Factors Controlling In Situ Uranium and Technetium Bioreduction at the NABIR Field Research Center

Oregon State University

J. Istok, M. Sapp, J. Jones, M. Park

University of Oklahoma

A. Spain, J. Senko, L. Krumholz

Pacific Northwest National Laboratory

J. McKinley, T. Resch

Oak Ridge National Laboratory

B. Gu, P. Zhou and S. Yan.

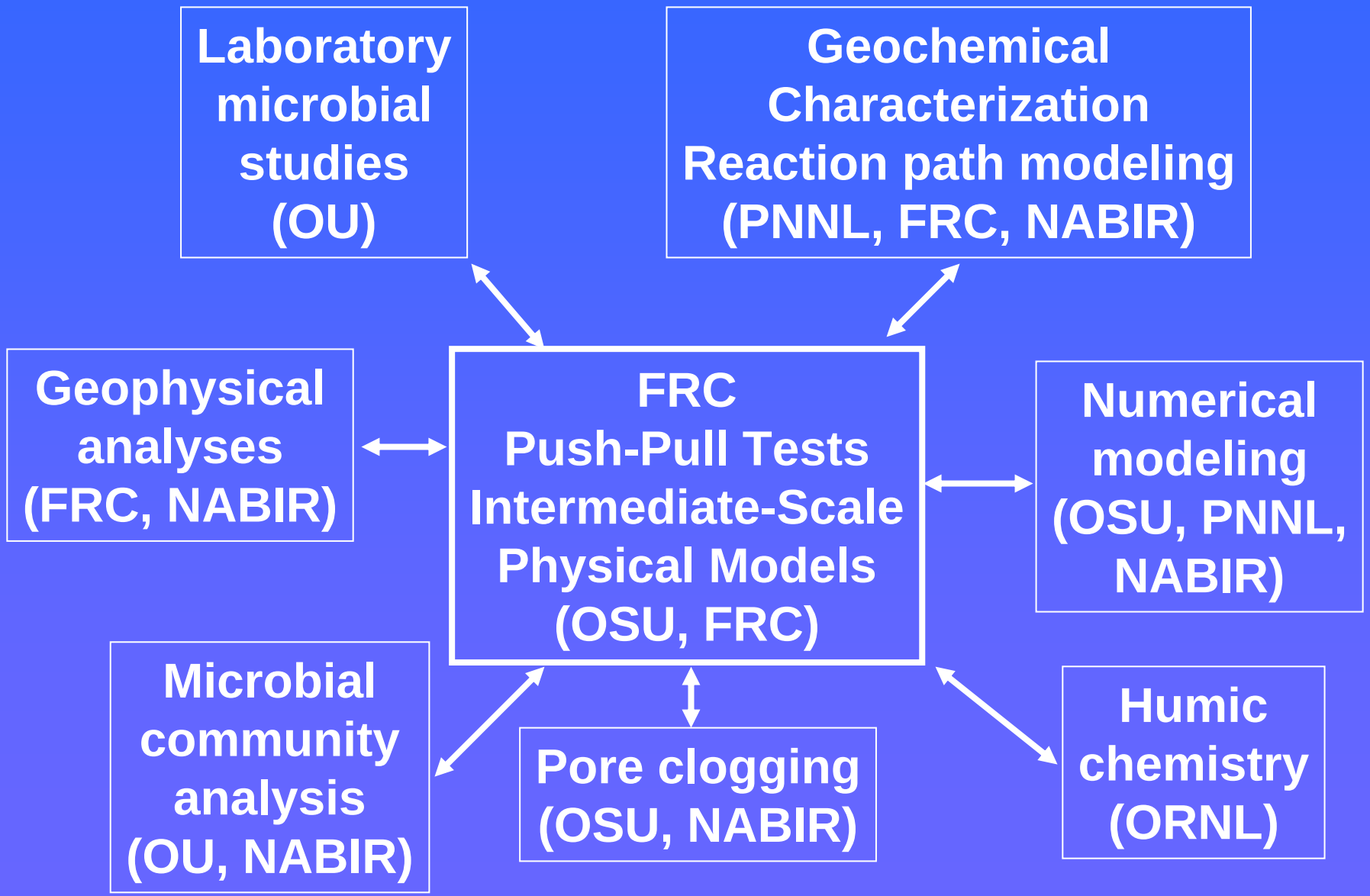
FRC/ORNL

D. Watson, M. A. Bogle, K. Lowe

Research Hypotheses

- Indigenous subsurface microorganisms at the FRC have the capability to reduce complex mixtures of NO_3^-, U(VI) and Tc(VII)
- Conditions that favor U(VI) and Tc(VII) reduction can be created by adding electron donors to :
  - Increase biomass and microbial activity
  - Remove competing electron acceptors
- Electron donor additions can be controlled to sustain high reduction rates and maintain the stability of U(IV) and Tc(IV)

Project Organization



Summary of In Situ Testing

- Desired metabolic capability is widespread and ethanol additions stimulated desired microbial activity in a wide range of subsurface environments in FRC Areas 1 and 2:

Initial Conditions				
pH	NO_3^- (mM)	SO_4^{2-} (mM)	U(VI) (μM)	Tc(VII) (pM)
3.3-3.9	100-140	0-1	5-12	10000-15000
5.2-5.6	90-100	0-1	5-12	10000-15000
5.6-7.2	0-6	1-2	1-7	200-1000

In Situ Microbial Activity Quantified in Extensive Series of “Push-Pull” Tests

Rate Summary					RATES			
Conditions		Donor Target	Number of	Donor	Nitrate	Sulfate	U	Tc
Nitrate	Donor	Conc (mM)	Tests	(mM/hr)	(mM/hr)	(mM/hr)	(uM/hr)	(pM/hr)
~120mM	Acetate	300-500	2	0.80-24.00	0.51-0.69		0	9-39
		50	2	0.14-0.40	0.12-0.36		0	107
~120mM	Ethanol	300-440	10	0.30-7.60	0.03-3.10		0.00-0.01	4-189
		30-100	8	0.04-0.25	0.02-0.40	0.00-0.01	0.00-0.03	1-150
~120mM	Glucose	200	3	0.94-4.30	0.04-3.20		0.02-0.03	45-460
		20	4	0.02-0.16	0.44-0.76		0.001	10-143
~120mM	None	0	8		0.00-0.10		0	0
~0.5mM	Acetate	50	1	-	>.01		0.021	-
~0.5mM	Ethanol	15-80	14	0.02-0.30	0.00-0.06	0.00-0.02	0.00-0.04	0-5
~0.5mM	Glucose	200	1	0.31	>.05		0.034	-
		20	1	0.1	0.012		0.041	-
~0.5mM	None	0	8	0	0	0.00-0.001	0.00-0.01	0-1

