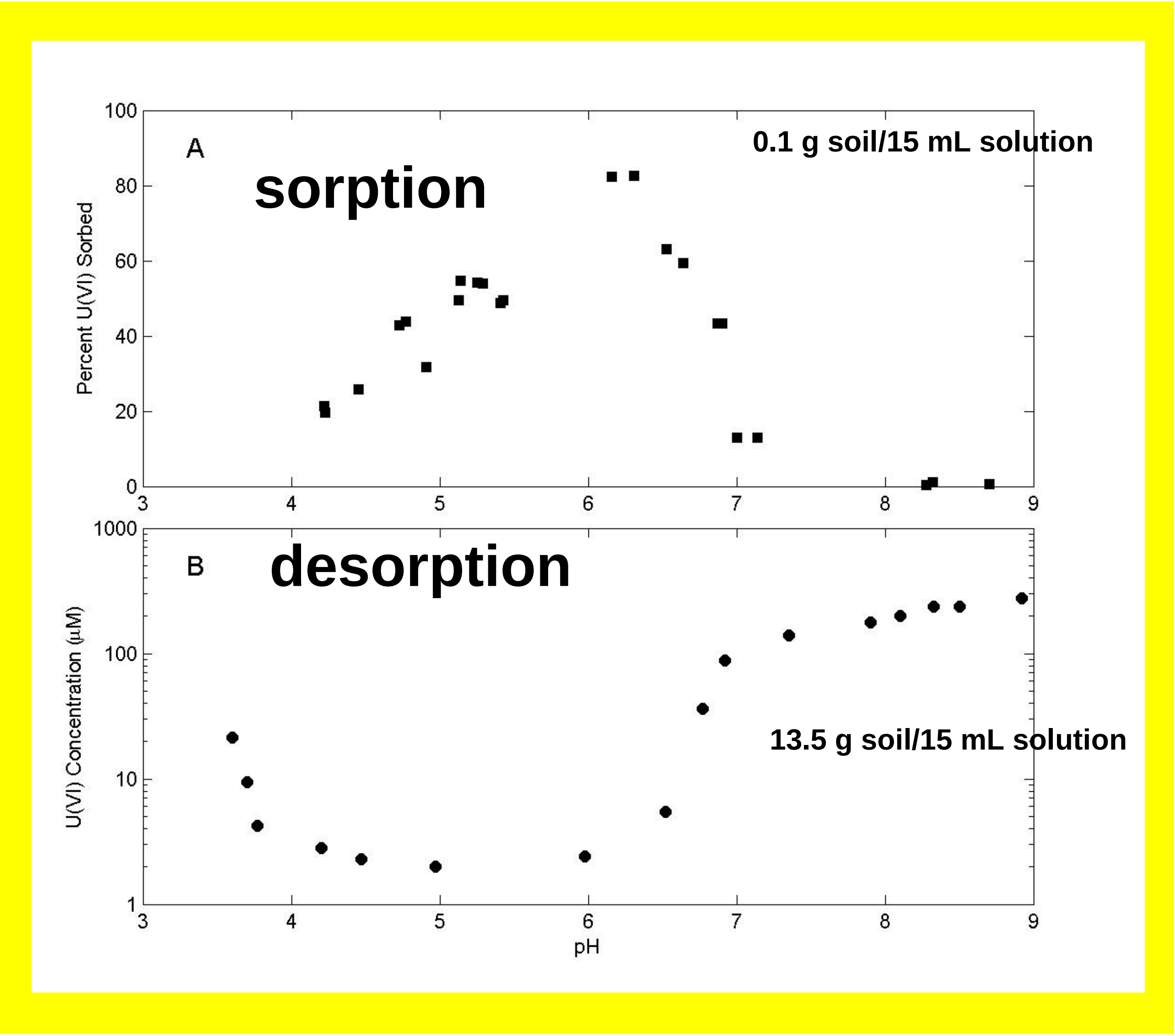


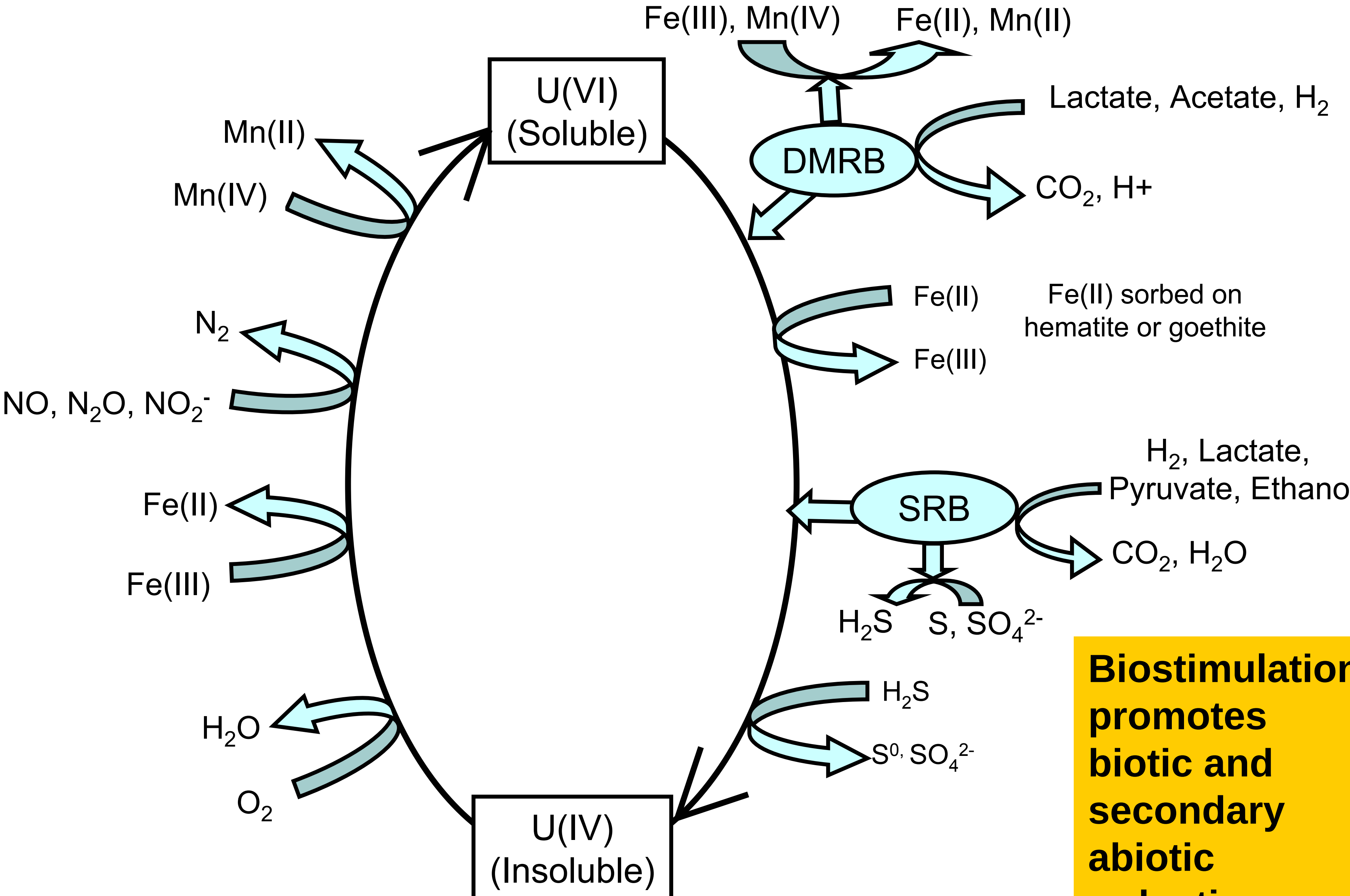
U sorption and desorption are strongly pH dependent.

Complexes at surfaces:



Source: Catalano (2004)





Biostimulation promotes biotic and secondary abiotic reductions

Chemistry considerations

High U(VI) on solid phase: is it accessible?
~98% on the soil (~400 mg/kg)
~2% in groundwater(~ 40 mg/L) - 40 mg U/L inhibits sulfate-reducer growth

Low pH (~3.5): bad for robust microbial activity
buffered by Al^{3+} acidity (~20 mM), Al precipitates at pH 4.5-5

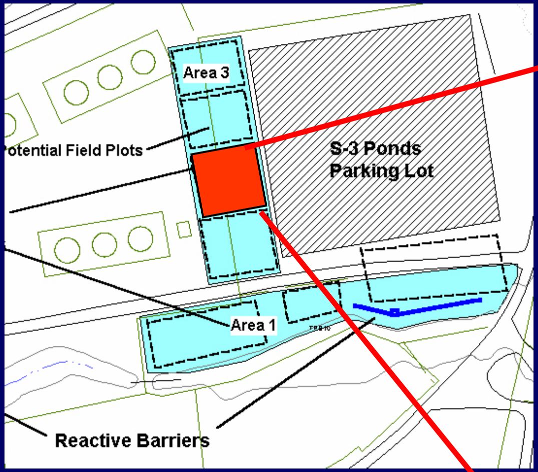
High NO_3^-: inhibits U(VI) reduction, precursor to N_2 clogging, oxidizes U(IV), present in the matrix
130-480 mM in groundwater

High Ca^{2+}: inhibits U(VI) reduction at 5 mM; precipitates at pH>7
~20 mM in groundwater

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

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

Field Research Center



Overview

- Selection of a treatment zone
- Gaining hydraulic control
- Flushing and conditioning
- Biostimulation
- Stability tests

Location: adjacent to the source zone.

Rationale:

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

Conversion of solid-associated U(VI) into highly insoluble U(IV) will prevent dissolution and desorption, decreasing the time and cost of remediation.

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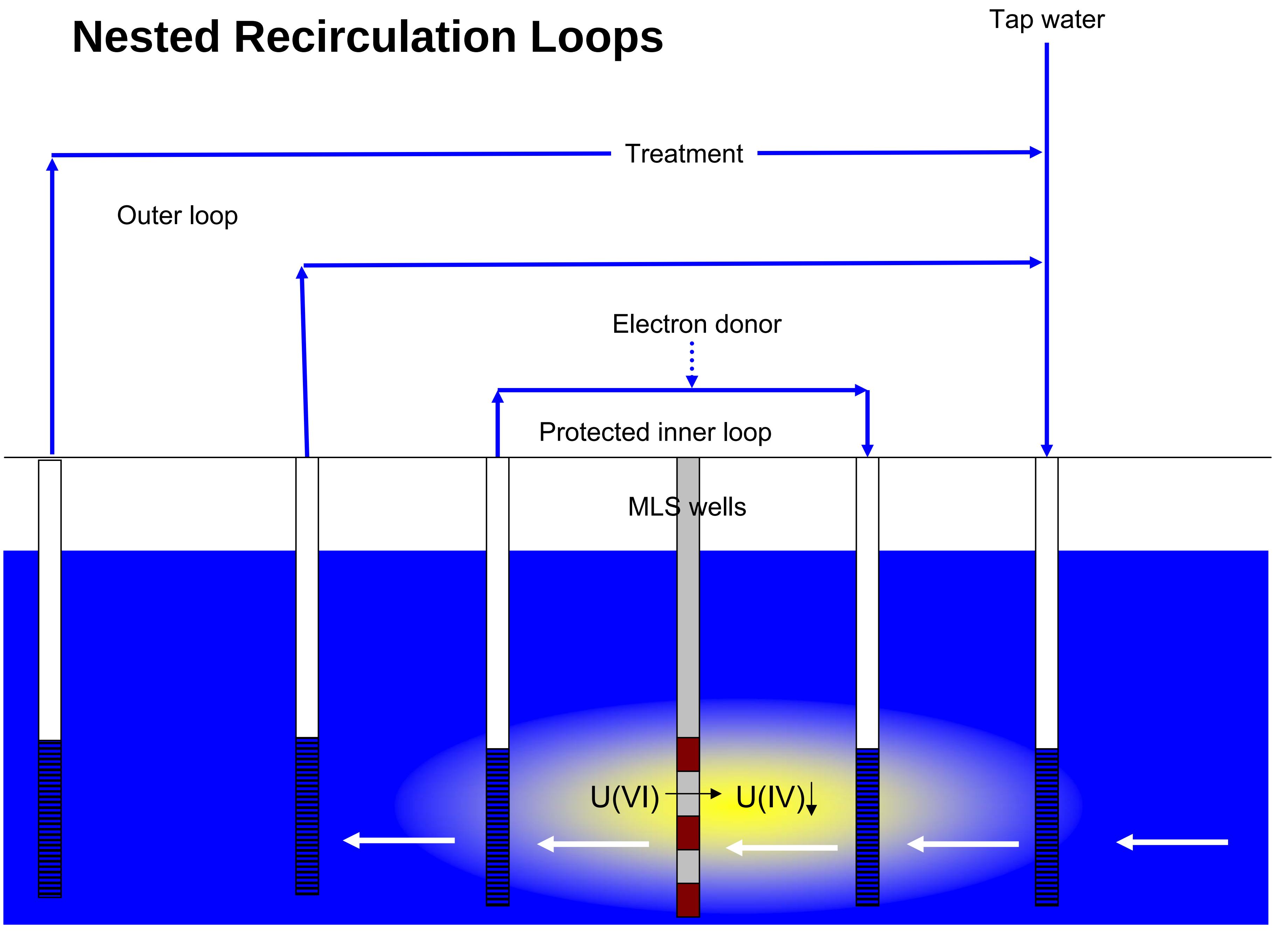
Stepwise strategy

