Field-Scale Evaluation of Biostimulation for Remediation of Uranium-Contaminated GW at FRC Area 3:

Project Update and Modeling Issues

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October 2006

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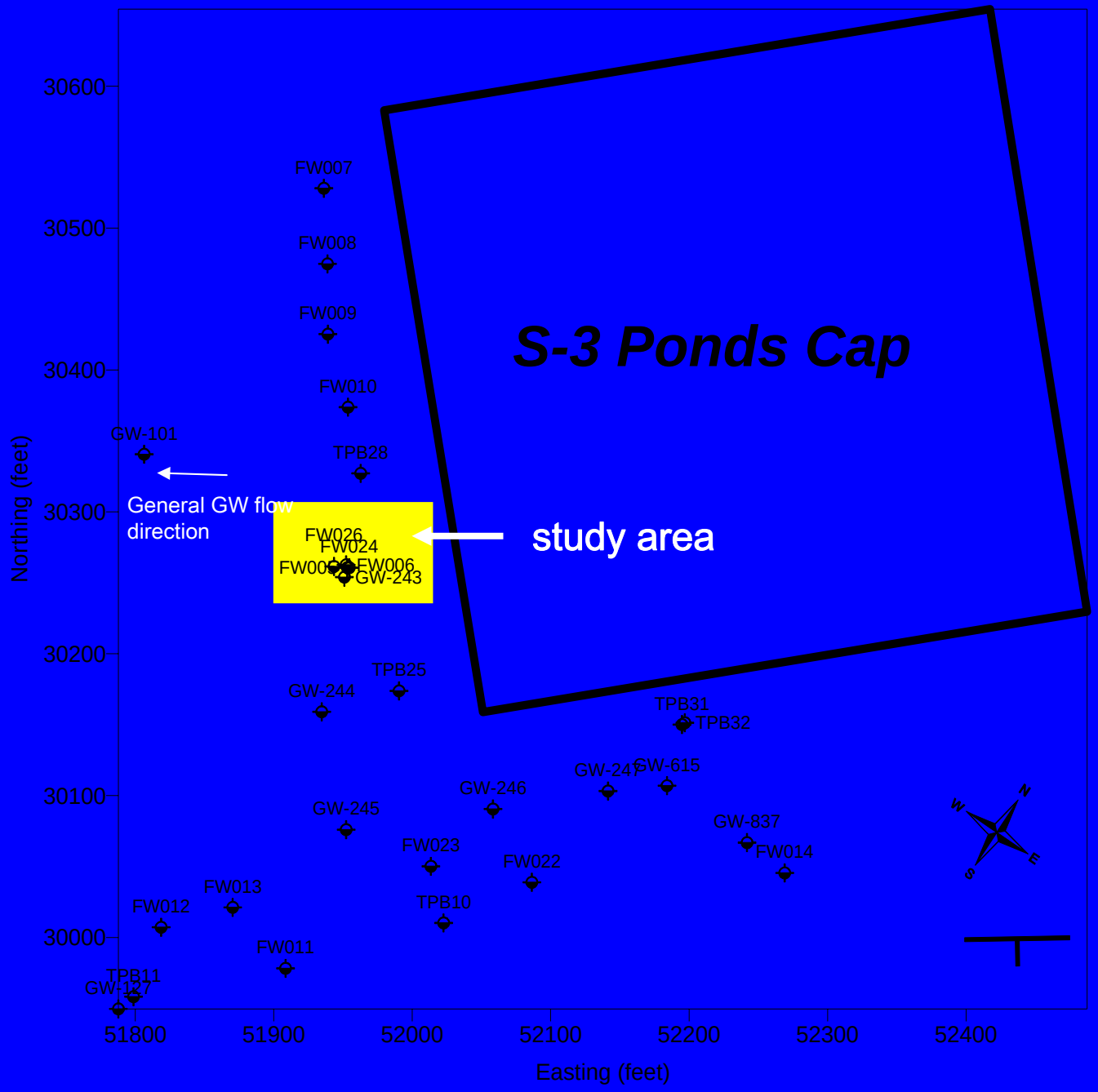
Outline

- Review of Important Milestones and Contributions of this Project.
- Update on Most Recent Work (Re-Oxidation).
- Comments on the Role of Modeling.

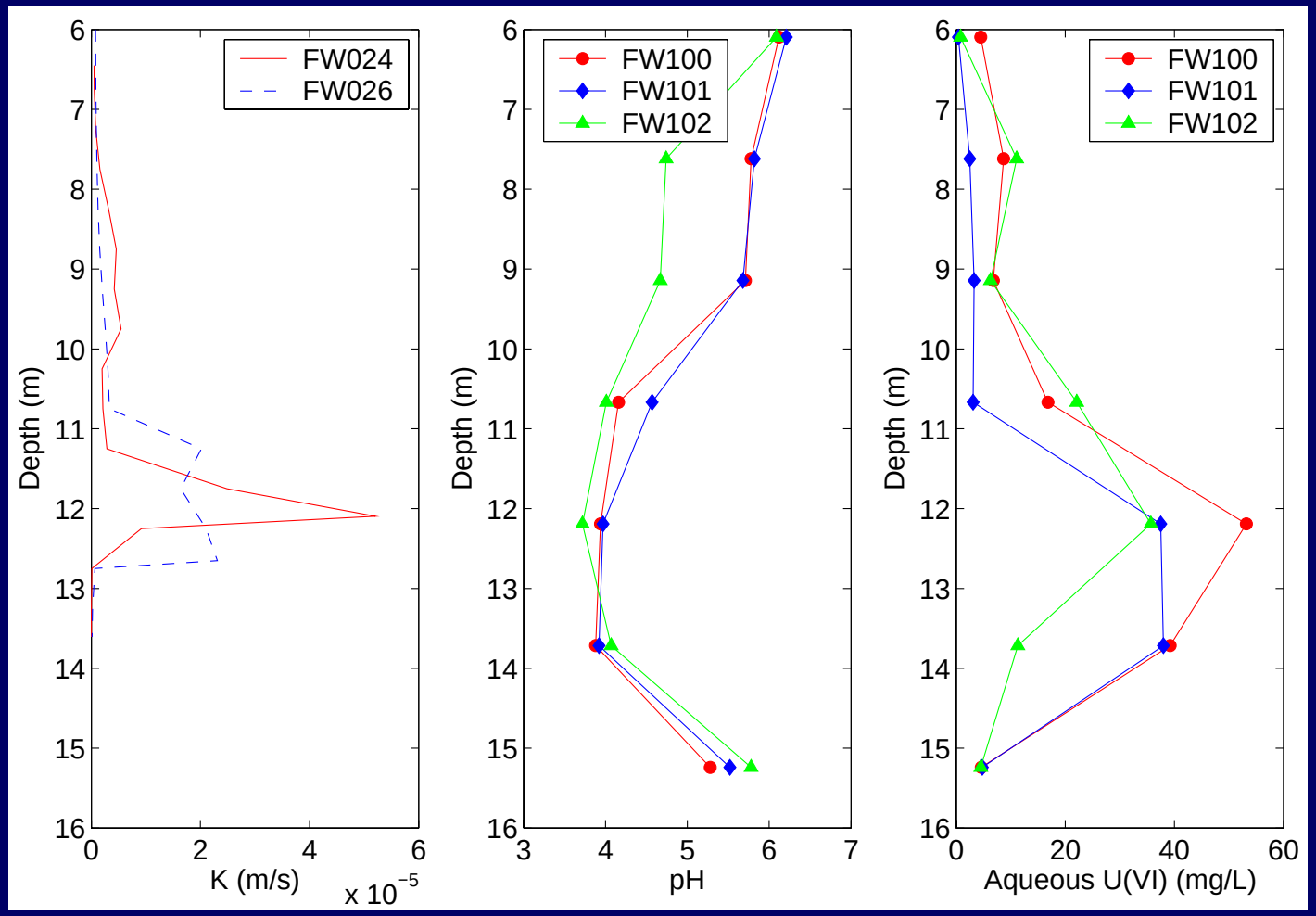
Site characterization (Jan. 2001 to August 2003)

- Characterization of hydrogeology, geochemistry, and microbial background.
- Feasibility study of uranium reduction and immobilization.
- Column tests for bioreduction-immobilization of uranium


S-3 Ponds Cap
study area
General GW 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
30600
30500
30400
30300
30200
30100
30000
51800
51900
52000
52100
52200
52300
52400
Northing (feet)
Easting (feet)
N
W
E
S