Lines of Evidence

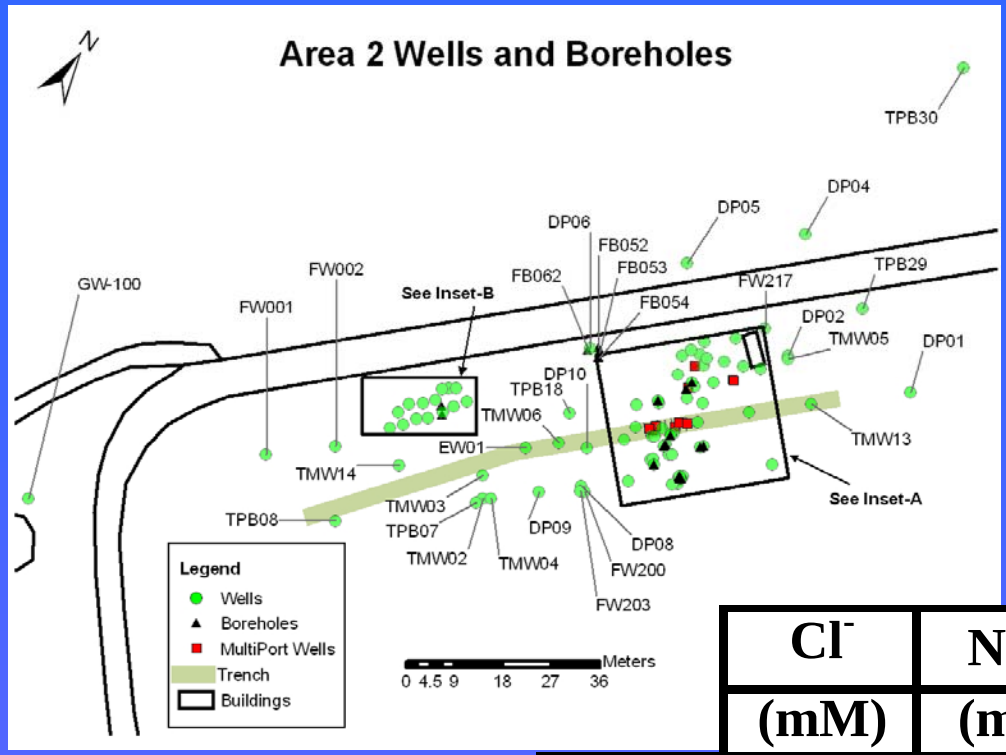
Conclusion that donor additions stimulated the growth and activity of metal-reducing organisms supported by:

- **Aqueous chemistry (dilution adjusted concentrations of added electron donors, electron acceptors; formation of diagnostic metabolic products; response to inhibitors)**
- **Microbial characterization of groundwater and sediments (diagnostic organisms)**
- **Geochemical characterization of sediments (reduced metals)**

Recent Field Activities

- High (120 mM) NO_3^- concentrations inhibit U(VI) reduction and promote oxidation of U(IV)
- Geochemical reductants may stabilize U(IV)
- "Sulfate Amendment" Study (In progress)
  - Ten new wells in Area 2
  - Inject GW835 groundwater with added sulfate (20 mM) and ethanol (40 mM) to precipitate sulfides
  - Challenge with added nitrate/nitrite