Step 1: Establishing hydraulic control

- Nested recirculation wells

Above ground treatment system in tent
S-3 Ponds parking lot
Well field for the below ground treatment system
On site lab trailer
Image © 2005 DigitalGlobe
© 2005 Google
N
W
E
S
Pointer 35°58'38.22" N 84°16'26.60" W elev 1009 ft
Streaming |||||||||| 100%
Eye alt 1945 ft

Nested Recirculation Loops



Step 2: Conditioning of subsurface by removal of clogging agents and inhibitors

- Acidified clean water tracer study and flush
- Aboveground removal of clogging agents and inhibitors
- pH increase

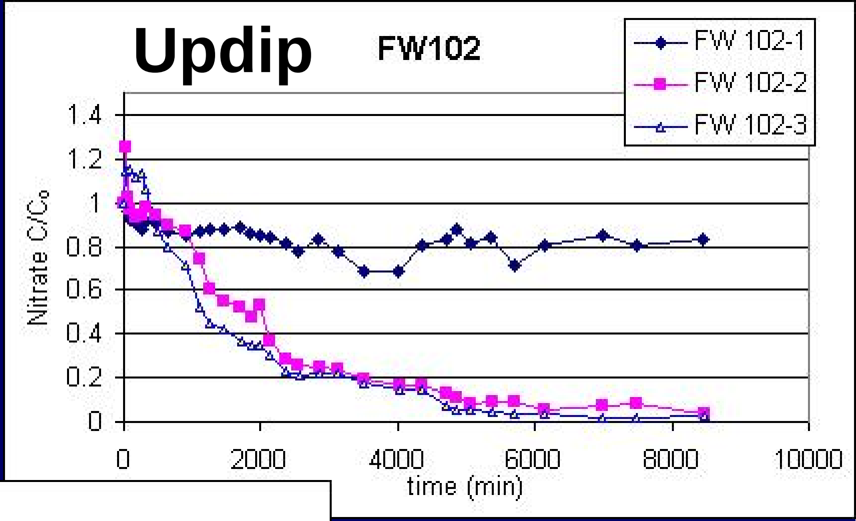
MLS wells

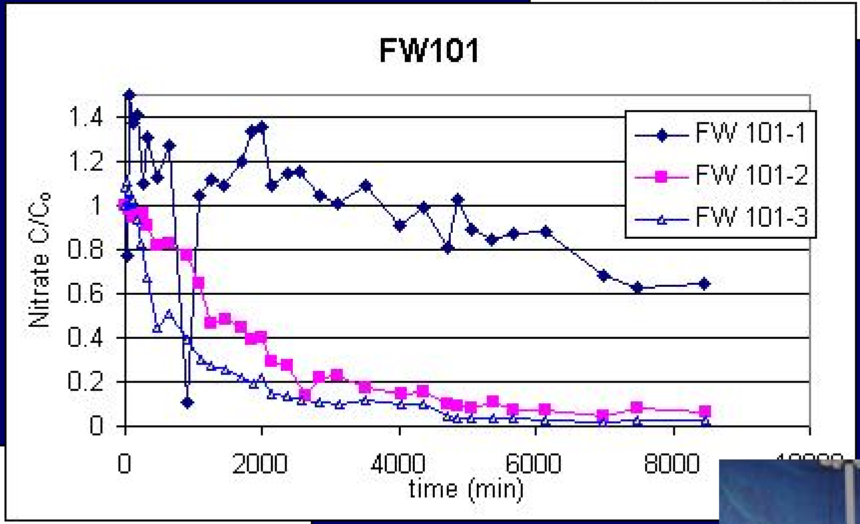
Well B

Well C

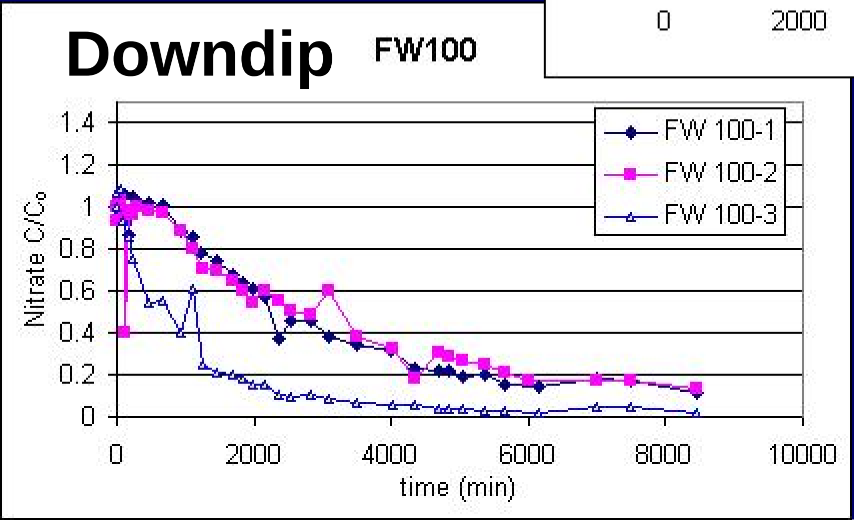
QuickTime™ and a
TIFF (PackBits) decompressor
are needed to see this picture.

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

Removal of clogging agents and pH adjustment

1. Recirculate and flush at pH 4-4.5

   Sorption of U increases compared to pH 3.4

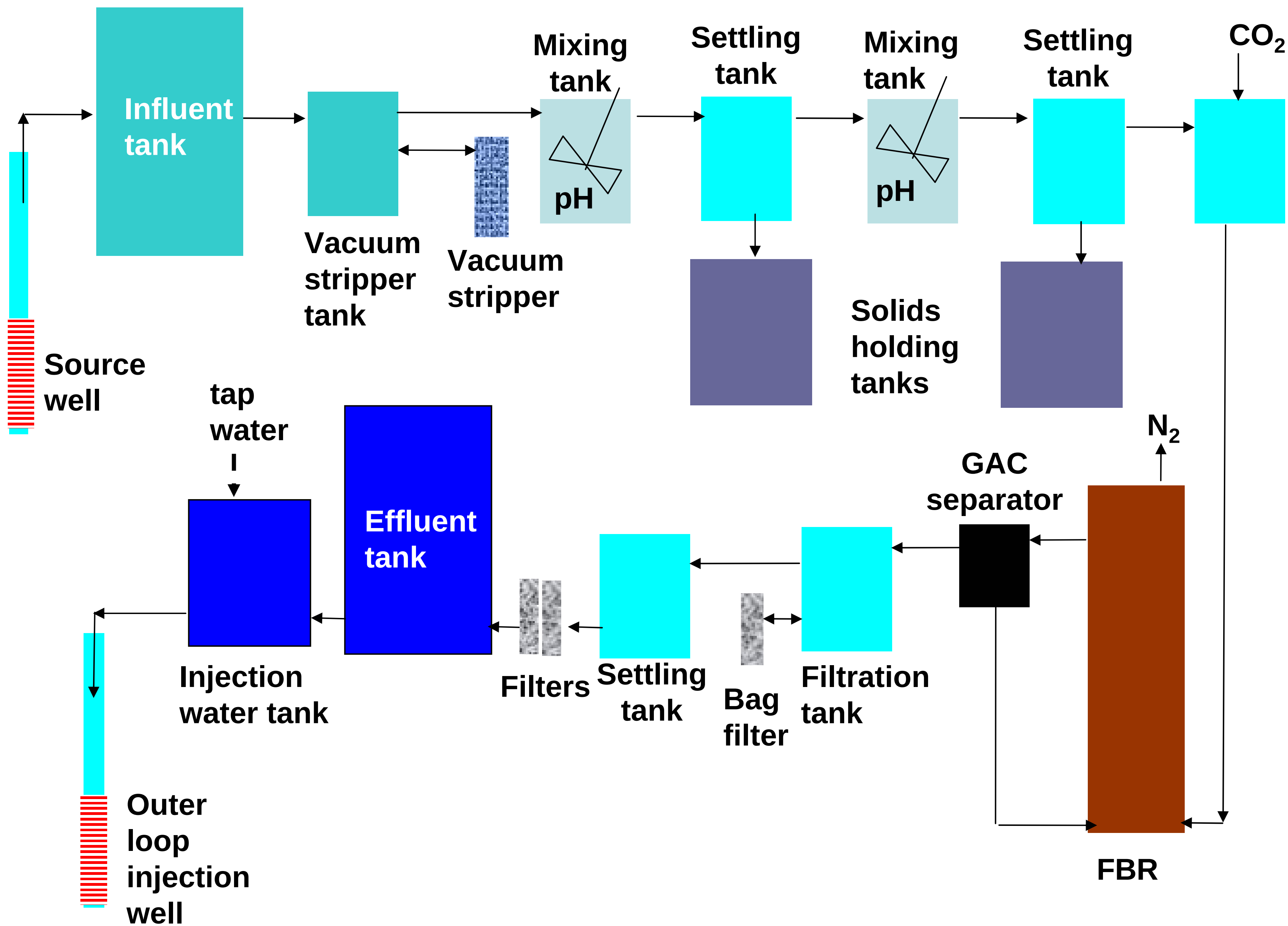
   While recirculating, remove clogging and inhibitory agents ex-situ: Al, Ca, NO_3^- , VOCs, N_2