S-3 Ponds
parking lot
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

Initial Depth Profiles



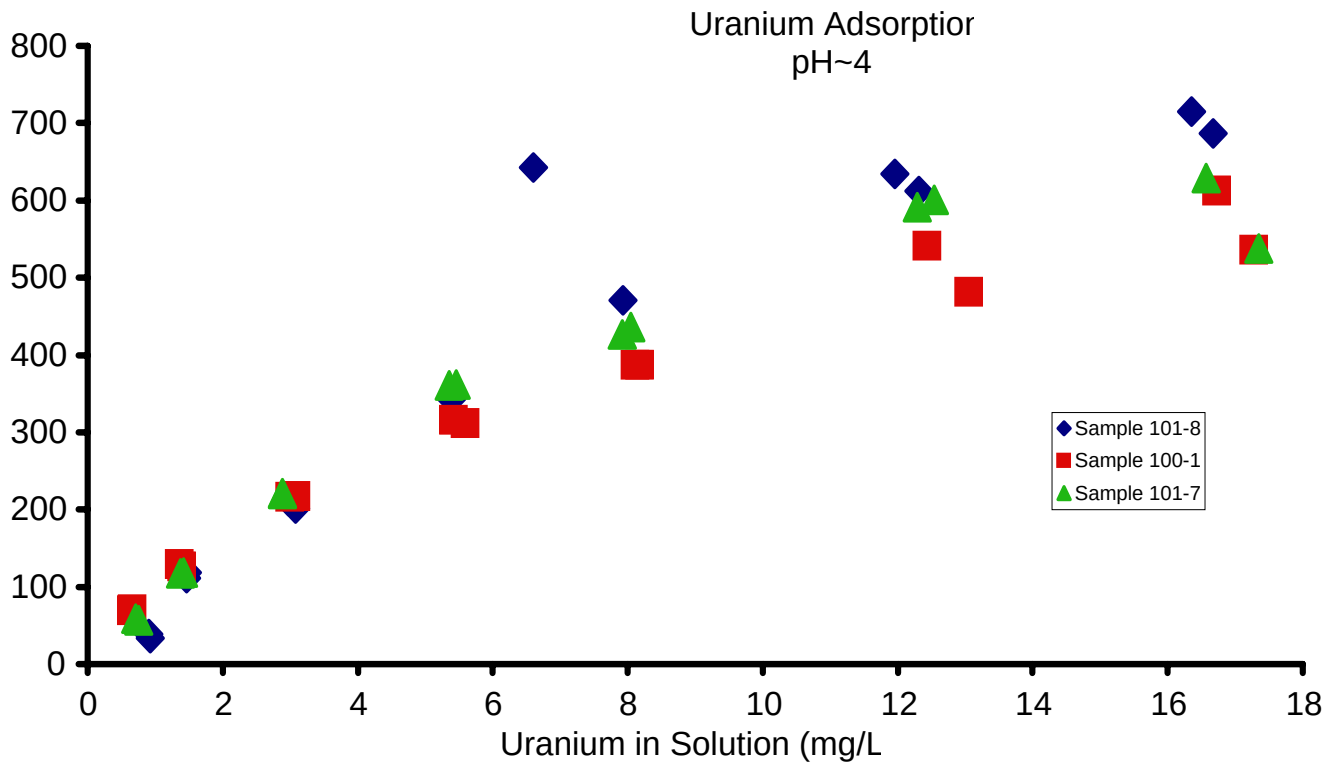
Representative Initial Groundwater Composition

Inorganic	Concentrations	Organic	Concentrations
pH	3.4-3.6	BOD5	100 mg/L*
TIC	202-401 mg/L	COD	200 mg/L*
Chloride	249-298 mg/L	TOC	65-81 mg/L
Sulfate	843-1116 mg/L	2-Butanone	69-84 µg/L
Nitrate	7500-8963 mg/L	Acetone	340-700 µg/L
Nitrite	Low	Ethanol	200 µg/L
Uranium	42-51 mg/L	Chloroform	34-36 µg/L
Technetium-99	35-40 nCi/L (80-89 dpm/ml)	Tetrachloroethene	2100-3300 µg/L
Ni	11.5-14 mg/L	Trichloroethene	94-130 µg/L
Cd	0.45 mg/L	cis-1,2 Dichloroethene	700-740 µg/L
Al	541±45 mg/L	1,1,2-trichloro-1,2,2-trifluoroethane	1200-1500 µg/L
Ca	931±74 mg/L	Methylene chloride	39-42 µg/L
Mg	174±11 mg/L	Citric acid	~6 mg/L #
Mn	130±9 mg/L	Acetic acid	~120 mg/L #
Sb	<0.003 mg/L		
Cr	0.17 mg/L		
Pb	0.03 mg/L		
Se	0.02 mg/L		

(* estimated values; # values for MLS FW101, 40’ depth)

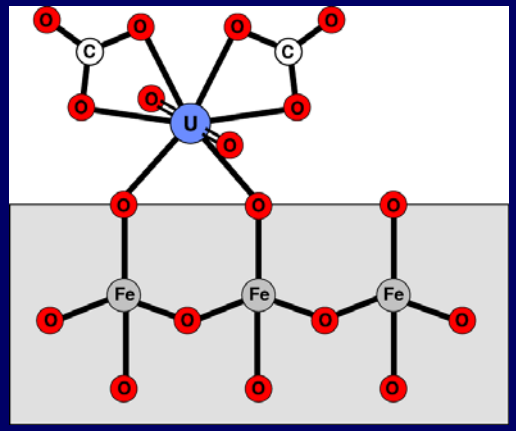
- U 40-50mg/l
- pH 3.4-3.6
- Nitrate 7500-8963 mg/L
- Al 541 mg/L
- Ca 931 mg/L

The aqueous phase U concentrations exceed the U.S. EPA drinking water (0.03mg/l) standard by 1000 times.
Much more U is on the soil, as illustrated by the sorption isotherm at pH 4.

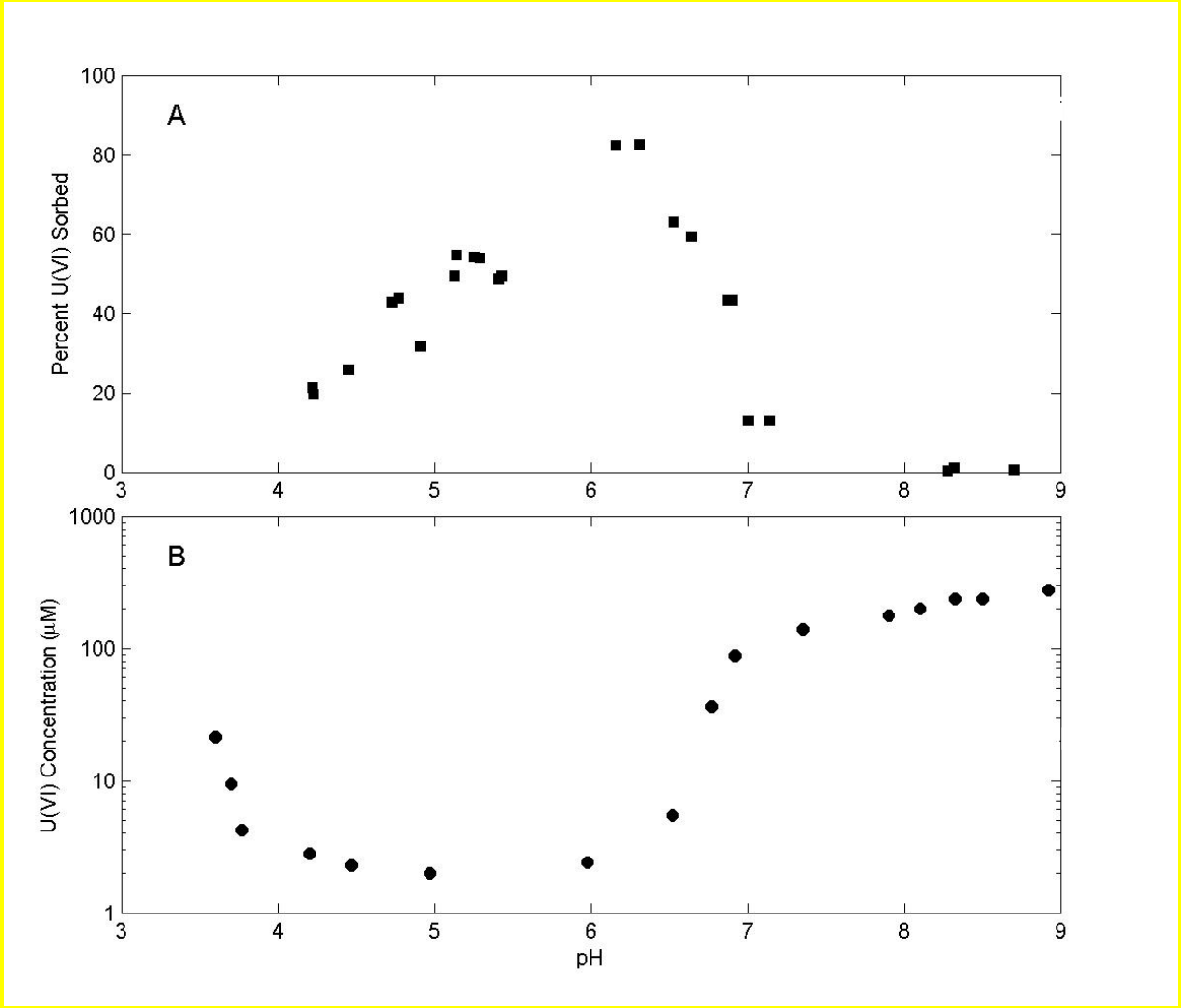


U sorption and desorption are strongly pH dependent.