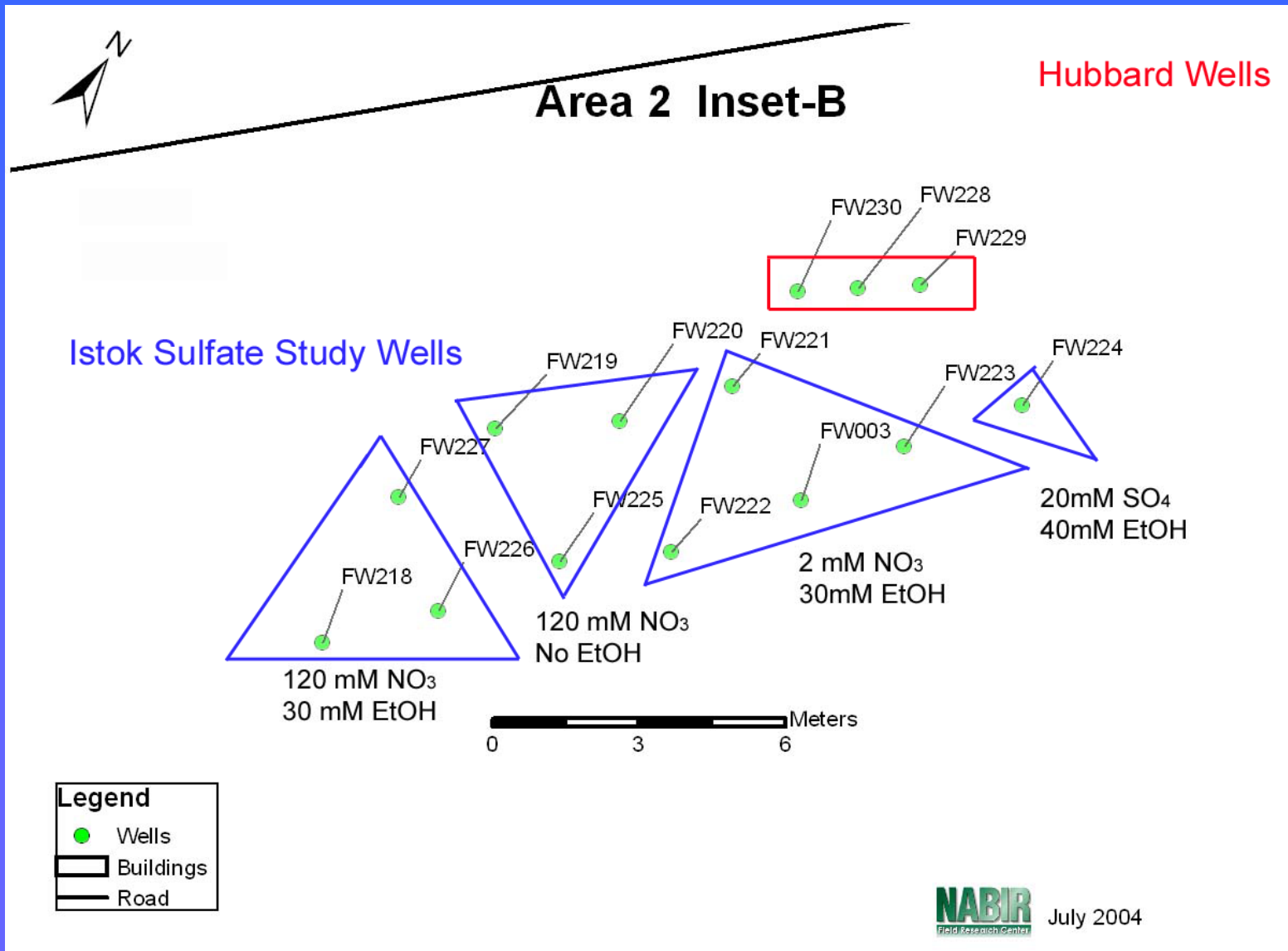
Sulfate Amendment Study



Background Geochemistry

	Cl^- (mM)	NO_3^- (mM)	SO_4^{2-} (mM)	U (uM)	Tc (pM)	pH
FW218	1.7	12.9	0.4	0.0	152	7.0
FW219	0.3	0.4	0.6	3.9	508	7.4
FW220	0.2	0.2	0.1	0.1	200	7.7
FW221	0.3	1.2	0.2	0.1	186	7.5
FW222	0.2	0.1	0.1	0.0	156	7.8
FW223	0.1	0.0	0.1	0.1	382	8.0
FW224	0.1	0.1	0.1	0.0	35	7.7
FW225	0.3	0.7	0.1	0.2	64	7.5
FW226	0.4	1.2	1.9	0.2	132	7.2
FW227	0.3	0.4	0.5	0.1	57	6.6

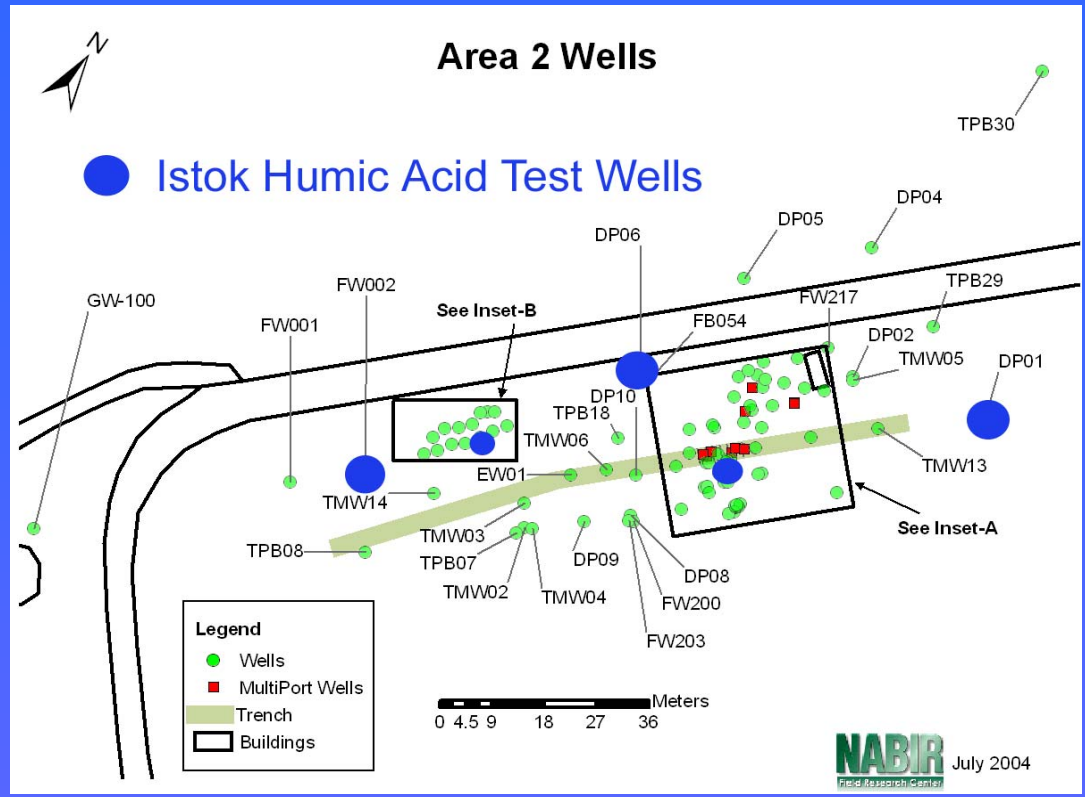
U(IV) Reoxidation Experiment (In Progress)



Recent Field Activities (cont.)

- **Will added humics increase rates of U(VI) reduction ?**
  - **Electron shuttling to solid Fe(III)**
  - **Complexation of potentially toxic metals**
  - **Three sets of 10 push-pull tests with and without added humics in Areas 1 and 2**

Humic Acid Study



Well	Ethanol	Humic Acid (100 mg/L)
DP15D	80mM	AL-HA
DP01	80mM	FRC-HA
DP06	80mM	FRC-HA
FW002	80mM	FRC-HA
FW003	None	AL-HA

