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

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Bioreduction/Bioimmobilization

Trace U(VI), Tc(VII)
Heterogeneous biogeochemistry
Largely sorbed U(VI)
Aerobic/oxidizing
Low pH
High Ca, Al, Ni, etc.
Very high NO_3^-
Moderate SO_4^{2-}

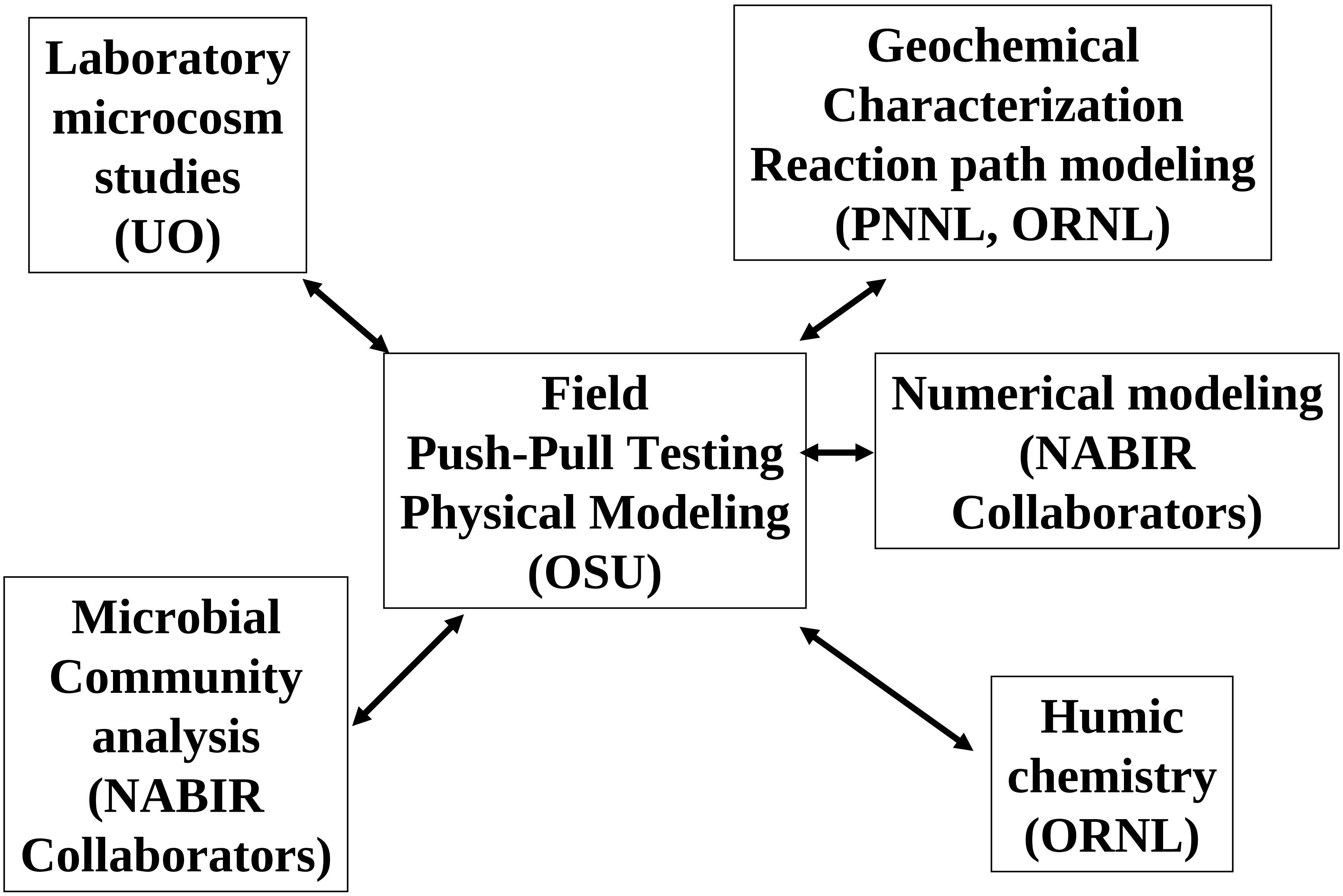
Donor Addition →

Anaerobic/reducing
Increase pH
Denitrification
Iron reduction
Sulfate reduction
U(VI) > U(IV)
Tc(VII) > Tc(IV&V)