Complexes at surfaces:



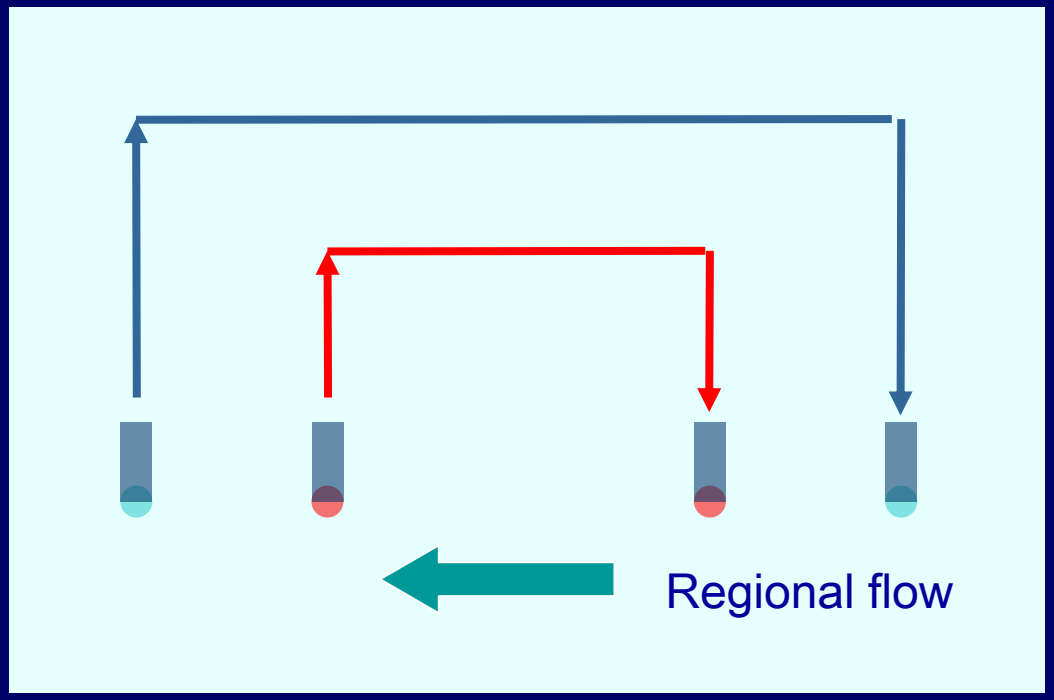
Source: Catalano (2004)

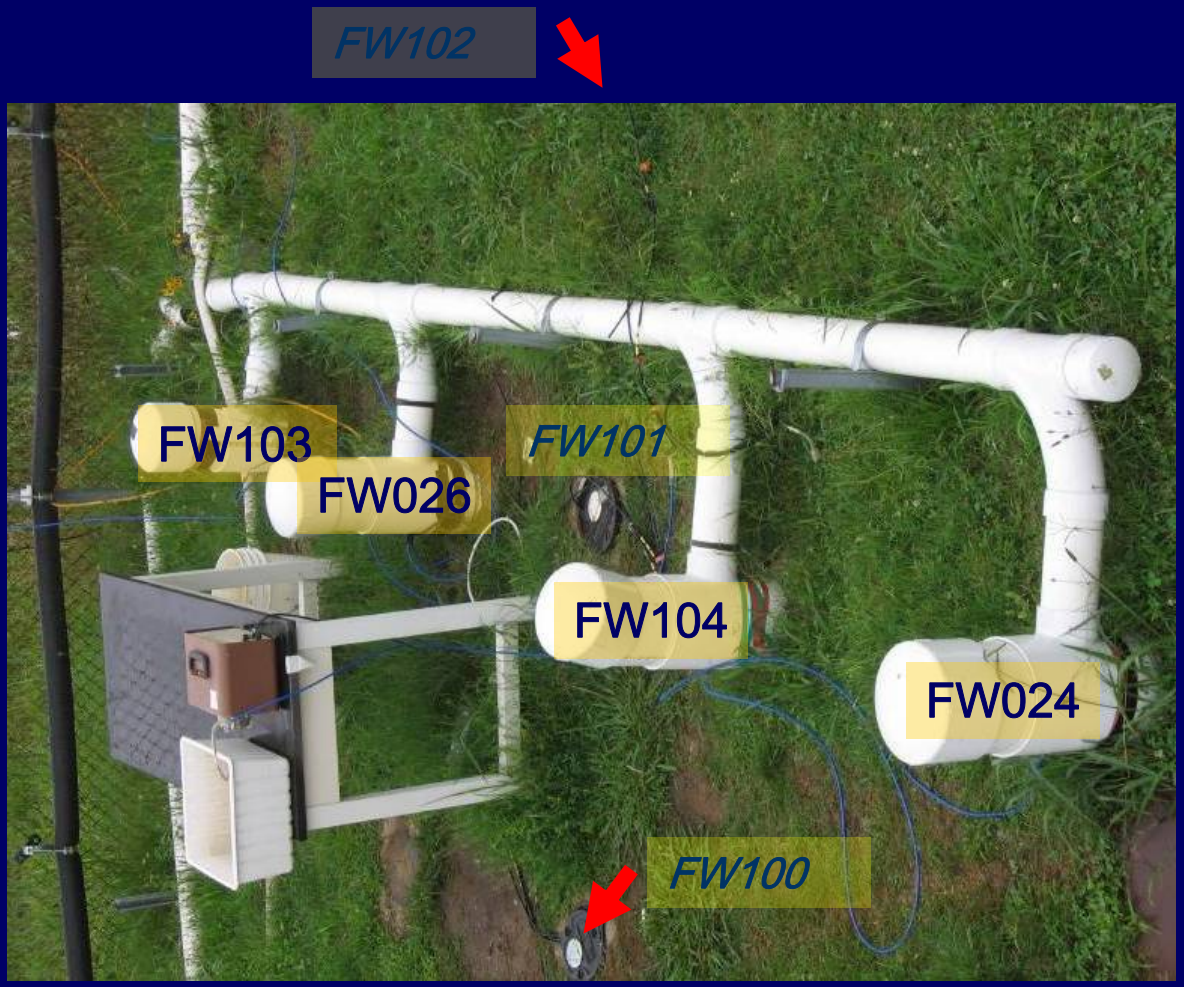


Design and installation of treatment system (Jan. 2002 to August 2003)

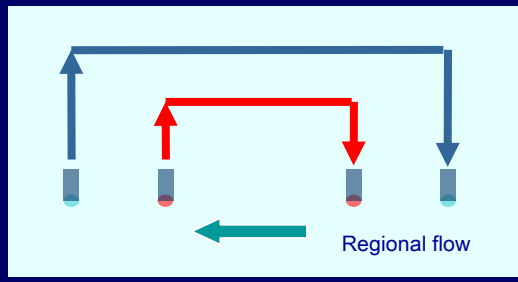
1) Development of a nested well system for hydraulic control of groundwater flow.
2) Design and installation of above-ground system to remove Al, Ca, and nitrate