2. Recirculate and flush at pH 6-6.3

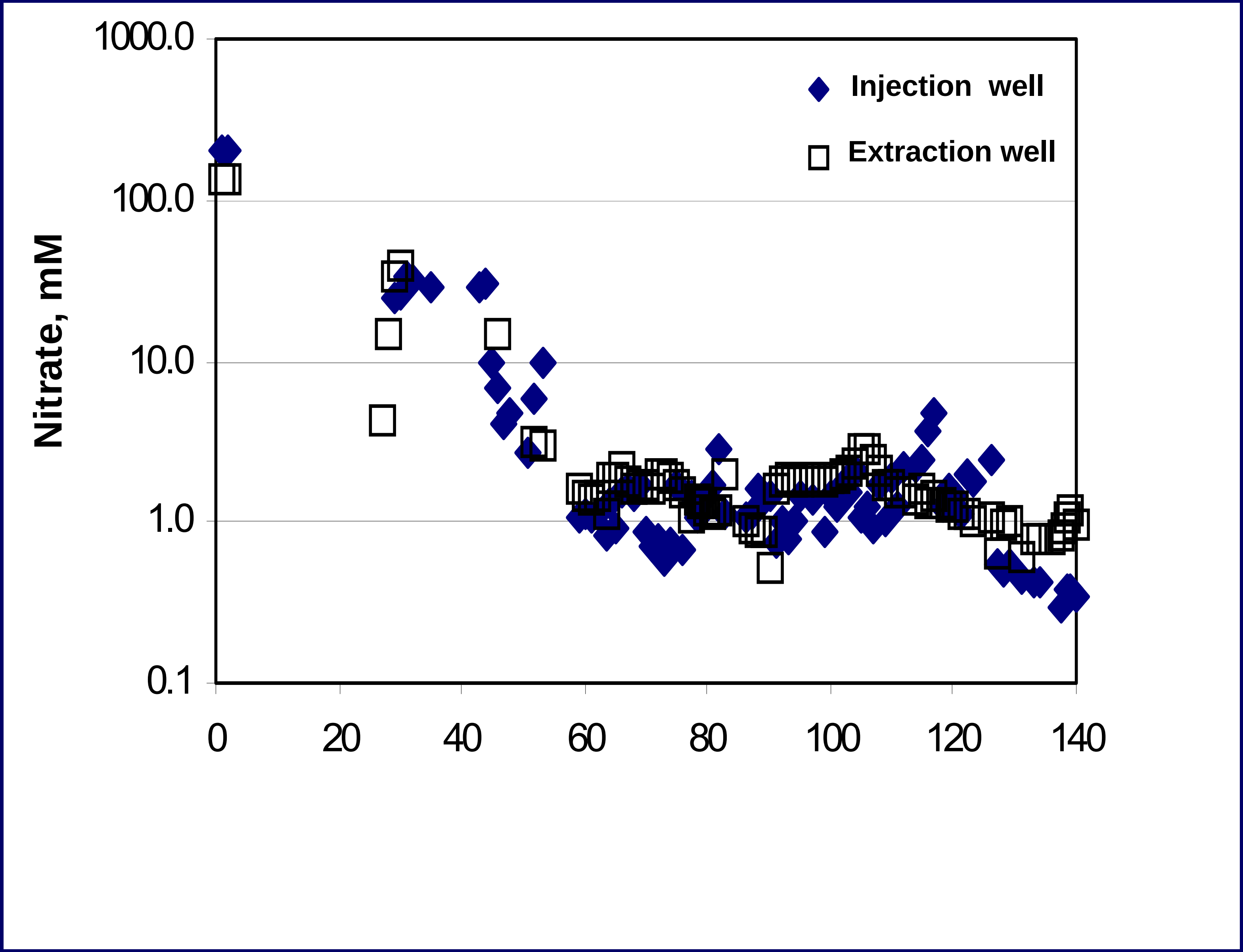
   Sorption of U now becomes maximum

   Favorable for SRB and FeRB, but not methanogens

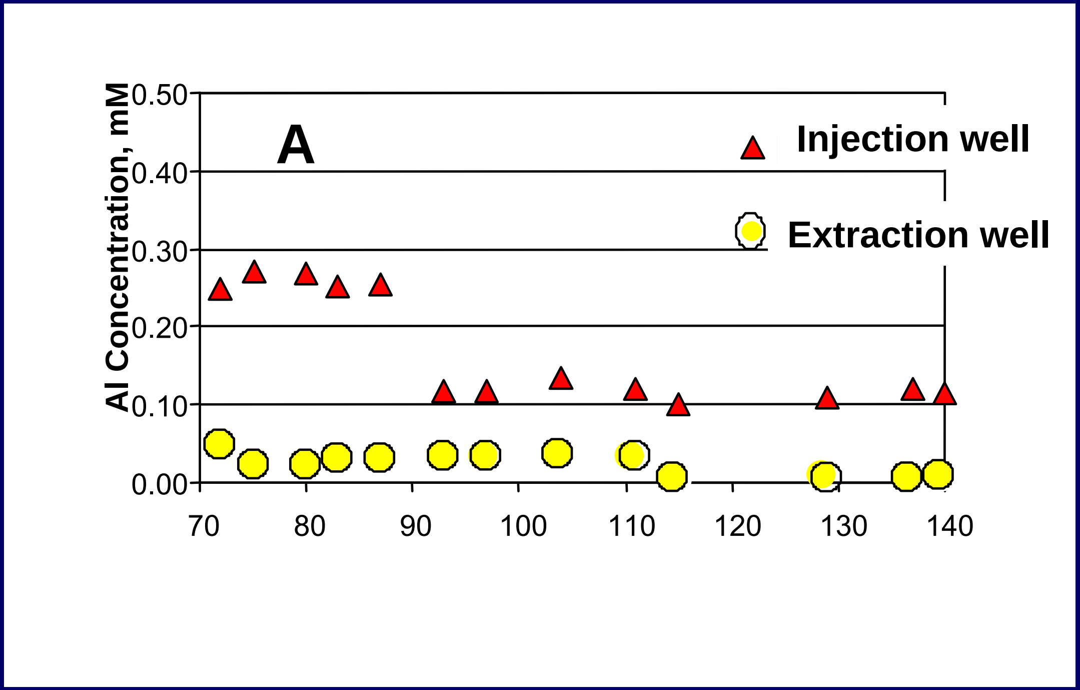
ABOVEGROUND PROCESS TRAIN

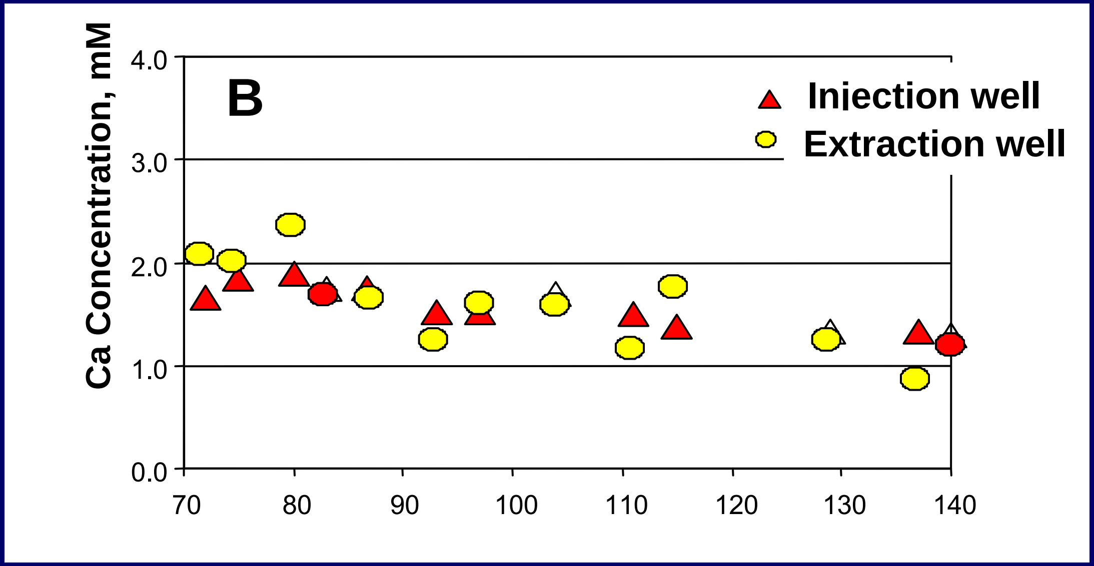


Nitrate removal at injection extraction wells



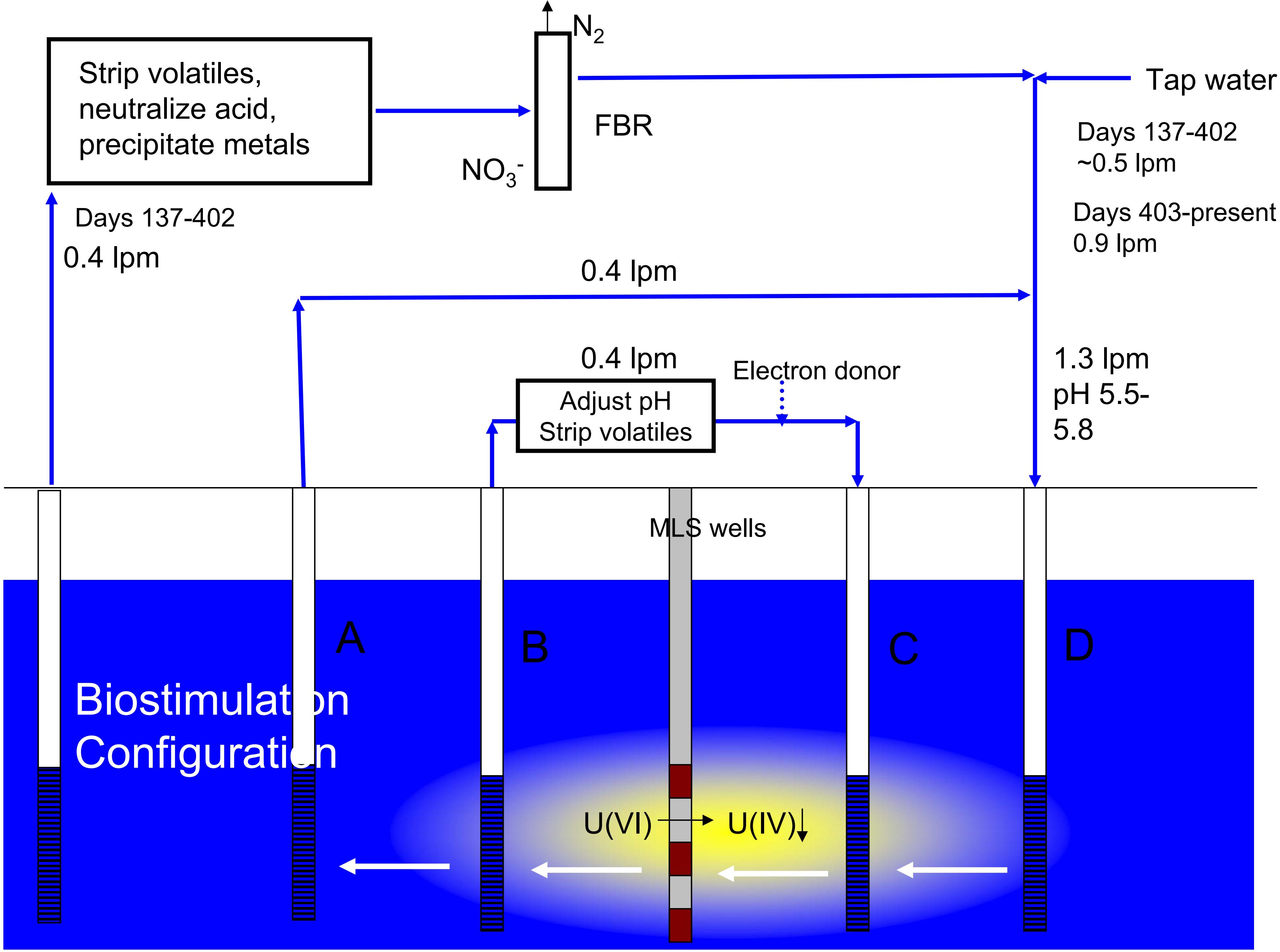
Al and Ca removal at injection extraction wells