Research Hypotheses

- **Indigenous microorganisms at the FRC have the ability to reduce U and Tc but rates are electron-donor limited**
- **Electron donor additions will result in conditions favorable for U and Tc reduction**
- **Microbially-reduced U will be rapidly reoxidized in the presence of high NO_3^- concentrations**
- **A donor addition strategy can be devised to maintain low U and Tc concentrations in groundwater**

Project Organization

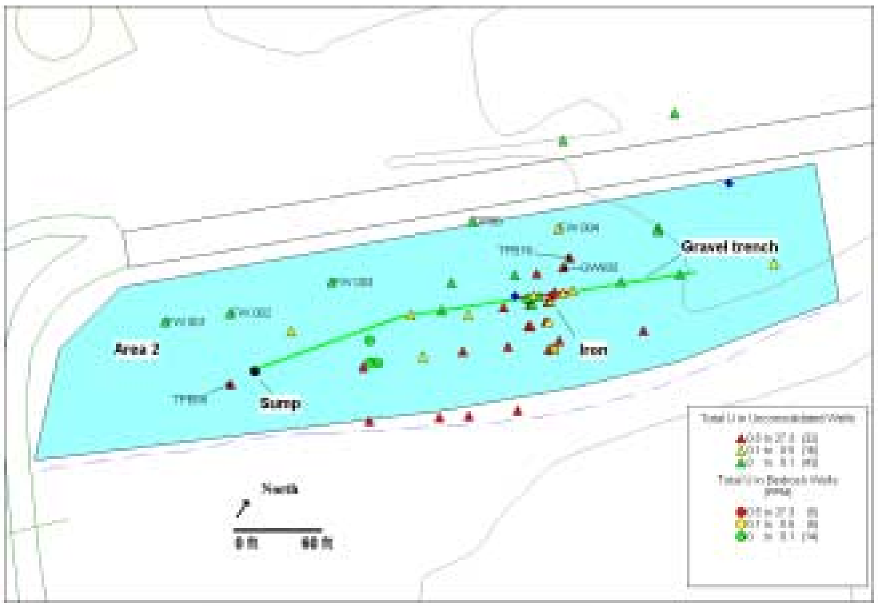


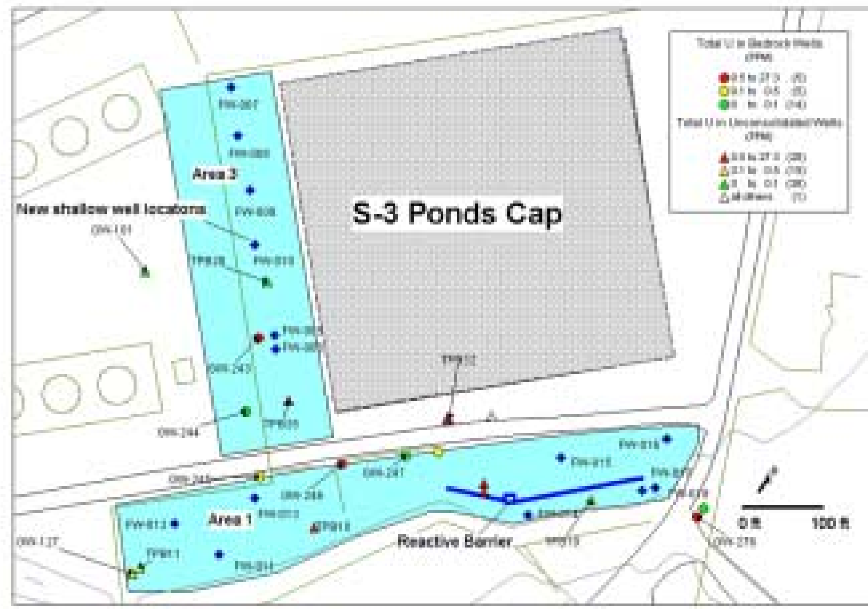