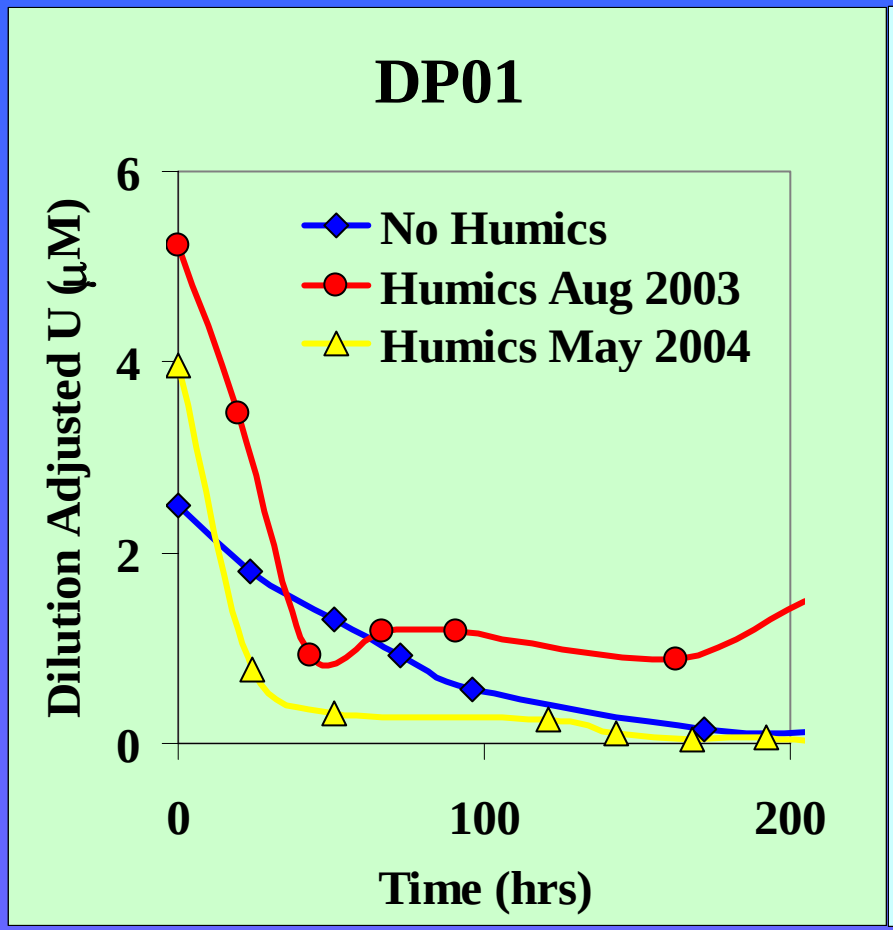
Experimental Design

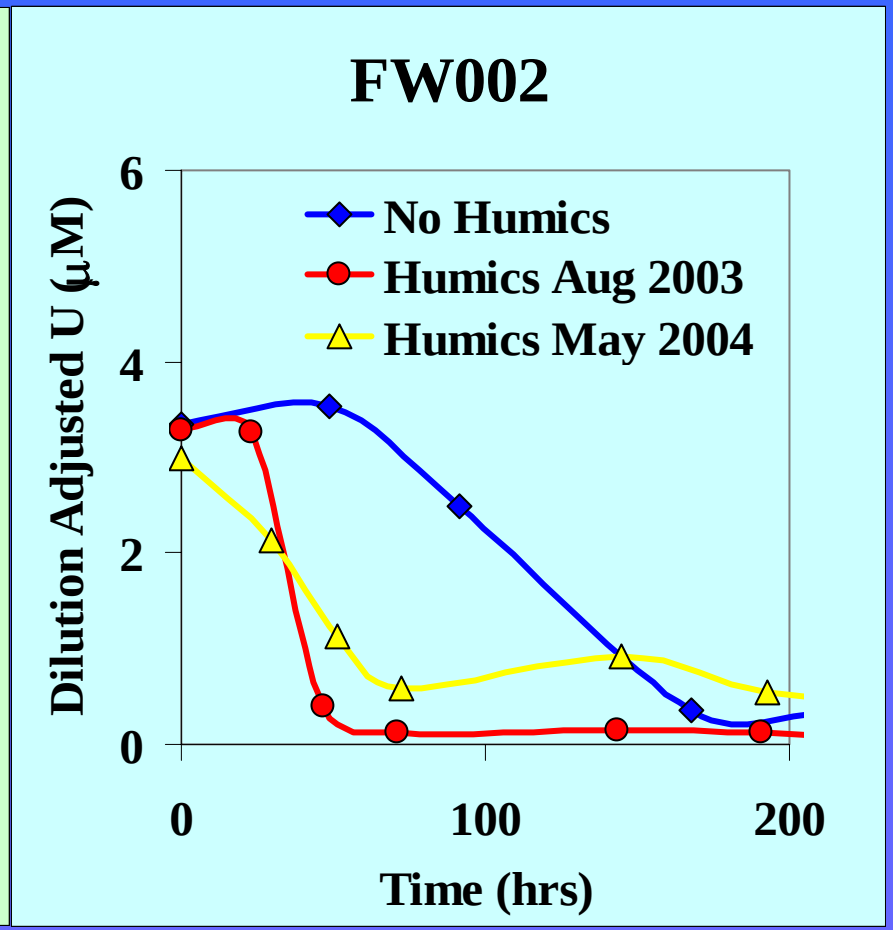
GW835 Water

10mM Bicarbonate

Tracer

Effect of Added Humic Acid on U(VI) Reduction





Recent Field Activities (cont.)

- Well (and perhaps aquifer) clogging occurs in field tests with low pH groundwater but mechanisms not clearly understood
  - Increased pH precipitates ~2 g/L solids
  - High donor concentrations (>300 mM) produces large amounts of biomass
  - Denitrification produces large quantities of N_2