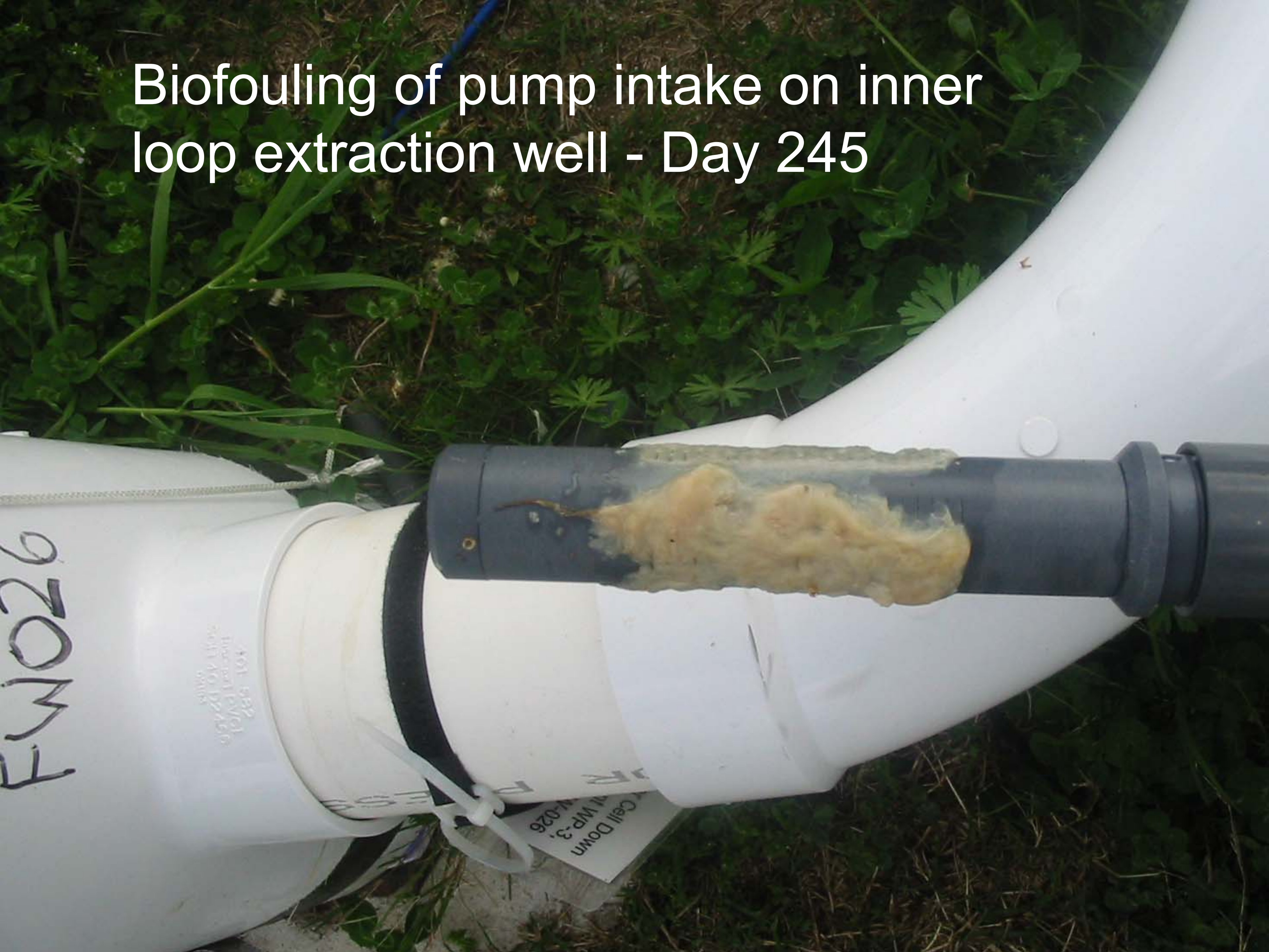


Overview

- Selection of the treatment zone
- Gaining hydraulic control (step1)
- Flushing and conditioning (step 2)
- Biostimulation (step 3)
- Stability tests



Strip volatiles, neutralize acid, precipitate metals
N2
NO3-
FBR
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
Electron donor
Adjust pH
Strip volatiles
1.3 lpm
pH 5.5-5.8
MLS wells
A
B
C
D
Biostimulation Configuration
U(VI)
U(IV)


Biofouling of pump intake on inner loop extraction well - Day 245
FW026

Surging allowed sediment sampling

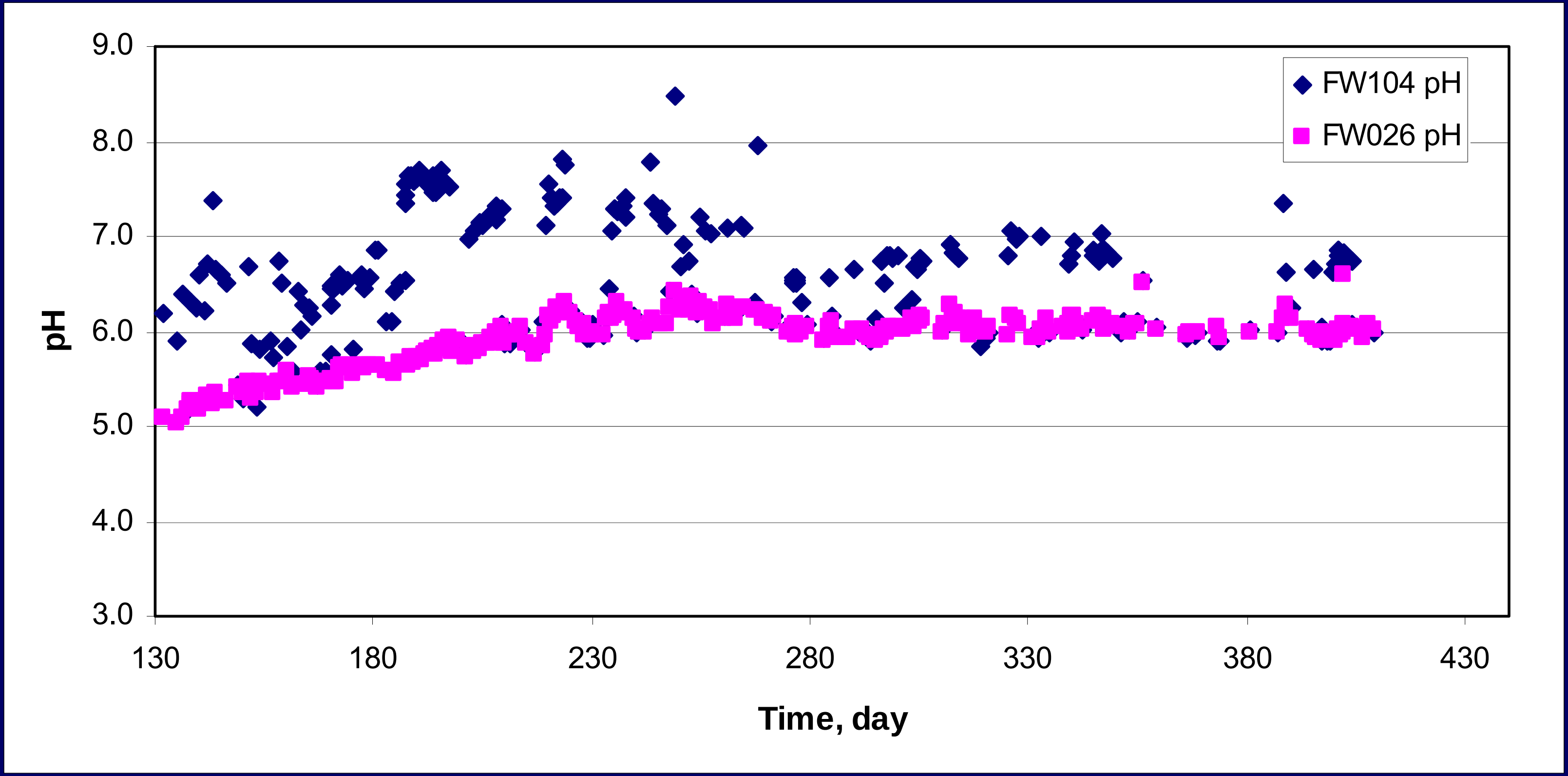
Preparing to surge

Surge block in use

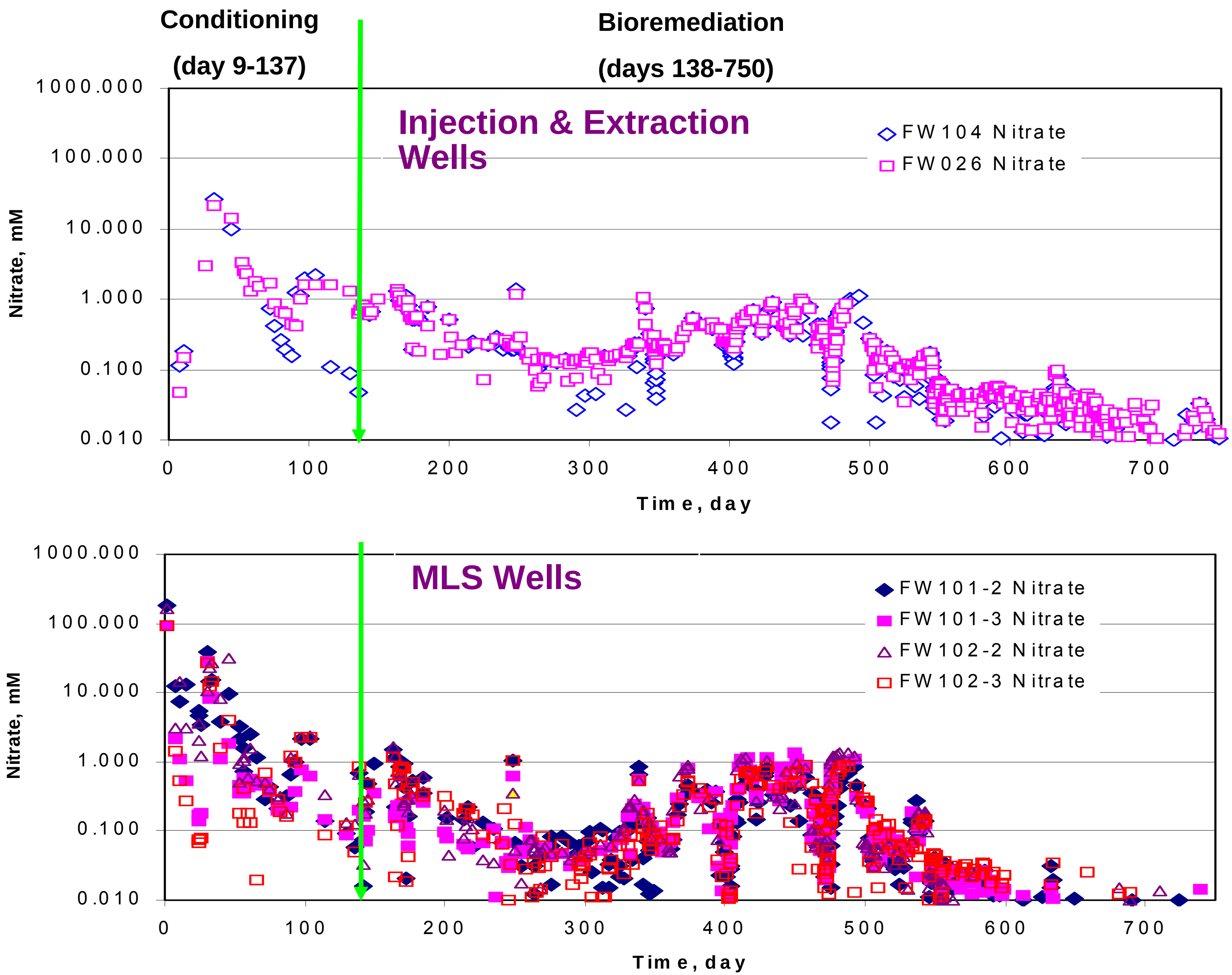
Anaerobically collected sediment

- Surging pulls sediment from around the well screen into the well
- Sediment is pumped to surface after settling
- Anaerobically stored at 4 °C until time of analysis
- Mounted as a wet paste for spectroscopy