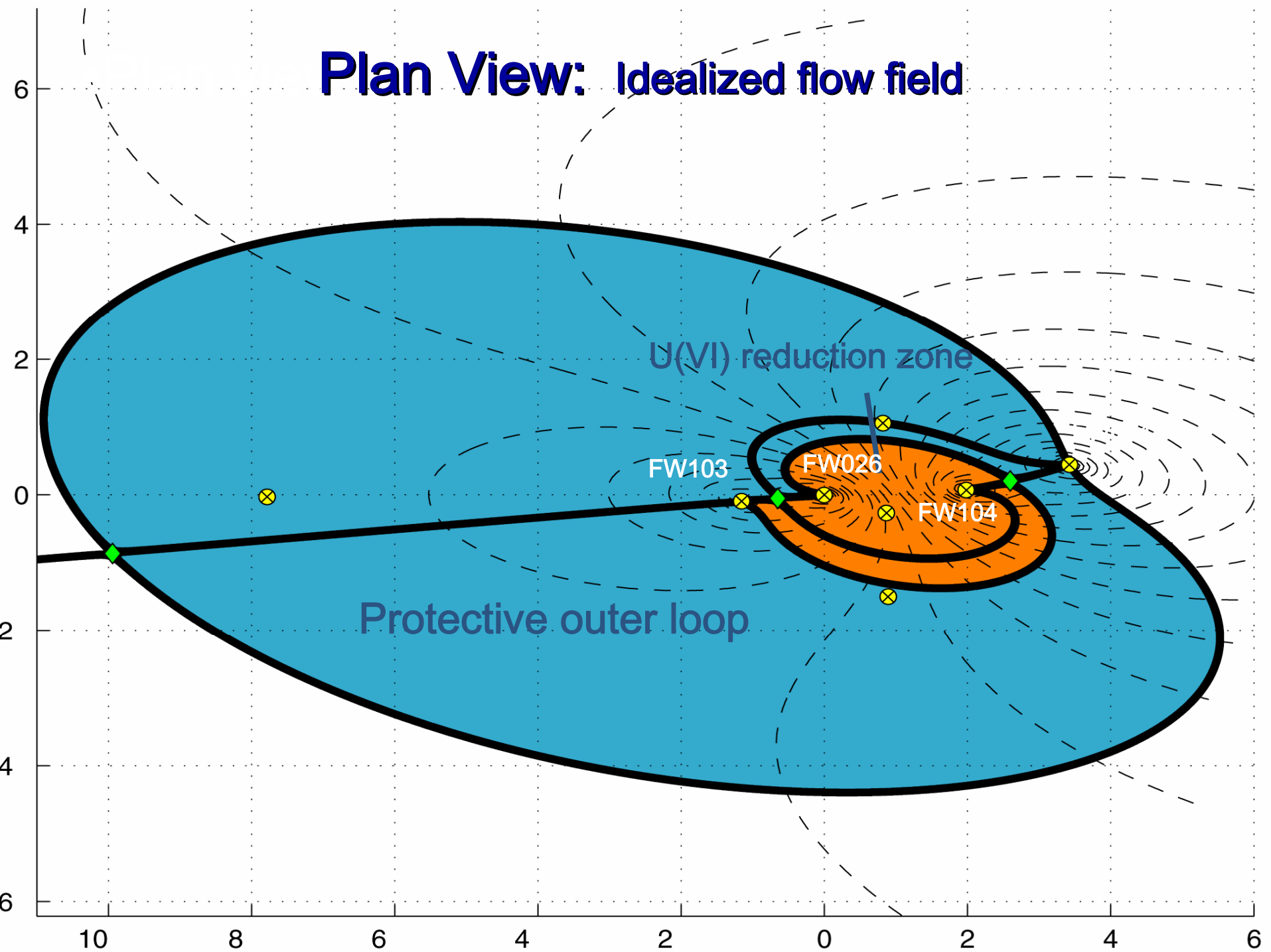
A Nested-Cell System





Injection Extraction And MLS Wells




Plan View: Idealized flow field
U(VI) reduction zone
FW103
FW026
FW104
Protective outer loop
6
4
2
0
2
4
6
10
8
6
4
2
0
2
4
6

The aboveground treatment train

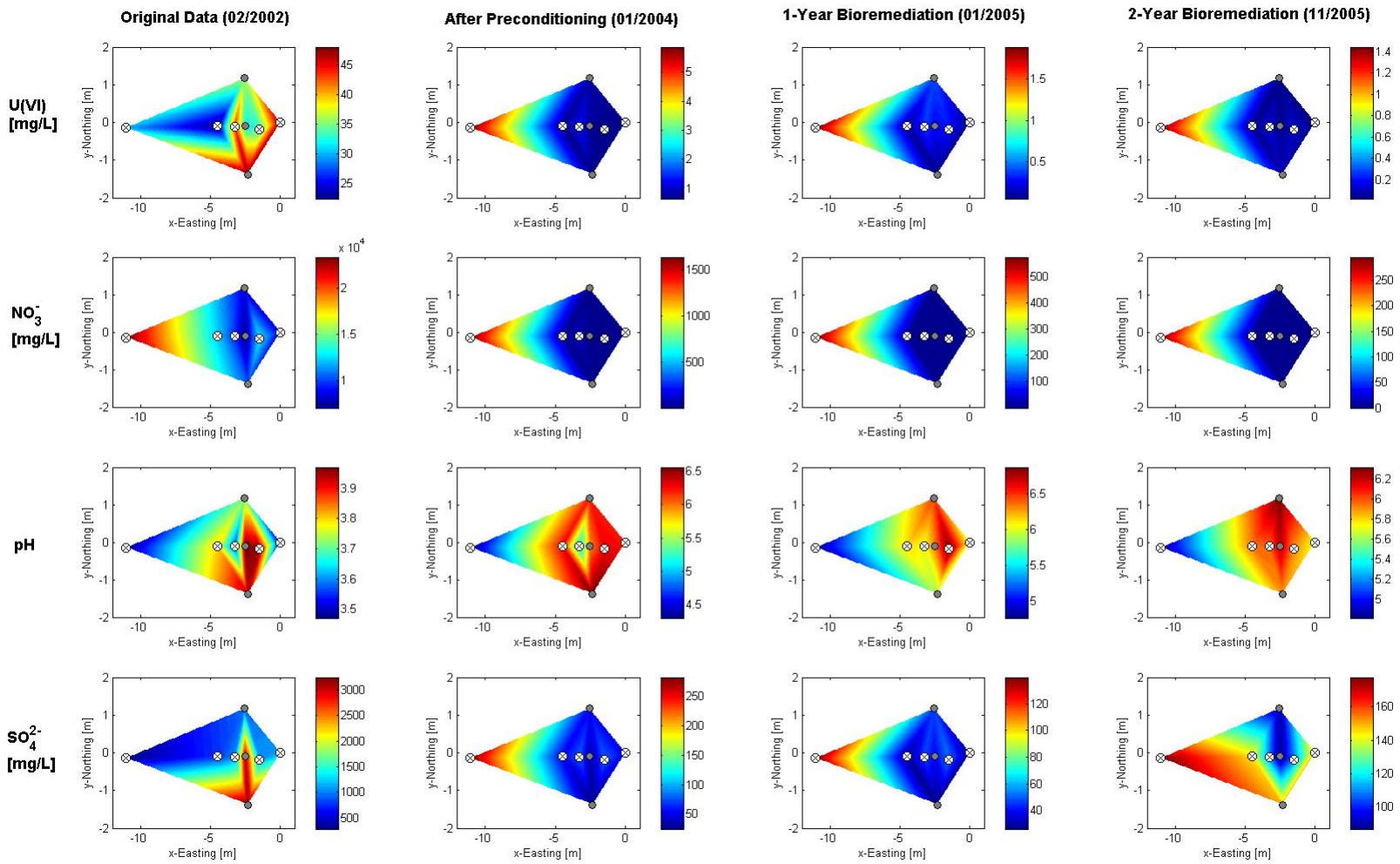
Vacuum stripper

Two-step chemical precipitation

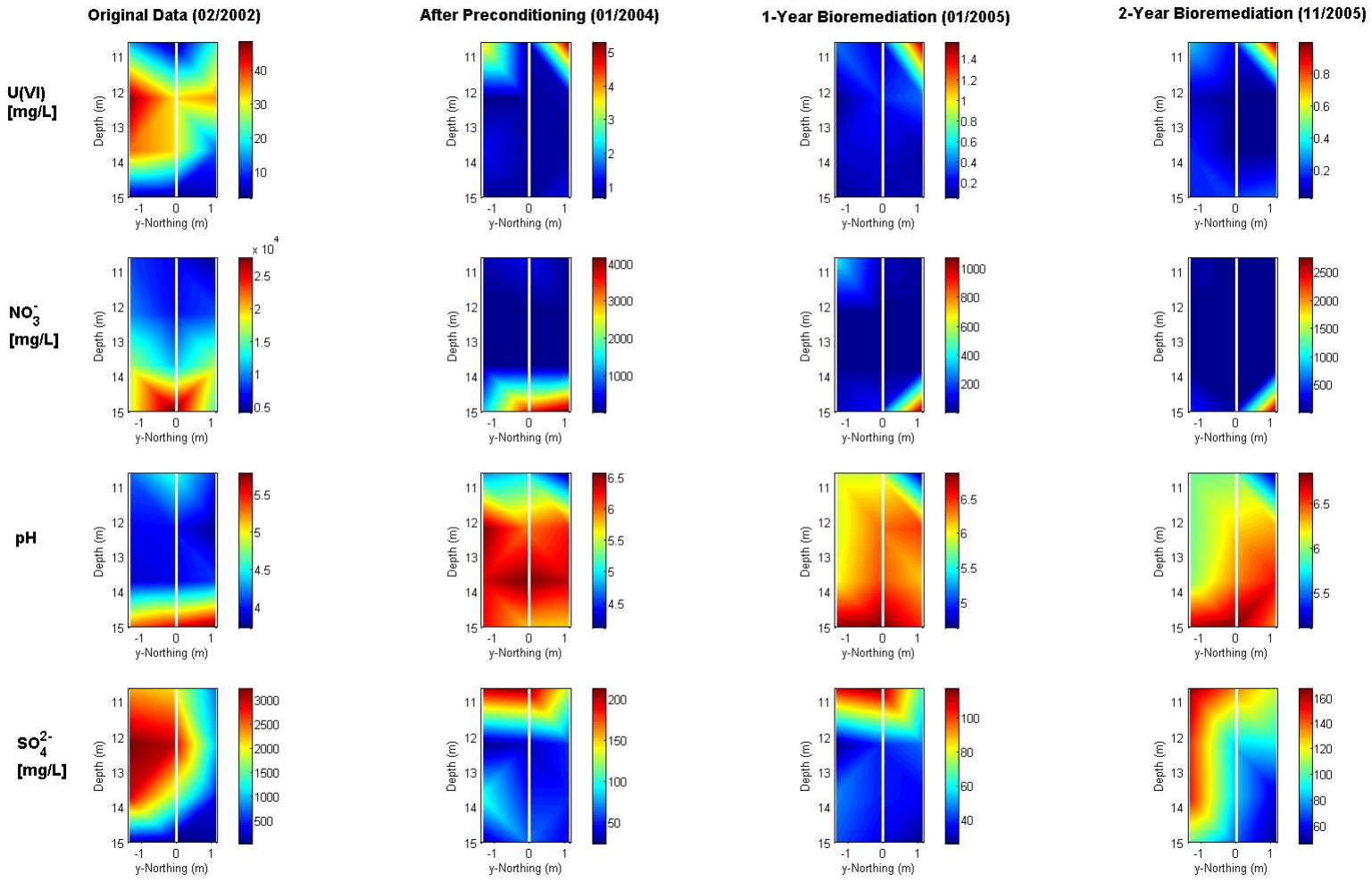
Fluidized bed reactor (FBR)