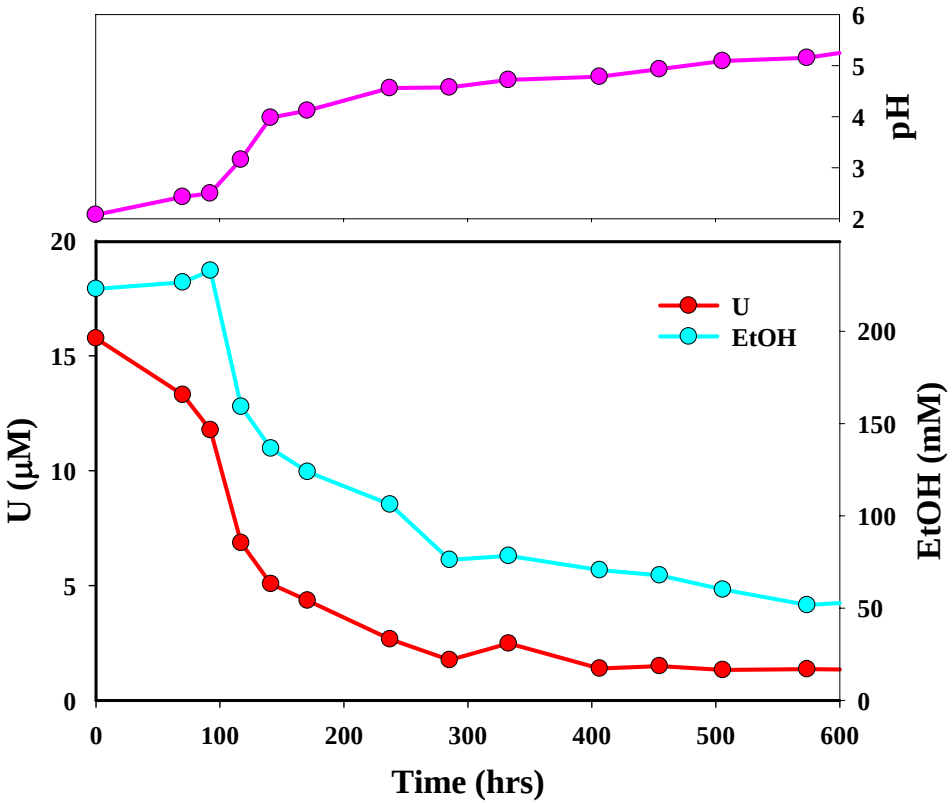
Area 1

Well Rehabilitation

HCl + Chlorox

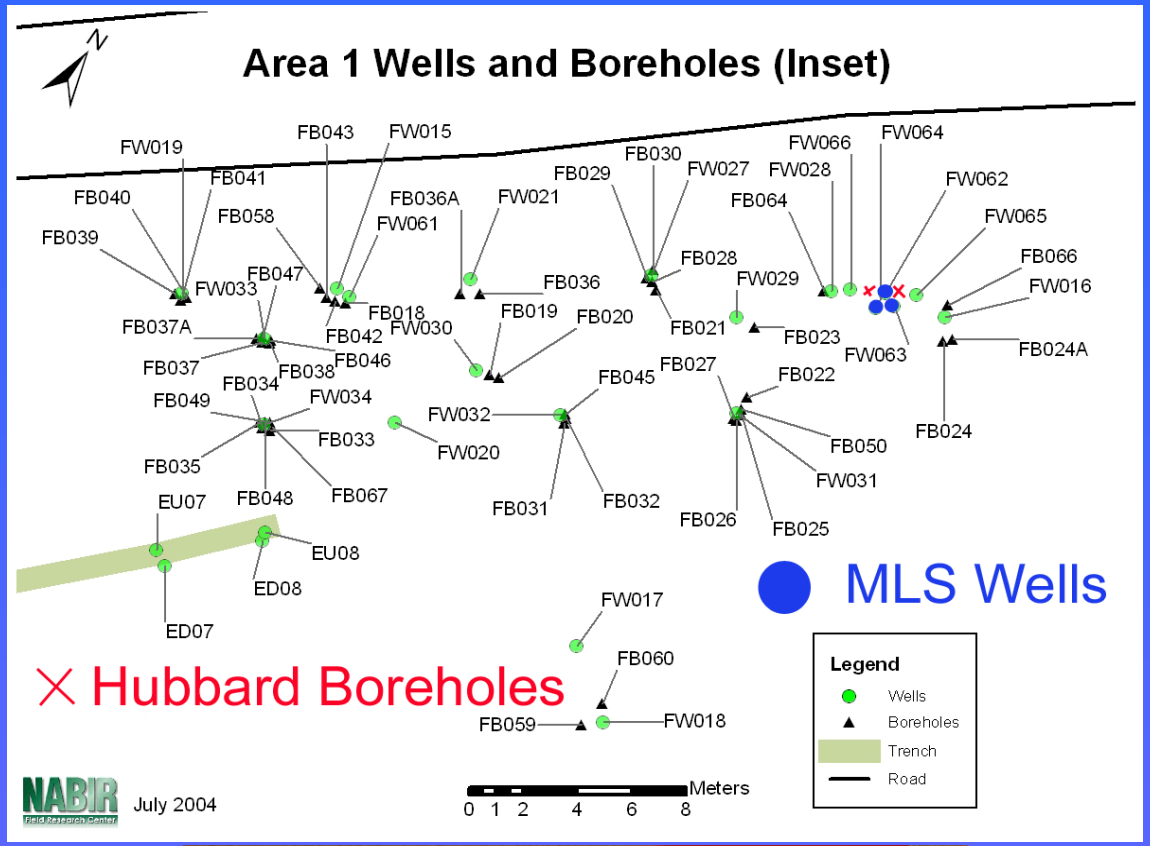
+ Surging

After Biostimulation (Jan 2004)			
Well	Volume Inj (L)	Time to Inj	Rate (L/day)
FW28	40-50	14 days	3
FW29	100	12 days	8
FW30	100	7 days	14
After Cleaning (May 2004)			
FW28	50	21 hrs	**57**
FW29	50	21 hrs	**57**
FW30	50	21 hrs	**57**