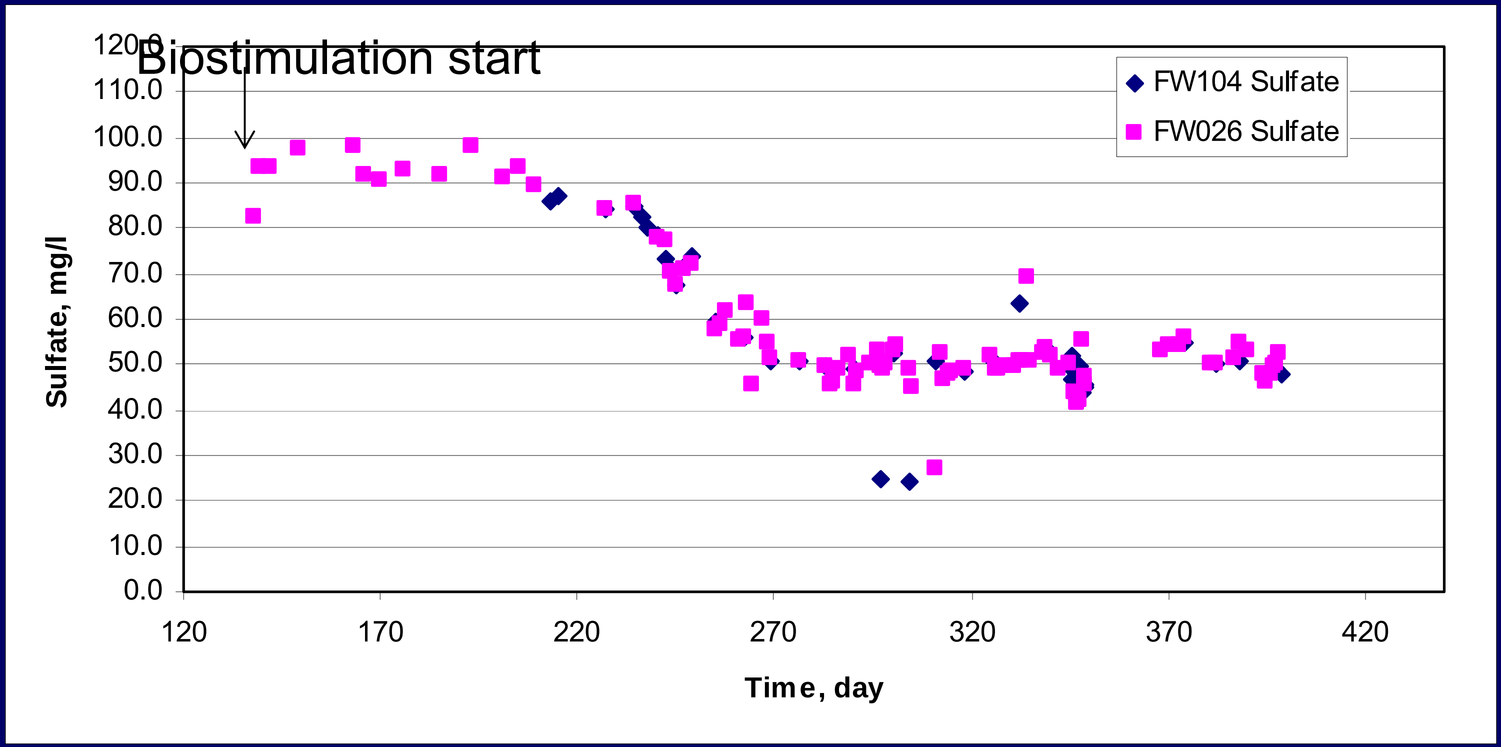
pH in inner loop injection and extraction wells during biostimulation



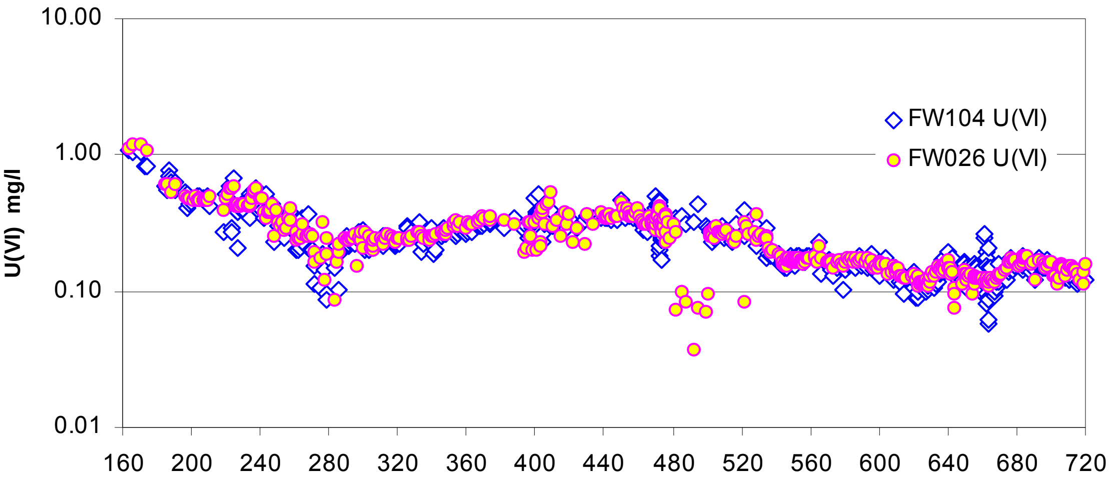
Nitrate removal during biostimulation

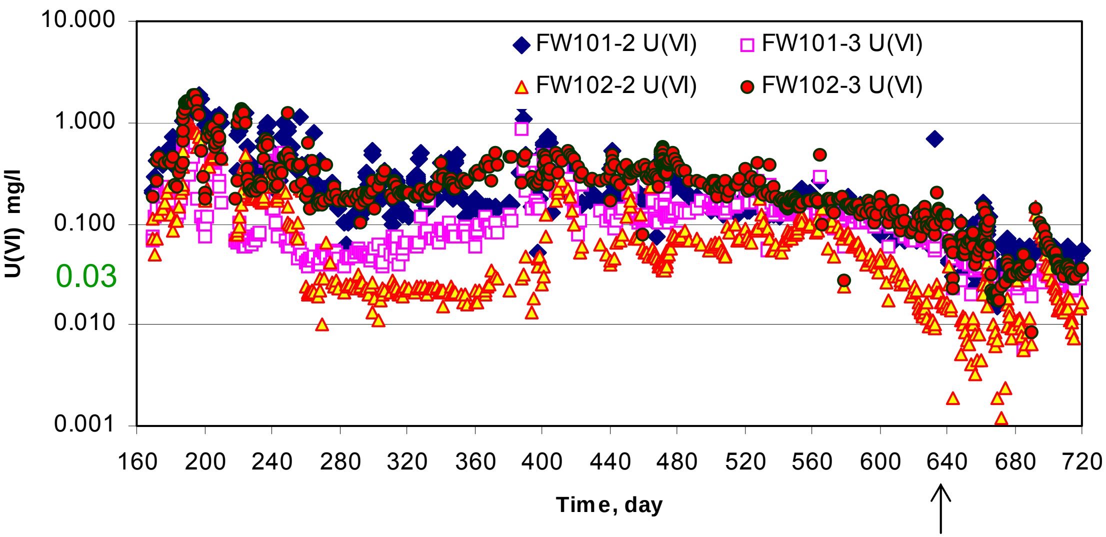


Sulfate in inner loop injection and extraction wells



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).

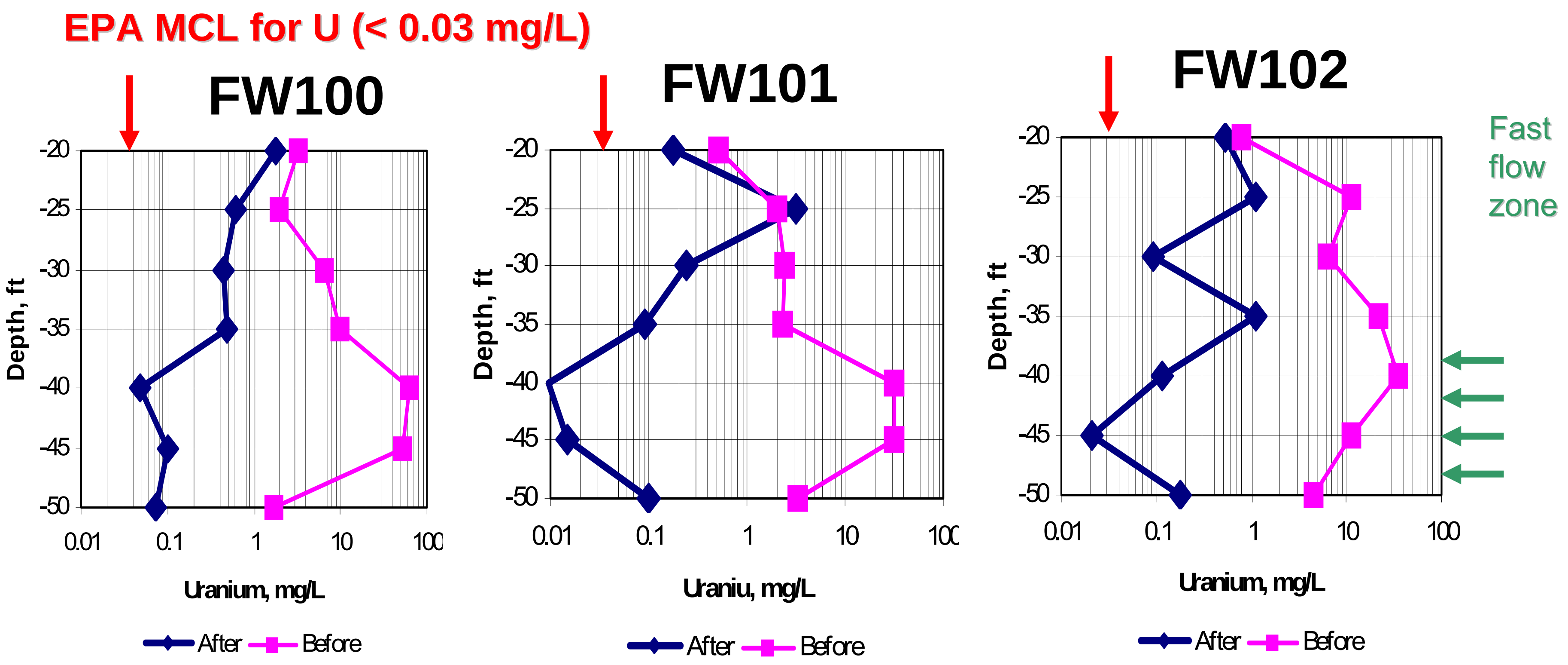
2. U(VI) concentration dropped below EPA MCL.

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

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

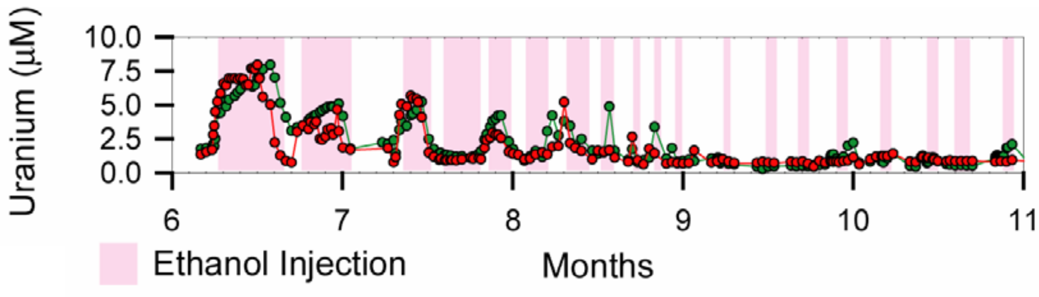
Maximum concentration of uranium in drinking water of 0.03 mg/l (US EPA) is achievable.