Field test
(August 23, 2003 to present)

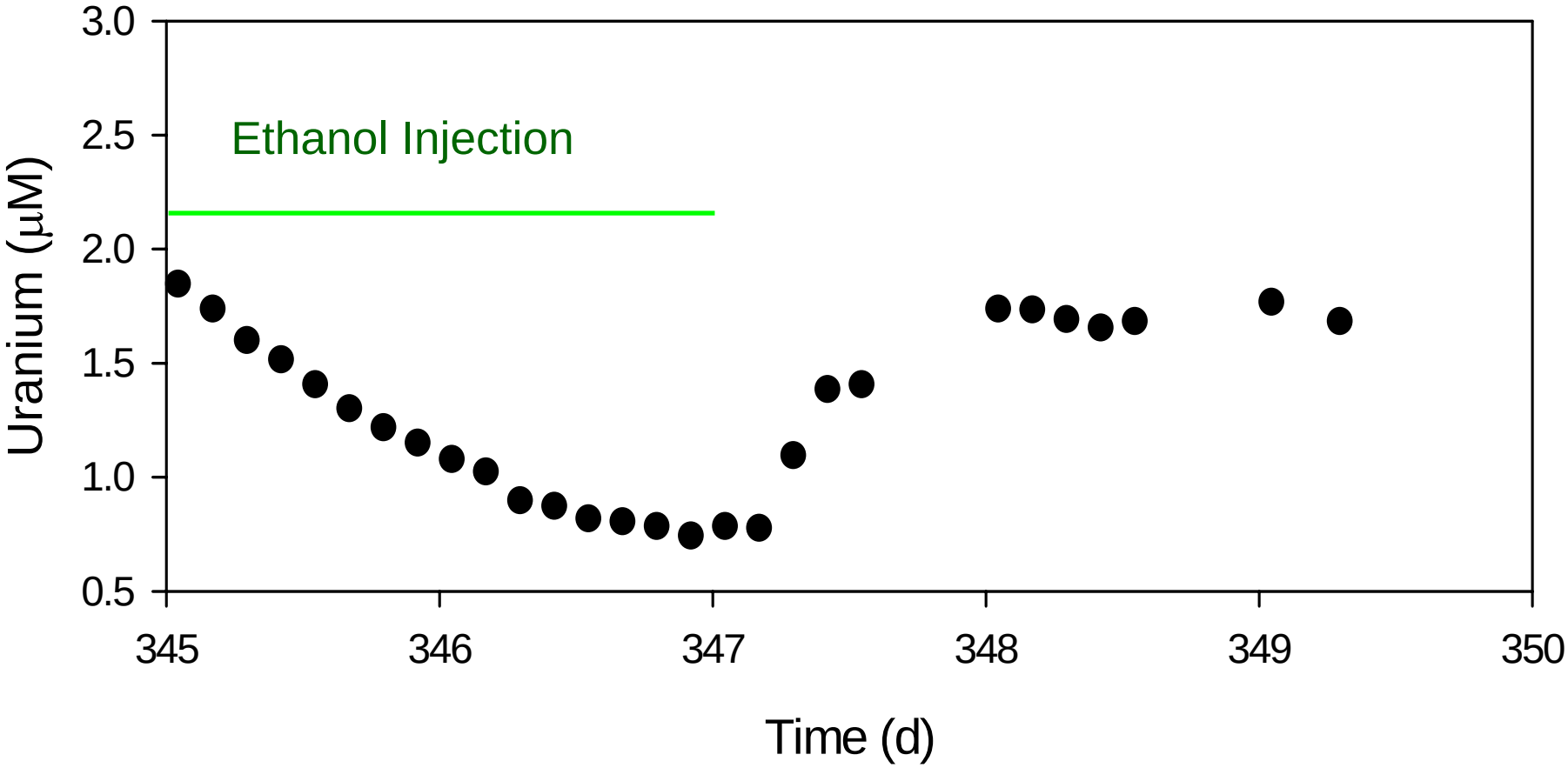
1) Flushing with clean water to remove bulk nitrate and Al, and to raise pH close to 6.0 (day 1-136).
2) In-situ denitrification to remove residual nitrate (day 137-184).
3) In-situ U(VI) reduction/immobilization (day 185-712).



The evolution of spatial distributions of concentrations over the in-situ bioremediation experiment. Horizontal plane is at depth 12m (i.e., the port “-3” of the MLS wells). Vertical scale is exaggerated.



The evolution of spatial distributions of concentrations over the in-situ bioremediation experiment. Vertical plane contains the MLS wells (represented by the white columns).

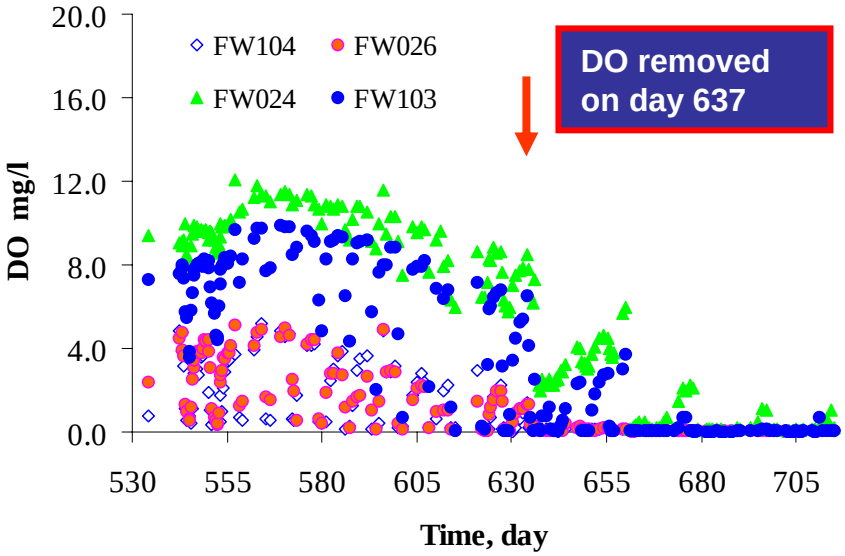


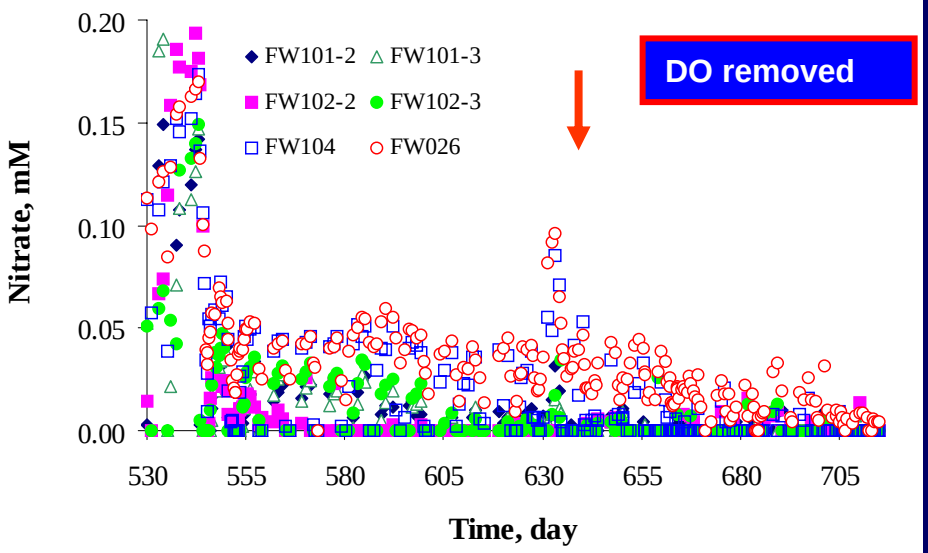
Representative dissolved U(VI) concentrations in a sampling well during and after ethanol injection.

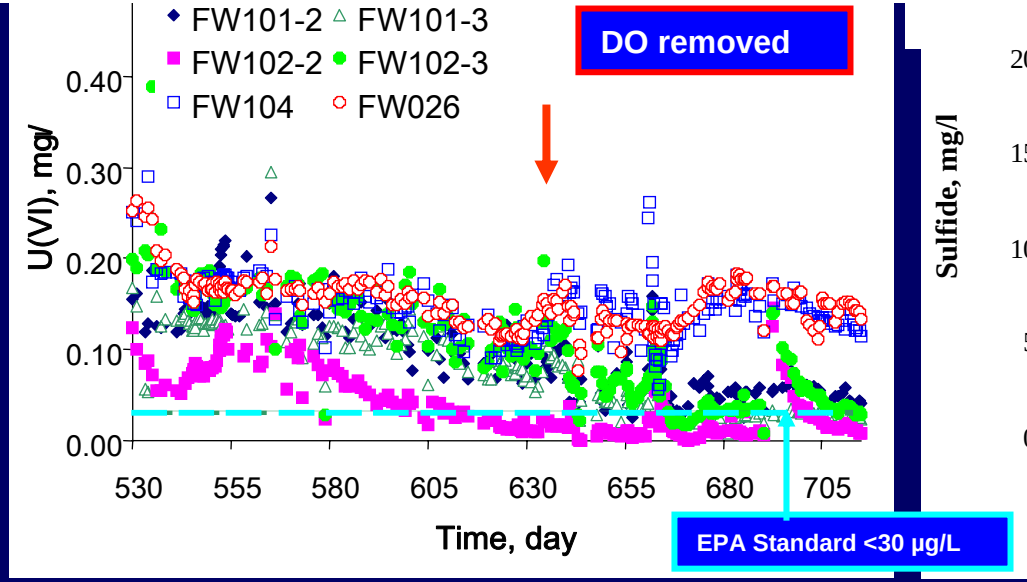
Field test (August 23, 2003 to present) (cont.)