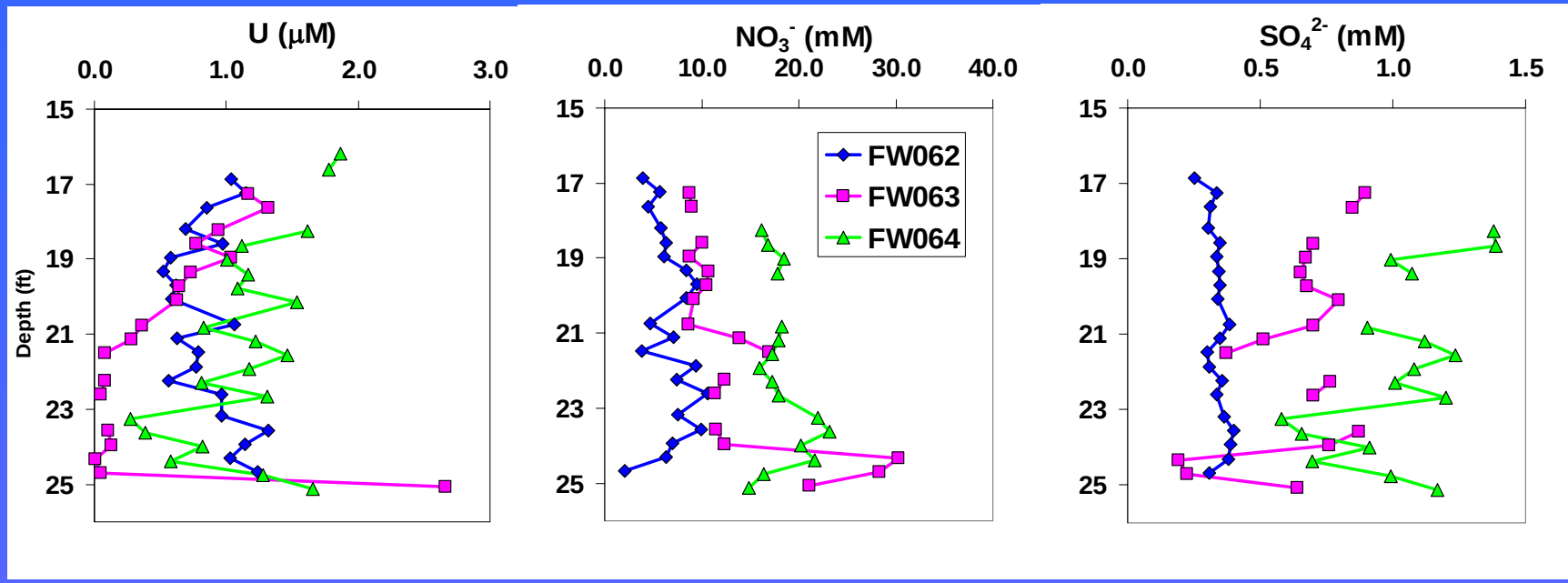


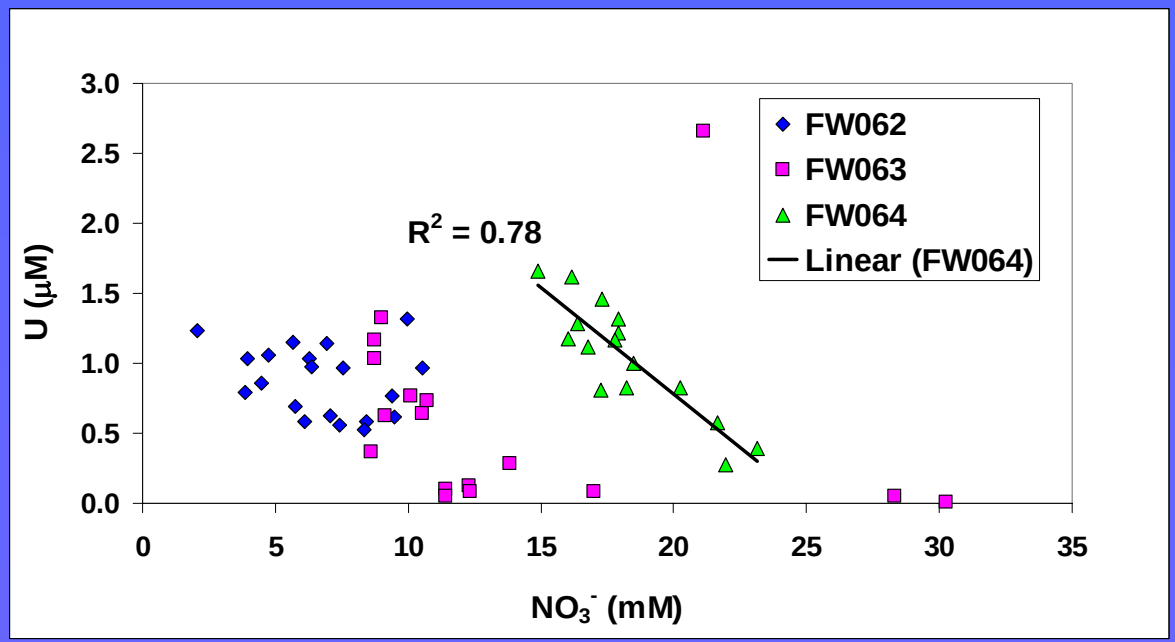
Recent Field Activities (cont.)

- **Multilevel Samplers (MLS)**
  - **3 Sets of closely-spaced MLS wells in Areas 1 and 2**
  - **Each MLS contains 20-30 cells vertically spaced on 10 cm intervals**
  - **Cells are used to monitor vertical variations in aqueous chemistry and to incubate sediment samples**