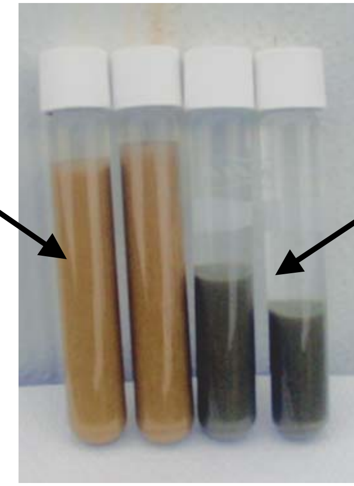
Aqueous U in the MLS Wells: Before and After



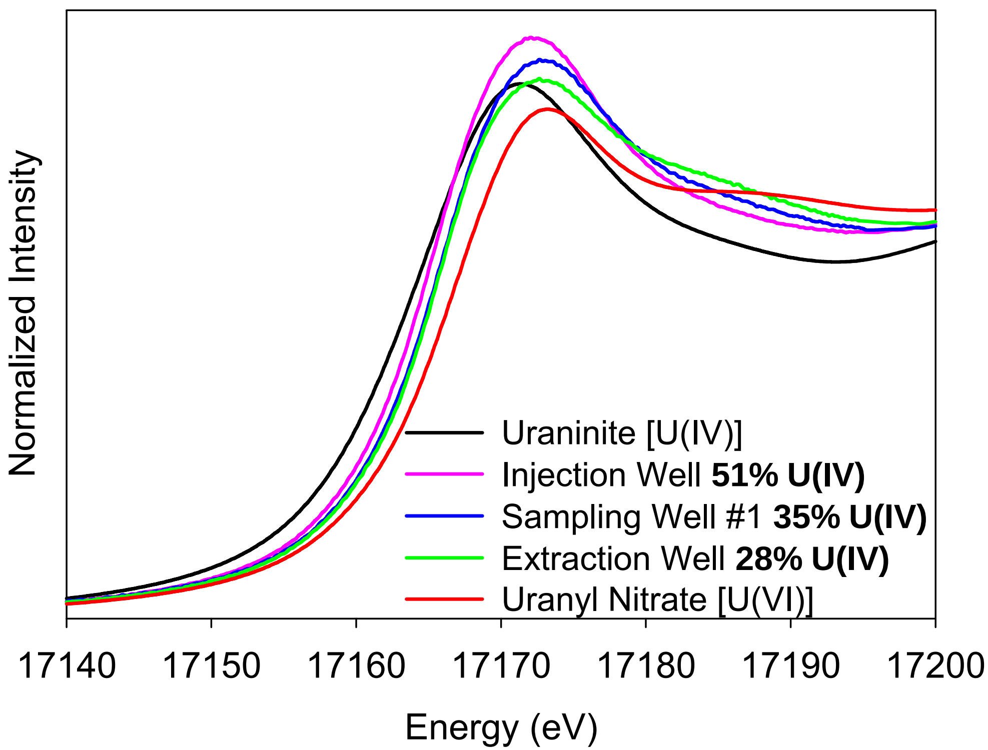
Samples before biostimulation: Feb - Apr, 2002
Samples after biostimulation: Oct 10, 2006

Solid Phase Uranium Speciation





Uranium L-edge XANES – Day 535

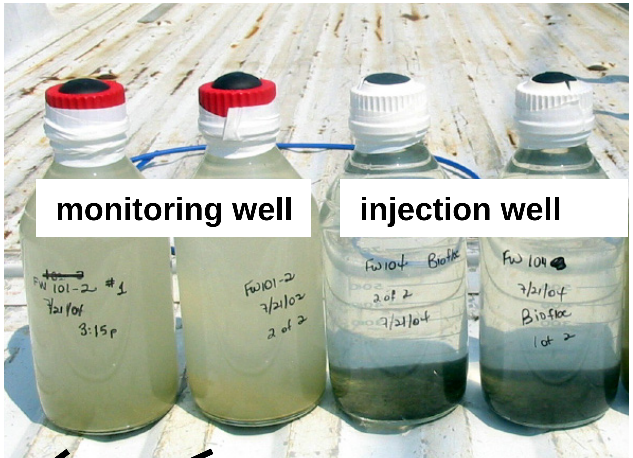


Summary of XANES data

Day	Well	U (g/kg)	% U(IV)
258	Inj.	2.60	39
271	Inj.	1.03	54
333	Inj.	ND	51
409	Extr.	1.29	0
409	Inj.	2.79	53
535	**Extr.**	**1.14**	**28**
535	**101-35ft**	**0.91**	**35**
535	**Inj.**	**4.32**	**51**

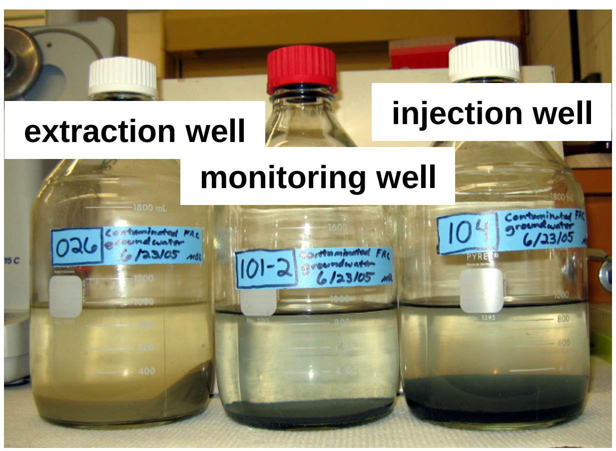
The sediment changes color as reduction progresses

Day 333



brown

Day 670



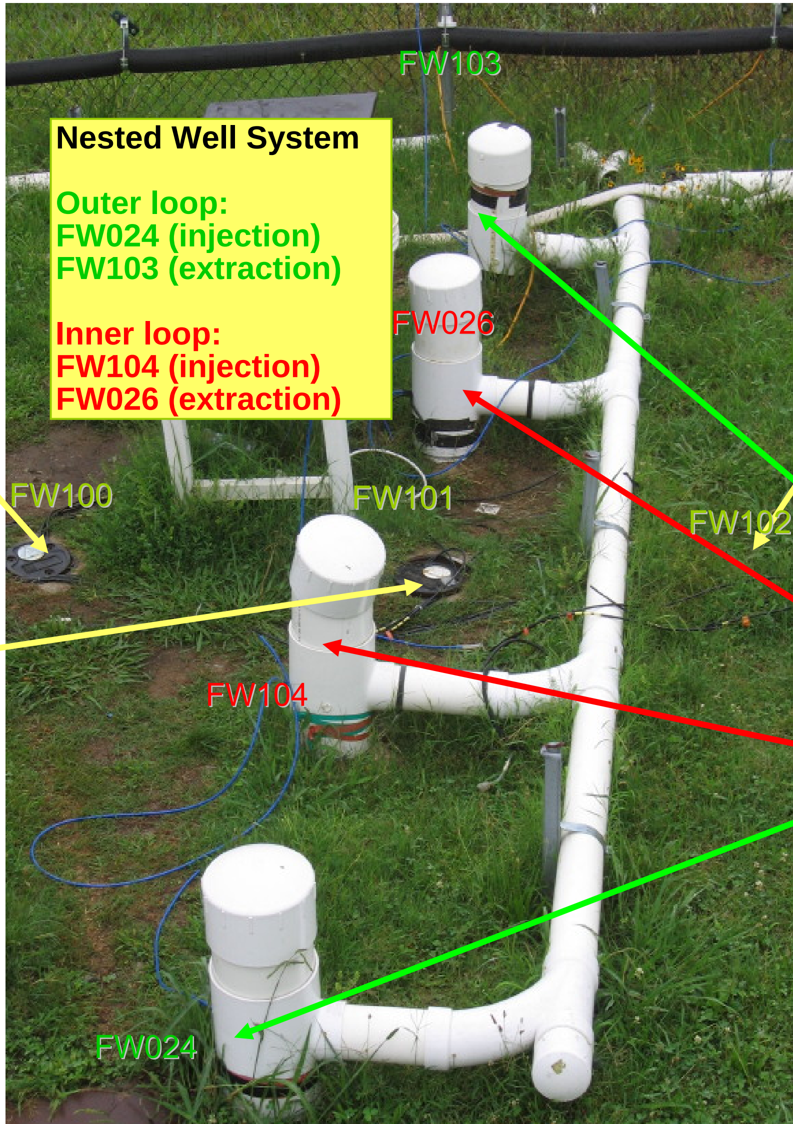
Now black

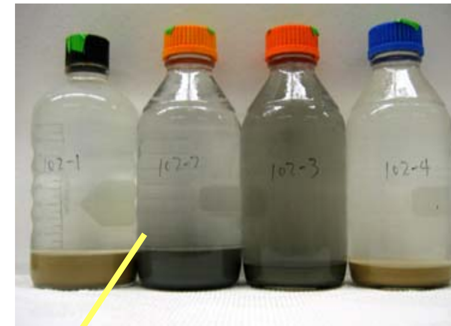
extraction well sample from day 670 incubated 3 days with no added ethanol

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

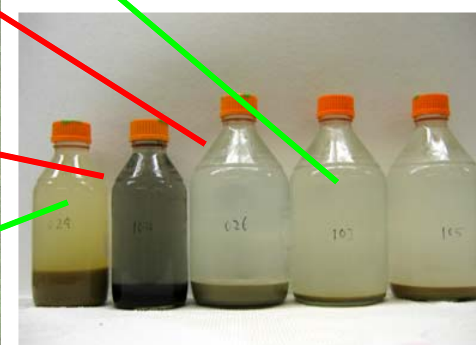
Samples from FW100 at 45ft, 40 ft, 35ft and 30ft.





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

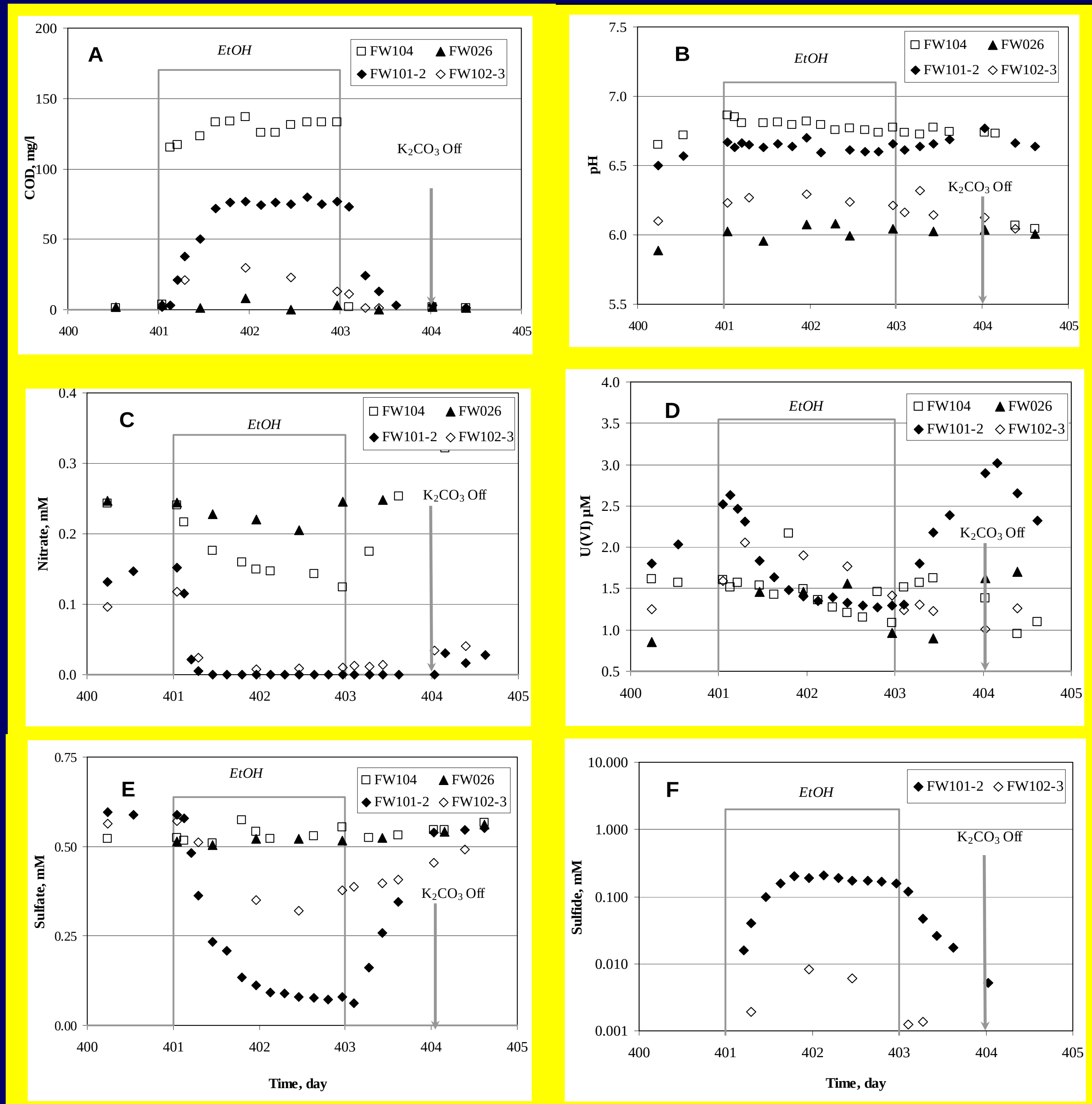
Samples from FW101 at 45ft, 40 ft, 35ft and 30ft.