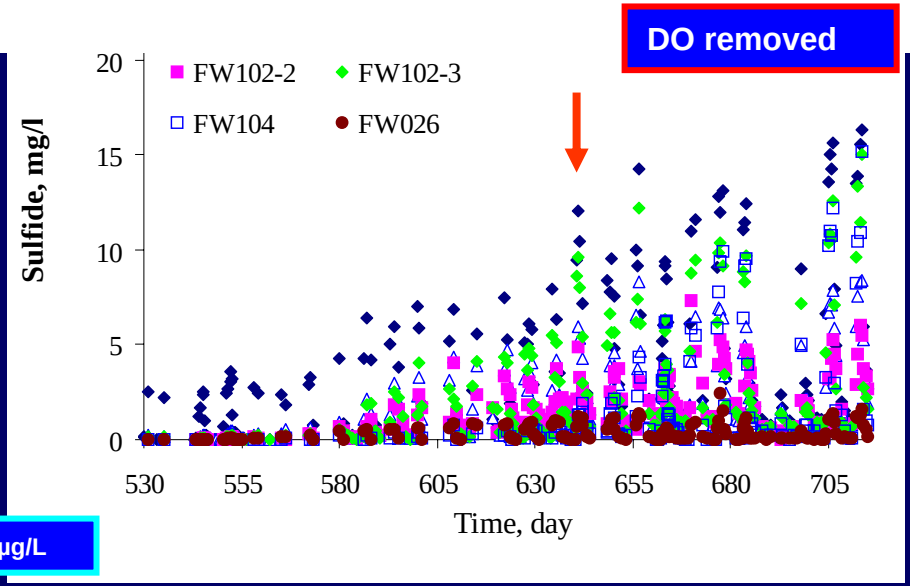
4) Evaluate factors that influence the stability of immobilized uranium (day 713-present).
5) Microbial community analysis of treatment area using clone library, MPN and microarrays
6) Characterization of uranium speciation in sediments using XANES & EXAFS to confirm bioreduction/immobilization of uranium.

Biostimulation with and without DO control (days 530-710)

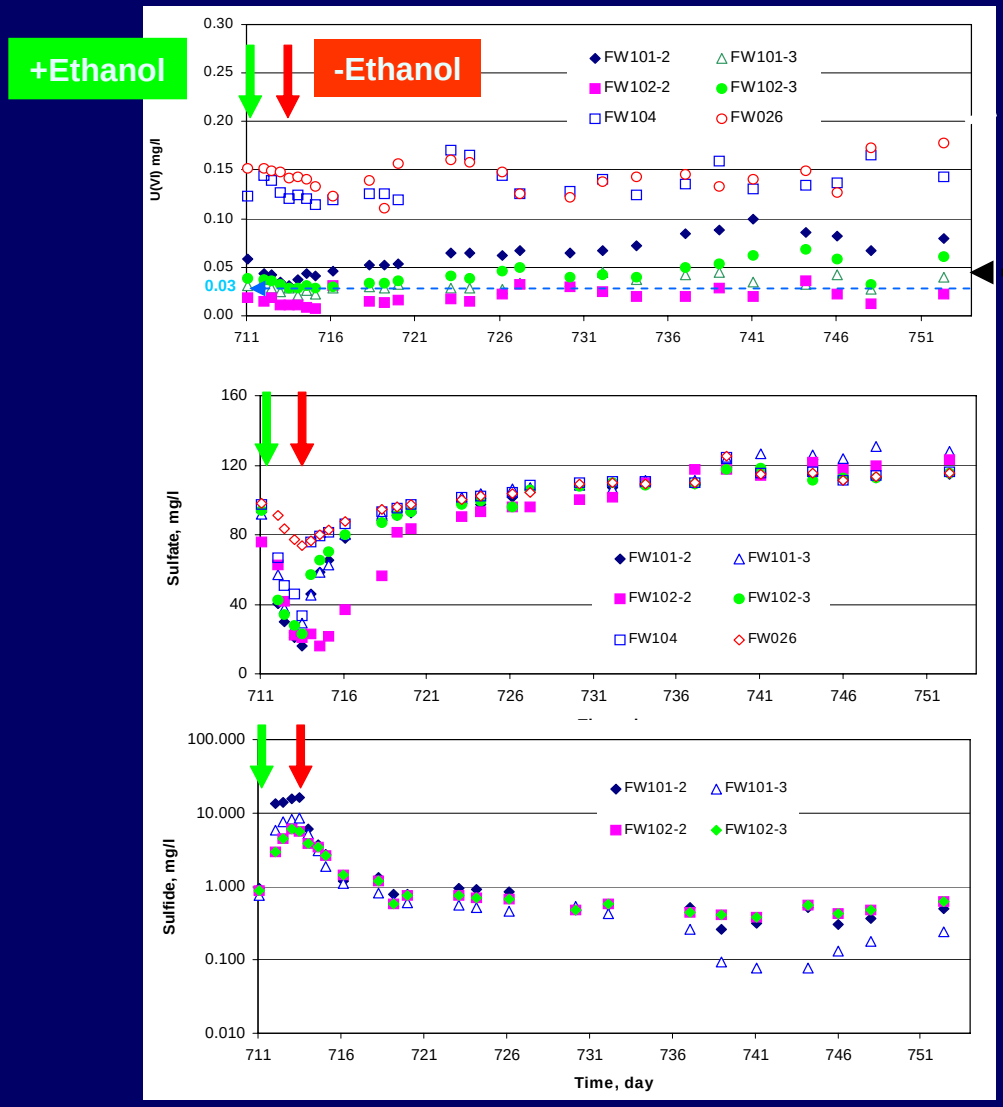








System stability in the absence of DO during a 41 day period of starvation (day 713-754)



Key findings

U(VI) concentrations in the injection and extraction wells were stable.

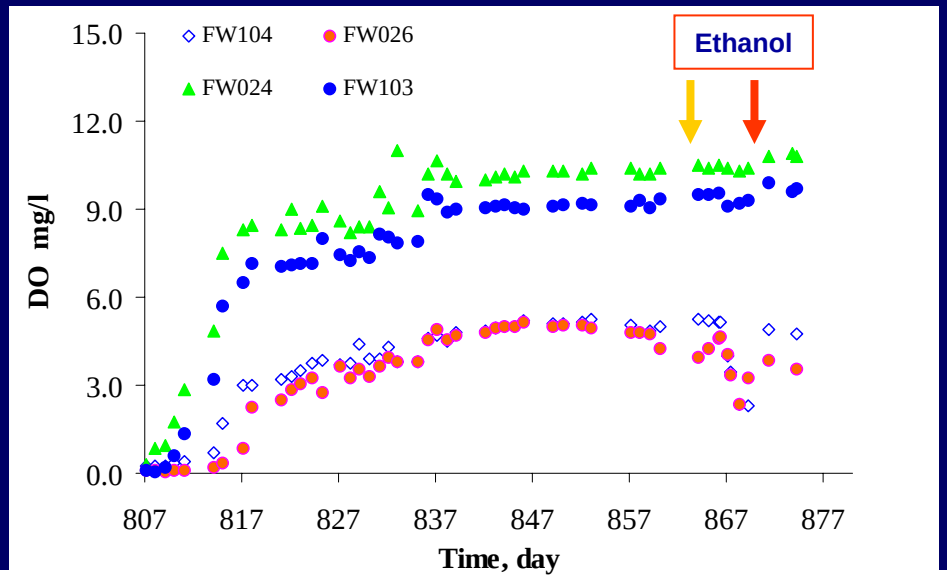
U(VI) concentrations in the MLS wells slowly increased, but never reached the concentration at the injection and extraction wells. (Desoprtion).

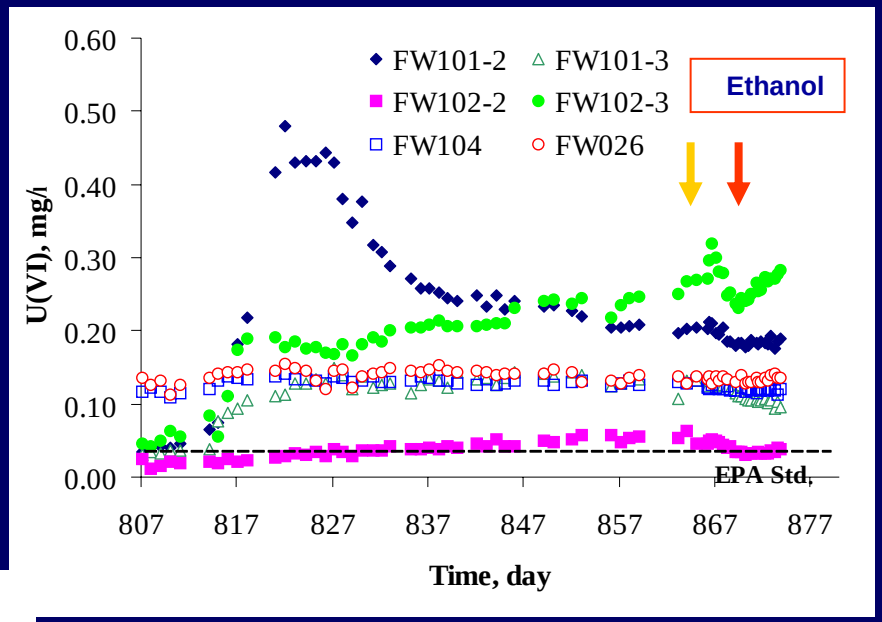
Sulfate concentrations in injection and extraction wells increased and became stable. Sulfate concentrations in MLS wells raised to the level of injection and extraction wells indicate low SRB activity.