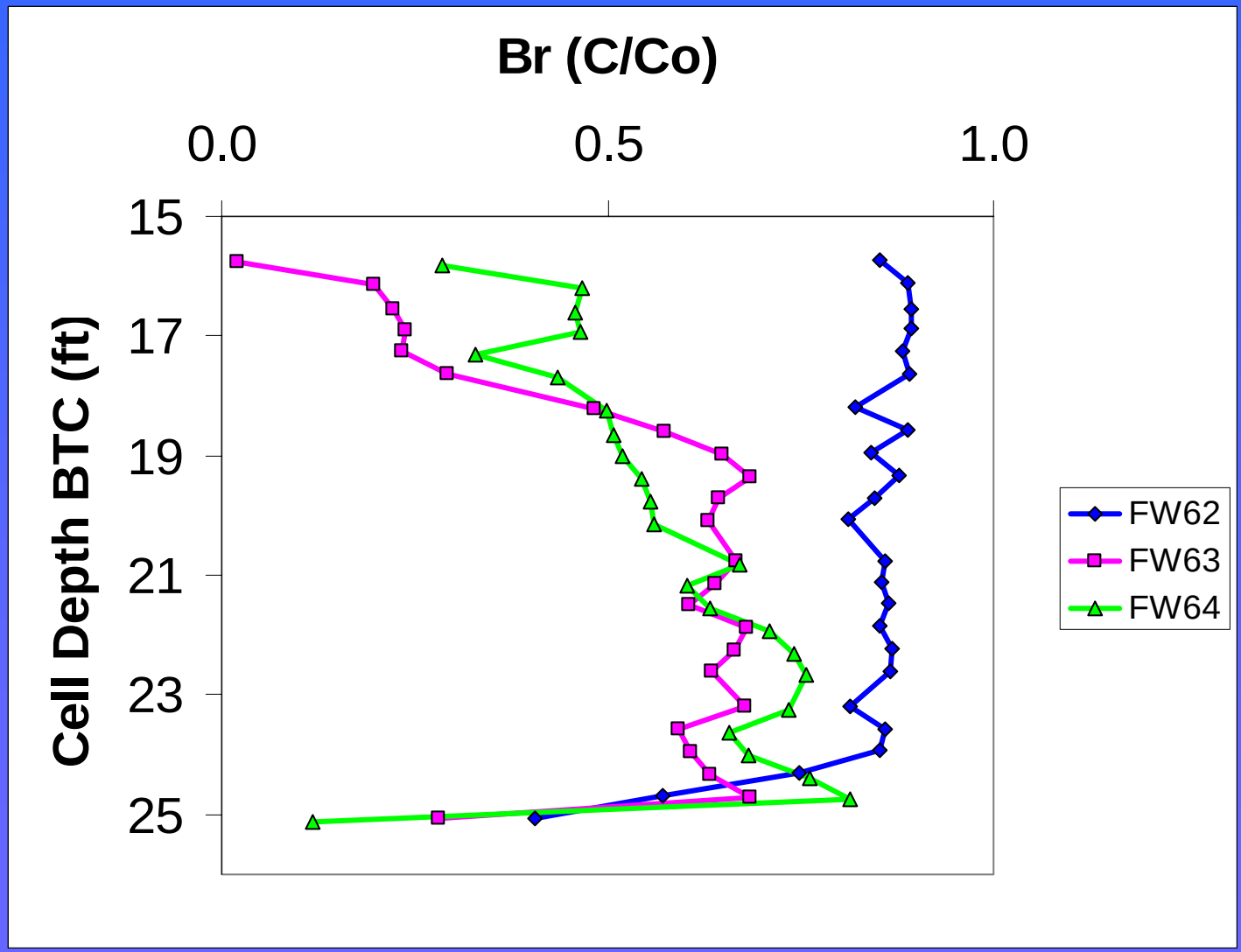

Area 1 Wells and Boreholes (Inset)
FW019
FB043
FW015
FB041
FB040
FB058
FB036A
FW021
FB030
FW027
FB029
FW028
FW066
FW064
FB064
FW062
FB039
FW061
FW065
FB028
FB066
FB047
FW033
FB036
FW029
FW016
FB018
FB037A
FB042
FW030
FB019
FB020
FB021
FB023
FW063
FB024A
FB037
FB038
FB046
FB034
FB045
FB027
FB022
FB049
FW034
FW032
FB024
FB033
FW020
FB050
FB035
FB048
FB067
FB031
FB032
FW031
EU07
FB026
FB025
EU08
ED08
ED07
FW017
FB060
FB059
FW018
MLS Wells
Hubbard Boreholes
Legend
Wells
Boreholes
Trench
Road
NABIR
Field Research Center
July 2004
Meters
0 1 2 4 6 8