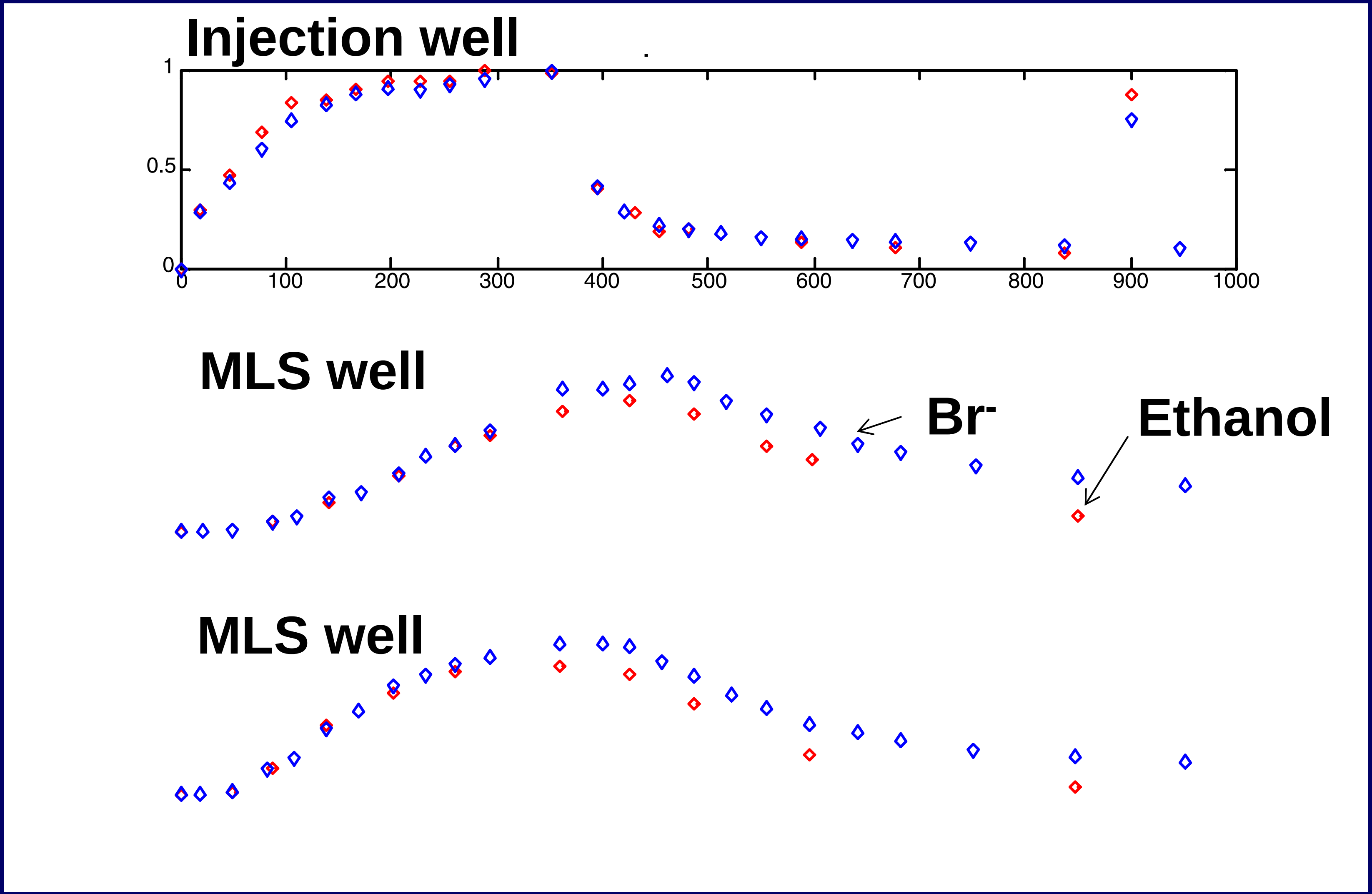
Samples from FW024, FW104, FW026, FW103 and FW105 (down gradient well).

Example sequence (days 399-409):

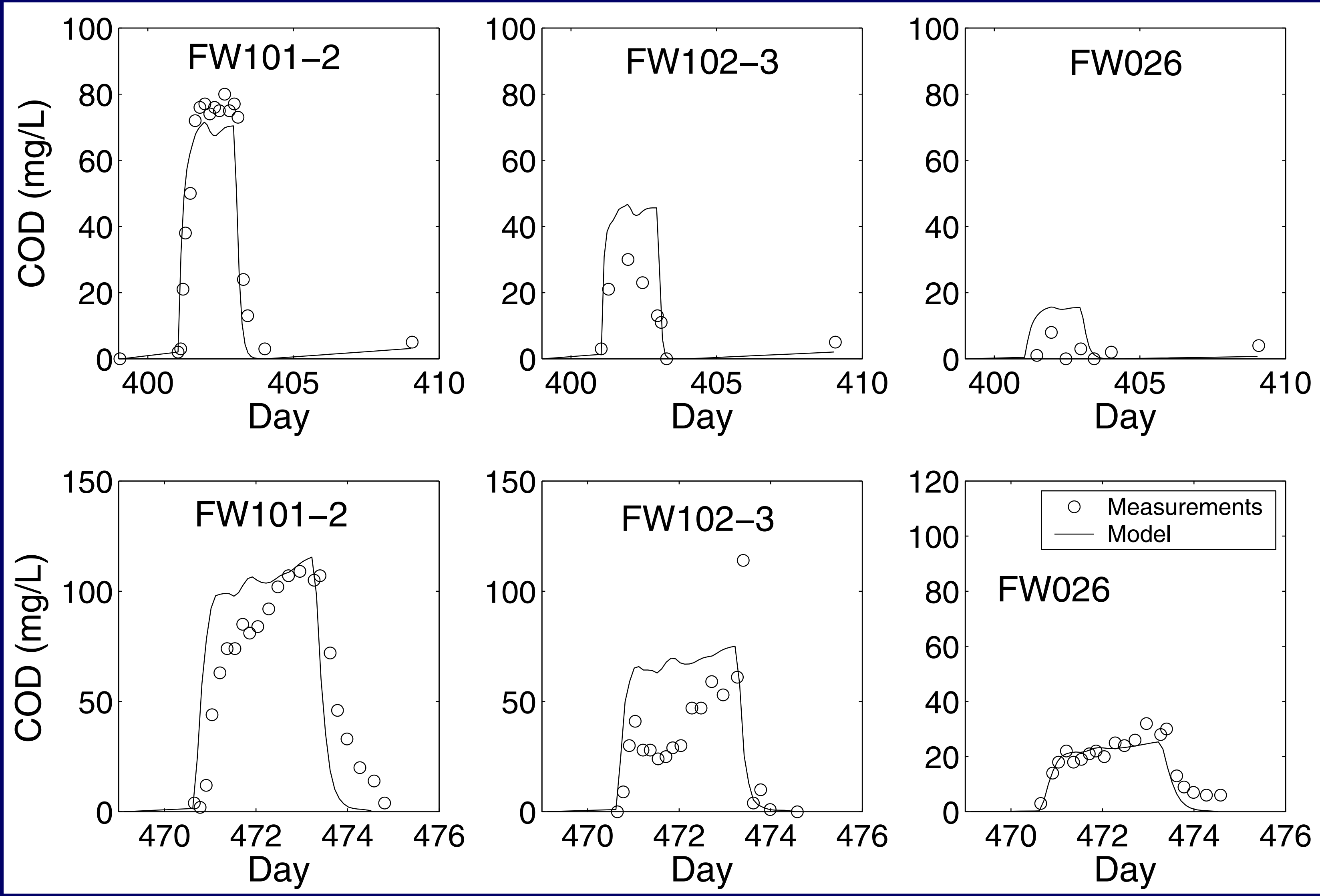
1. + carbonate
2. + ethanol
3. - ethanol
4. - carbonate



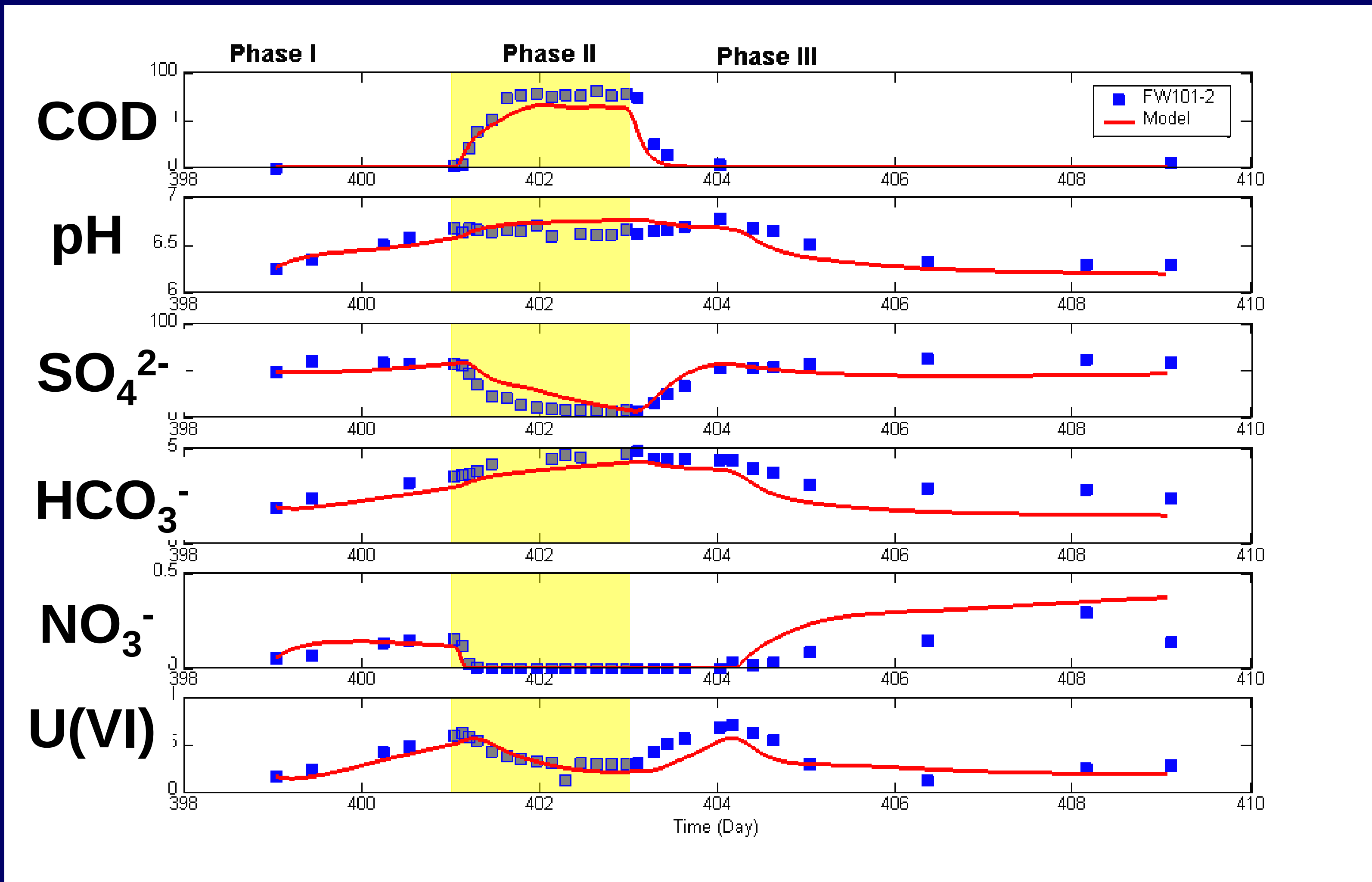
Model calibration: ethanol and bromide tracer study



Predictions for ethanol consumption



Reactive transport simulation (Days 399-409)



Snapshot of dominant sediment organisms

(Day 774)

Groups listed comprised at least 5% of the total 16S rRNA gene clone libraries.