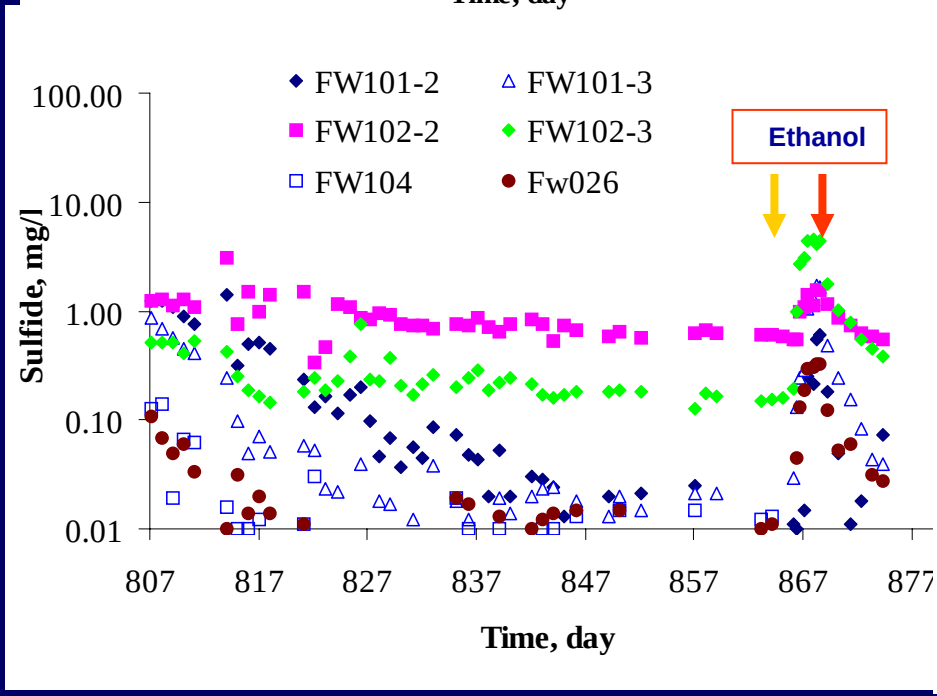
Sulfide concentrations at the MLS wells decreased but remained at significant levels throughout the 41 day starvation period.

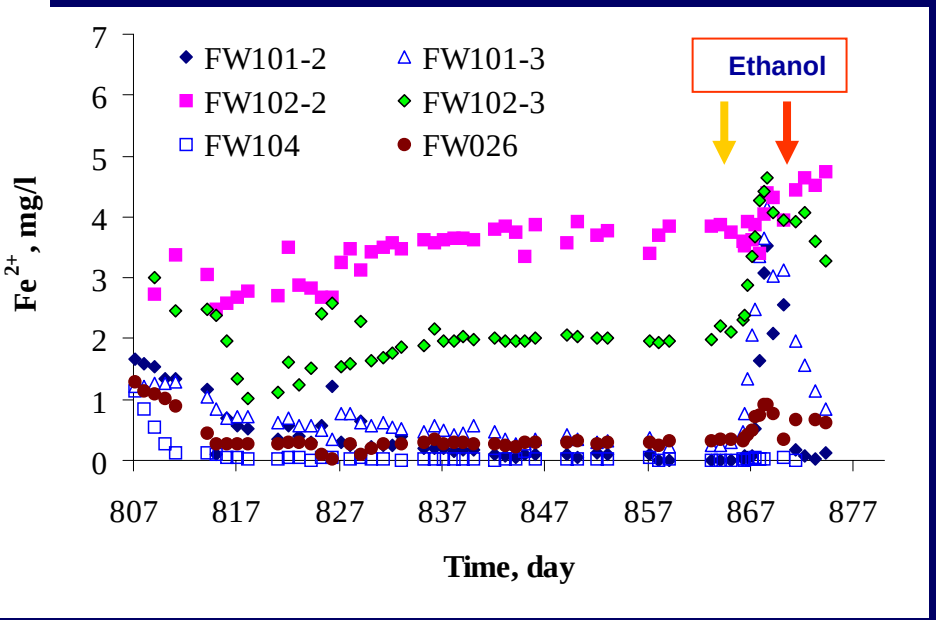
Thus, anaerobic conditions persisted without continued ethanol addition .

System stability in the presence of DO (Days 807-866): Reduced U is sensitive to DO









Modeling was:

- Instrumental in anticipating problems and devising engineering solutions.
- The means to organize, assimilate, and evaluate the plethora of information.
- The way to test hypotheses or understand complex situations.

Travel-Time Based Model (Steady Flow)

Transport equation in spatial coordinates (neglecting local dispersion)

$$\frac{\partial \mathbf{c}_{aq}^{m}(t,\mathbf{x})}{\partial t}+\frac{\partial \mathbf{c}_{sorb}^{m}(\mathbf{c}_{aq}^{m})}{\partial t}+\mathbf{v}(t,\mathbf{x})\cdot\nabla\mathbf{c}_{aq}^{m}(t,\mathbf{x})=\mathbf{r}_{m\leftrightarrow im}(\mathbf{c}_{aq}^{m},\mathbf{c}_{aq}^{im})+\mathbf{r}_{equi}(\mathbf{c}_{aq}^{m})+\mathbf{r}_{microbial}(\mathbf{c}_{aq}^{m},t)$$

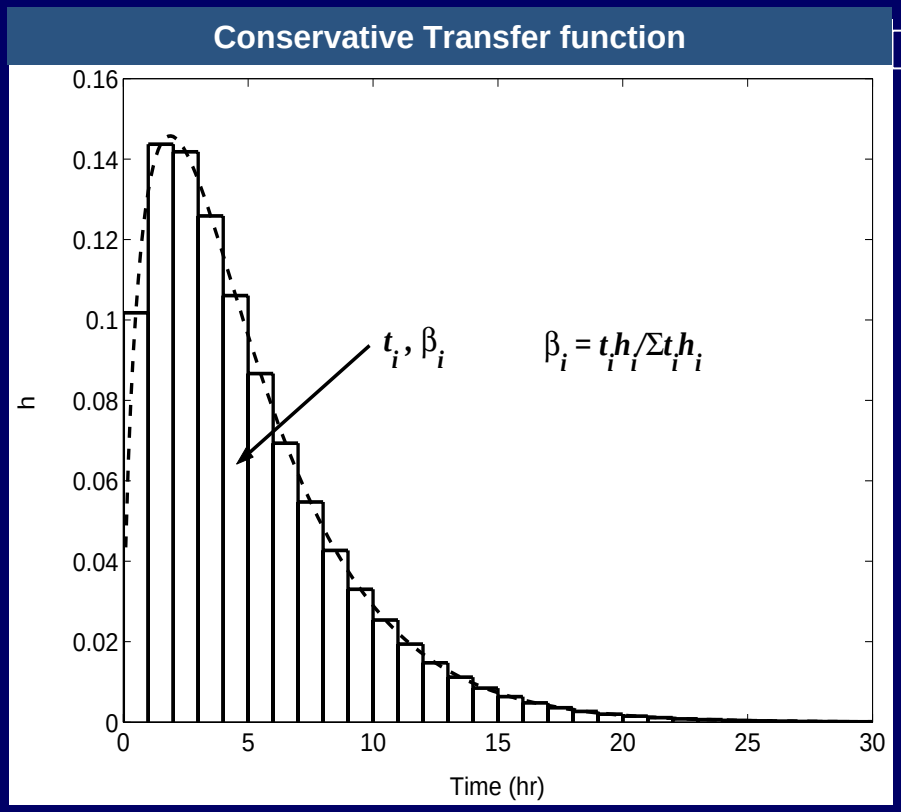
travel time τ along streamline

$$\tau(\mathbf{x})=\int_{\text{well}}^{\mathbf{x}}\frac{\mathrm{d}\xi}{\|\mathbf{v}(\xi)\|}$$

Transport equation in travel-time coordinate

$$\frac{\partial \mathbf{c}_{aq}^{m}(t,\tau)}{\partial t}+\frac{\partial \mathbf{c}_{sorb}^{m}(\mathbf{c}_{aq}^{m})}{\partial t}+1\cdot\nabla\mathbf{c}_{aq}^{m}(t,\tau)=\mathbf{r}_{m\leftrightarrow im}(\mathbf{c}_{aq}^{m},\mathbf{c}_{aq}^{im})+\mathbf{r}_{equi}(\mathbf{c}_{aq}^{m})+\mathbf{r}_{microbial}(\mathbf{c}_{aq}^{m},t)$$