Vertical Variability in Aqueous Geochemistry

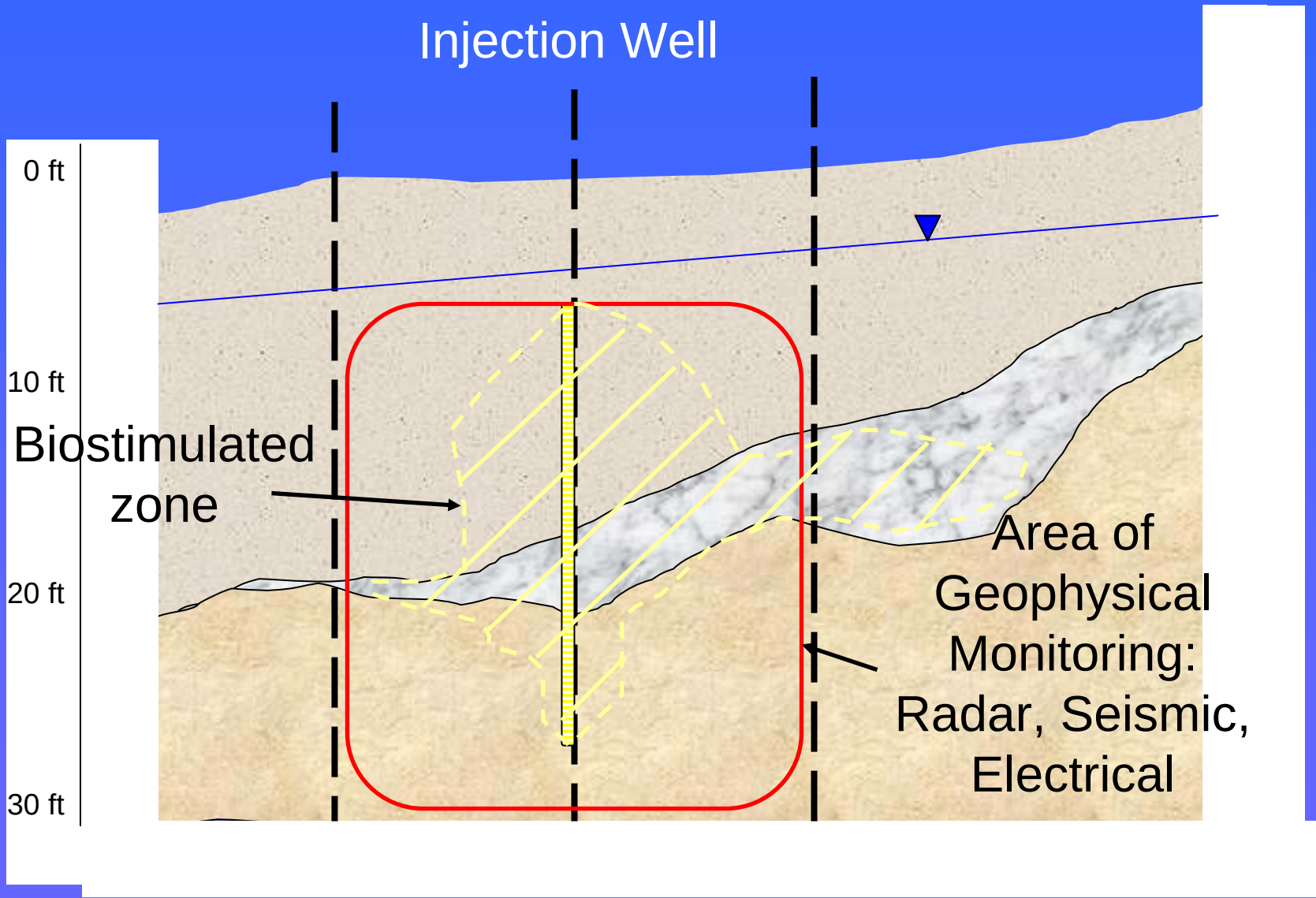




Example Area 1 MLS Tracer Test

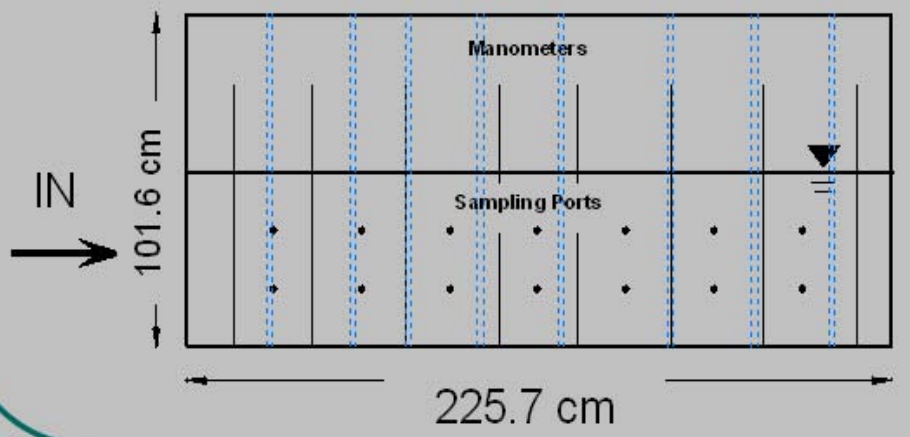


Geophysical Investigations

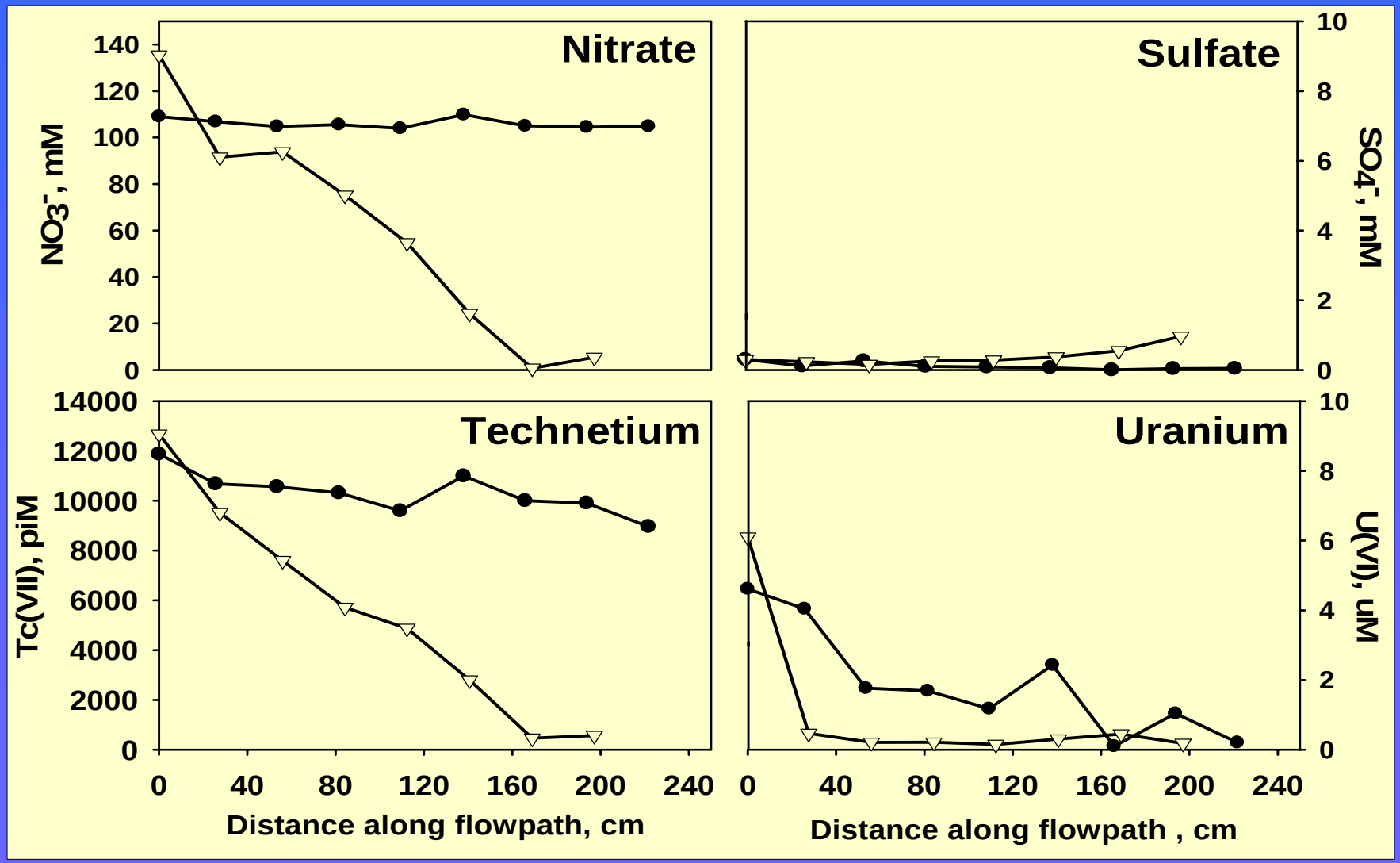


The Area 1 Physical Model

- Pack: stimulated FRC sediment, Maynardsville Limestone, Bicarbonate
- FW21 water pumped through Q ~ 3 mL/min
- EtOH injection system
- Samples collected thrice weekly
- Measured:
  - Q, Δh, U(VI), Tc(VII), SO_4^{2-}, NO_3^-, NO_2^-, EtOH, pH



Example Area 1 Results



Where does the N_2 gas go ?

- FRC Background Sediment and Maynardsville Limestone
- Denitrifying activity stimulated with ethanol
- Gas and liquid saturations monitored to track fate of N_2 gas

EMSL Flow Cell

Sequential Feeding with 300 mM Ethanol and 100 mM NO_3^-