Family	Dominant Genus	Relative abundance (% of total clones)					
		104	101-2	101-3	102-2	102-3	26
Desulfovibrionaceae	*Desulfovibrio*	7	15	5	4	12	5
Geobacteraceae	*Geobacter*	2	1	1	11	1	1
Rhodocyclaceae	*Ferribacterium*	12	6	38	10	17	18
Hydrogenophilaceae	*Thiobacillus*	5	27	0	1	4	5
Acidobacteraceae	*Geothrix*	12	7	10	4	10	16
Oxalobacteraceae	*Duganella*	9	10	2	2	11	2
Xhantomonadaceae	*Rhodanobacter*	6	2	0	5	5	0
Commanonadaceae	*Acidovorax*	2	1	2	1	2	6
Sphingomonadaceae	*Sphingomonas*	6	0	1	2	2	1
other families		39	31	41	60	36	46

Source: Cardenas et al., unpublished data

Time series for wells FW-101-2 and FW-104 (source: Hwang et al., unpublished)

	FW-101-2	**FW-104**
166d	Unc. bacterium clone 300I-F12 (26%) *Herbaspirillum* sp. isolate G8A1 (39%)	Unc. bacterium clone 300I-F12 (23%) *Herbaspirillum* sp. isolate G8A1 (27%) Unc. soil bacterium clone D04 (11%)
535d	*Acidovorax delafieldii* isolate N7-18 (10%) *Acidovorax delafieldii* isolate N7-18 (7%) Unc. δ-proteobacterium clone 177T36 (6%) Unc. *Actinobacteriaceae* clone Hrh678 (6%) *Dechlorosoma* sp. C6 (5%)	Unc. Sludge bacterium H22 (15%) Unc. bacterium clone 300I-F12 (7%) Unc. Bacterium clone 015B-B03 (7%) *Acaligenes defragans* strain:PD-19 (6%) *Dechlorosoma* sp. C6 (10%)
641d	Unc. bacterium clone TTMF87 (16%) Unc. δ-proteobacterium clone 177T36 (14%) Unc. *Desulfovibrionacaceae* bacterium (7%) *Desulfovibrio magneticus* (6%) Unc. δ-proteobacterium clone 036T7 (9%) Unc. *Geobacter* sp. clone KB-1 1 (7%) Unc. *Phyllobacterium* sp. clone Ph (6%) *Rhizobium* sp. SDW058 (6%)	Unc. δ-proteobacterium clone 177T36 (17%) Unc. *Desulfovibrionacaceae* bacterium (4%) *Desulfovibrio magneticus* (2%) Unc. *Actinobacteriaceae* clone Hrh678 (7%) Unc. δ-proteobacterium clone 036T7 (6%) Unc. *Geobacter* sp. clone KB-1 1 (4%)

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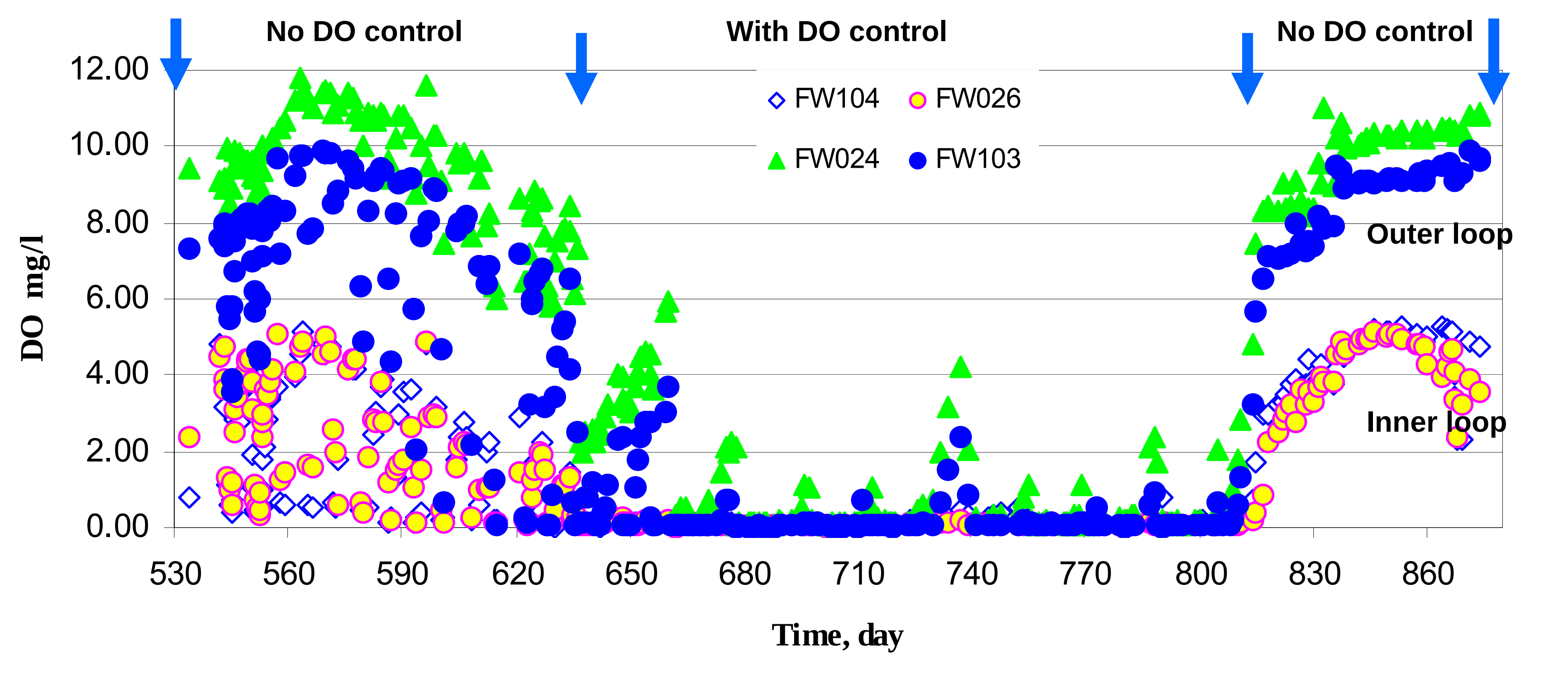
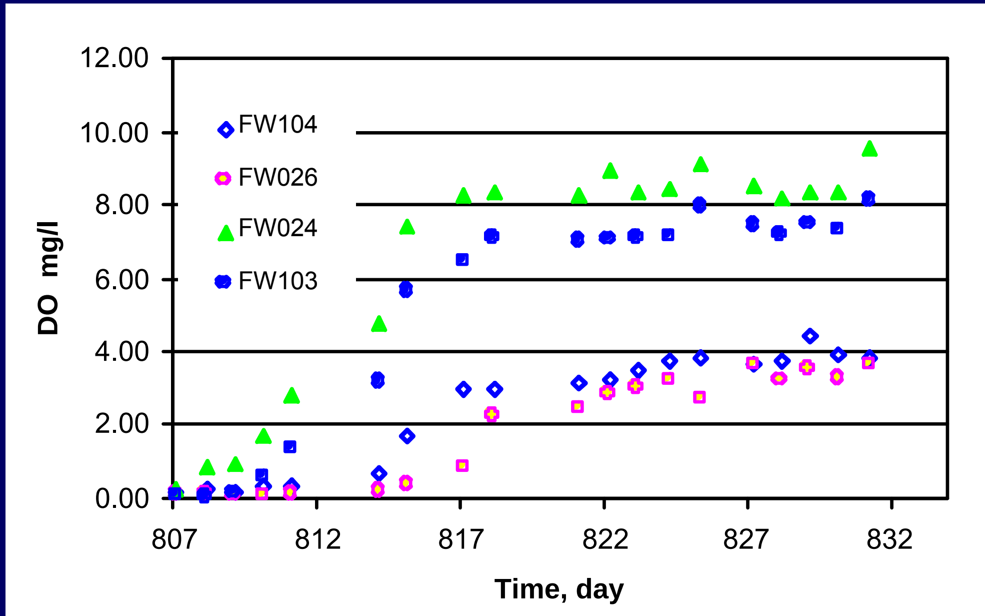
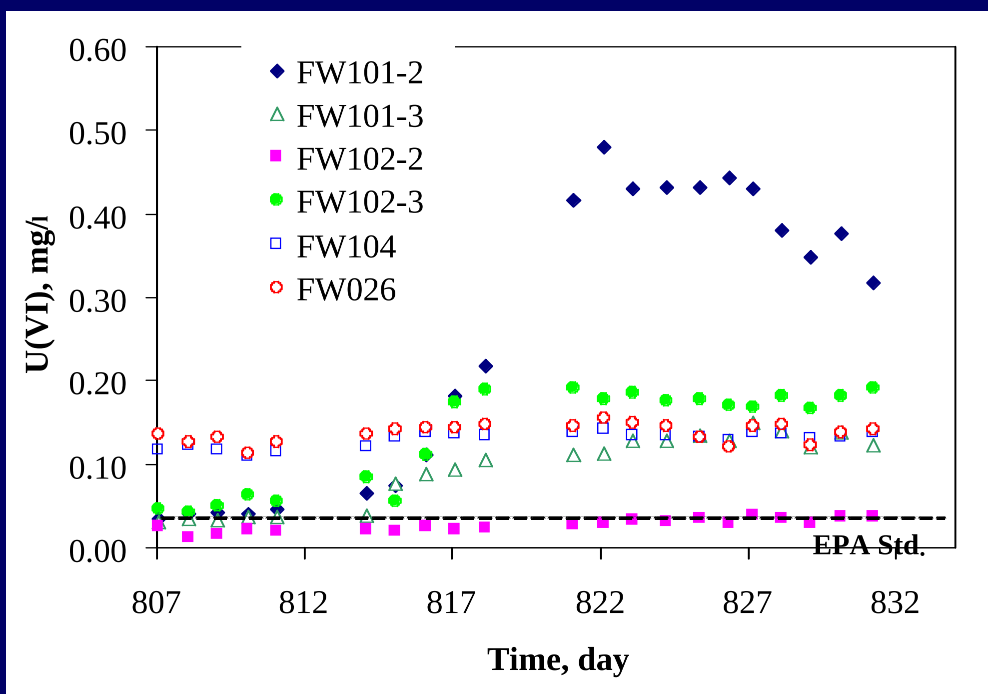
Changes in DO in the inner and outer loop







U stability was spatially variable with O_2 in system

Conclusions

- Stepwise remediation enabled process control & gave insight into mechanisms. Useful steps: geophysics, tracer studies, removal of inhibitors and clogging agents, pH control over sorption/desorption.

- The nested recirculation scheme is a useful pilot-scale strategy for highly contaminated sites.

- Very low aqueous phase concentrations can be achieved despite high solid phase concentrations. This is evidently due to the low solubility of U(IV) and low rates of desorption/dissolution relative to rate of reduction.

- For the anaerobic conditions tested (bicarbonate < 5 mM, Ca < 0.5 mM, pH near 6.0), bioreduced U(IV) is stable. Oxygen and nitrate reoxidize U(IV) in current system.