Nonlinear Systems



Travel-time pdf

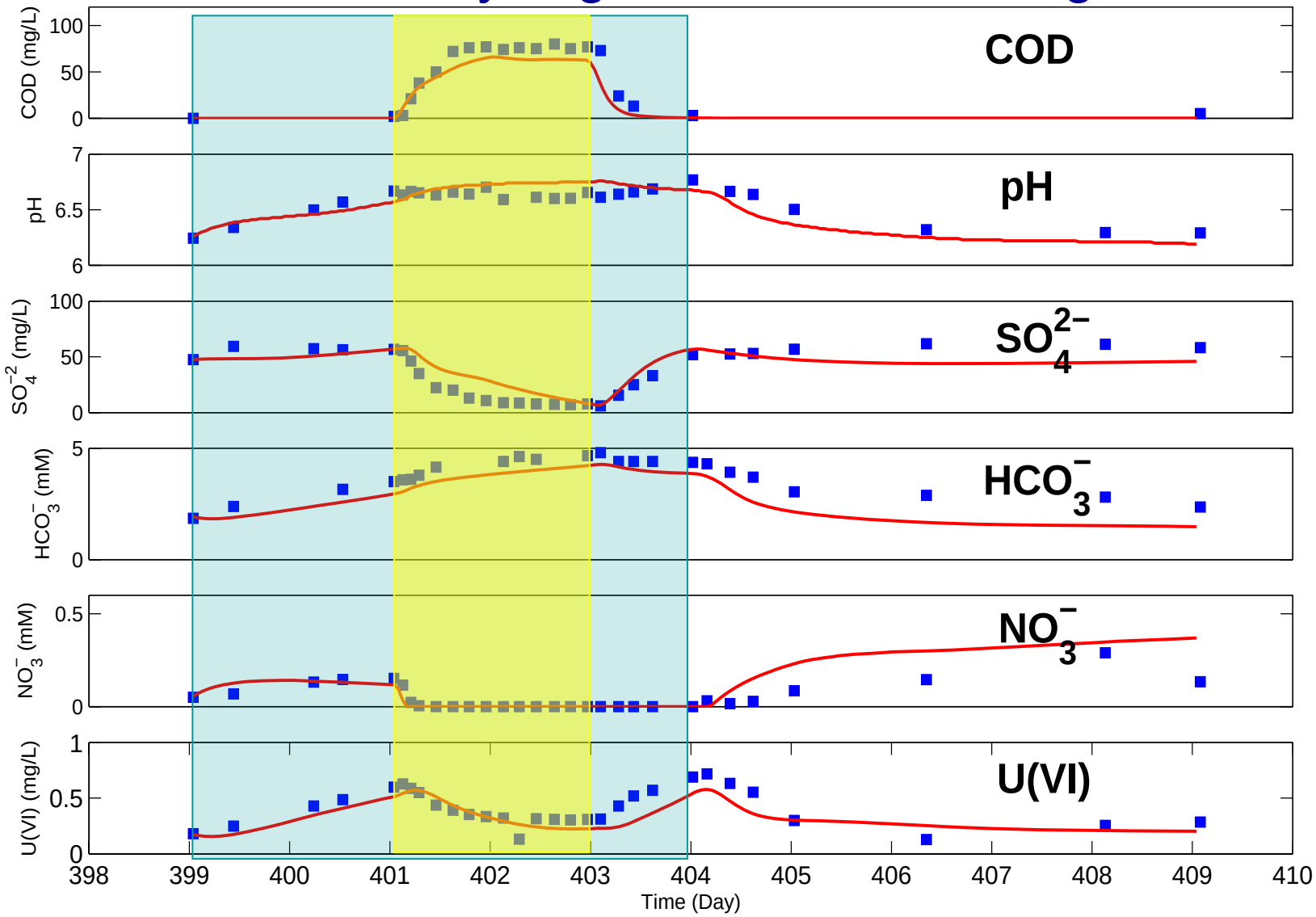
Travel-time based model, c_i

$$c = \sum \beta_i c_i$$

Modeling Reactions

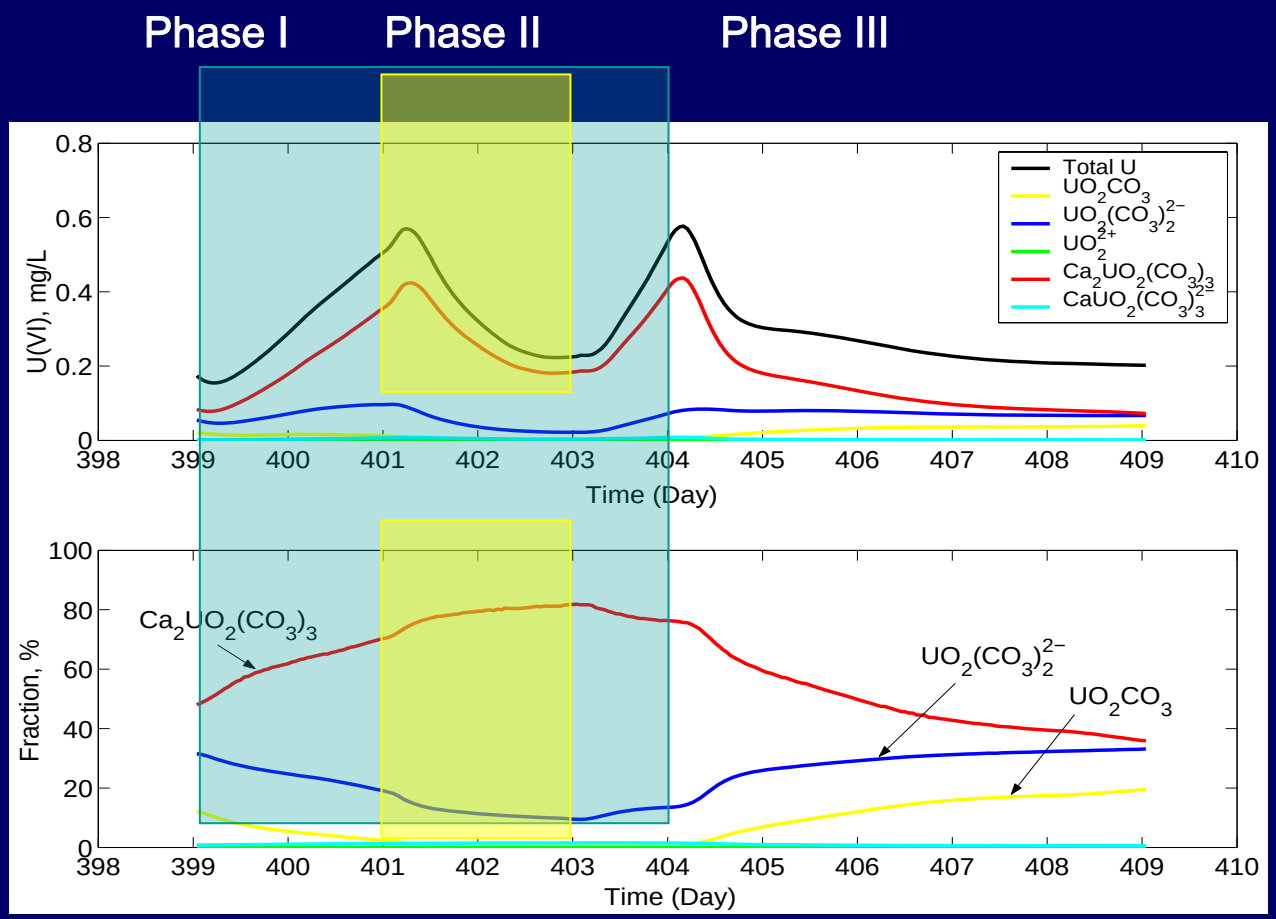
- Microbial reduction kinetics of U(VI) and sulfate in the presence of nitrate
- Equilibrium aquatic geochemical reactions
- Kinetic uranium sorption/desorption
  - Surface complexation model
  - Sorption sites: weak and strong
  - Mass-transfer limitations

Data and Hydrogeochemical Modeling



- Effective reduction rate: $v_{U(VI)}$=1mmol U(VI)/mg SRB-day

Aqueous U(VI) Species



Major Achievements

1. This project has demonstrated that U concentration below US EPA maximum contaminant limit (MCL) for drinking water and groundwater (< 0.03 mg/L) can be achieved by in situ bioreduction.
2. Bioreduced/immobilized U has been stable under anaerobic conditions for 1-2 years. No anaerobic re-oxidation was observed.
3. Dissolved oxygen reoxidizes and remobilizes bioreduced U(IV) but treated zone has "reducing capacity" that protects immobilized U.

Major Achievements (cont.)

4. U(VI) reducing bacterial community is selected and enriched in situ, including metal-reducing *Geobacter* spp., and sulfate reducing *Desulfovibrio* spp. etc.
5. XANES and EXAFS analysis confirmed the presence of bioreduced U(IV) up to 60-80% in reduced zone and the change in uranium species.
6. Mass-transfer limitations determine rates both during reduction and during re-oxidation.
7. We have many publications in peer-reviewed journals.