S-3 Ponds

Study Areas

Area 2

Area 1

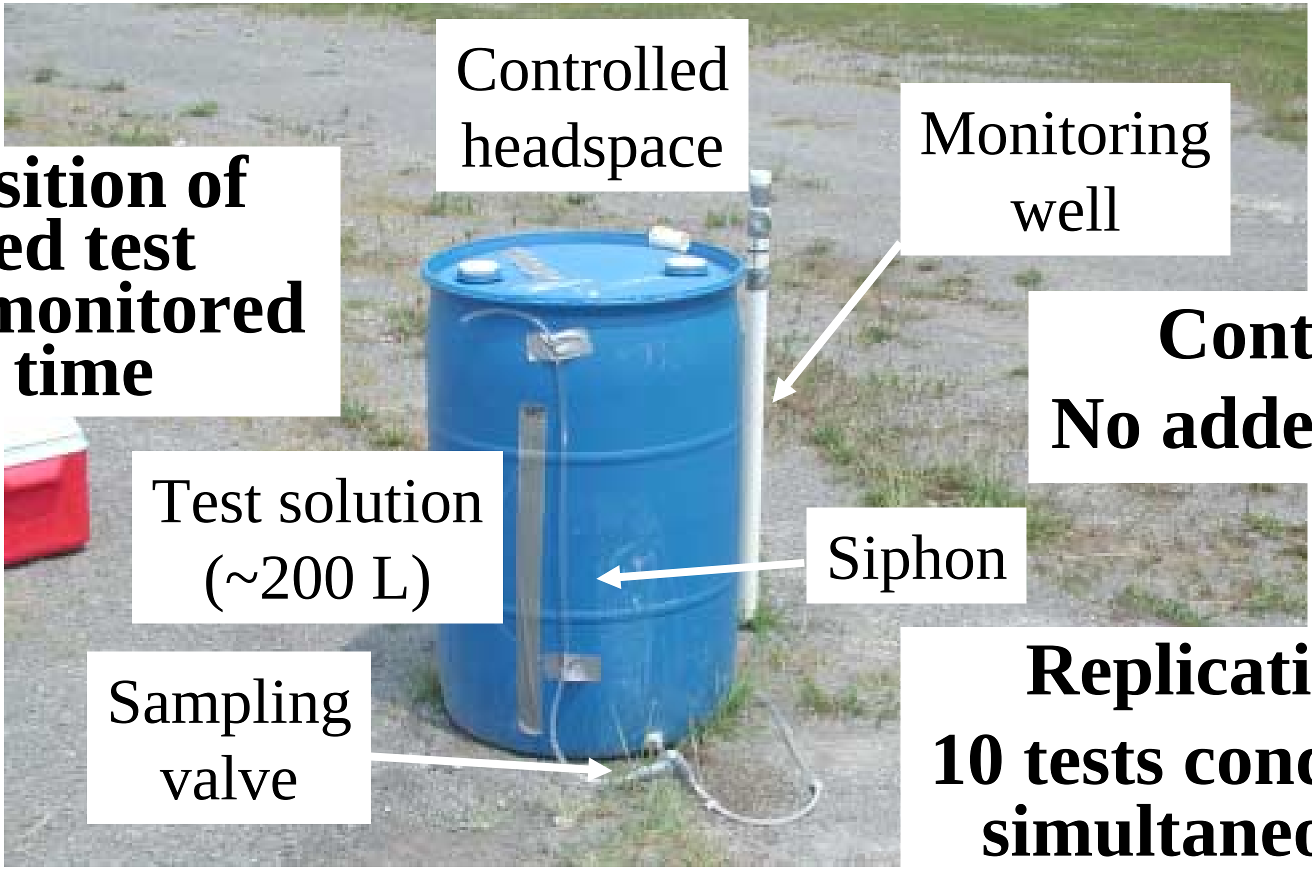




Processes Studied In Situ Using Push-Pull Tests

Site groundwater amended with tracers, +/-bicarbonate, +/- electron donor(s), +/- humics, +/- electron acceptors, +/- inhibitors and injected into existing monitoring wells

Composition of injected test solution monitored over time



Controls:
No added donor

Replication:
10 tests conducted simultaneously

Source Groundwater Used in Field Manipulation Experiments

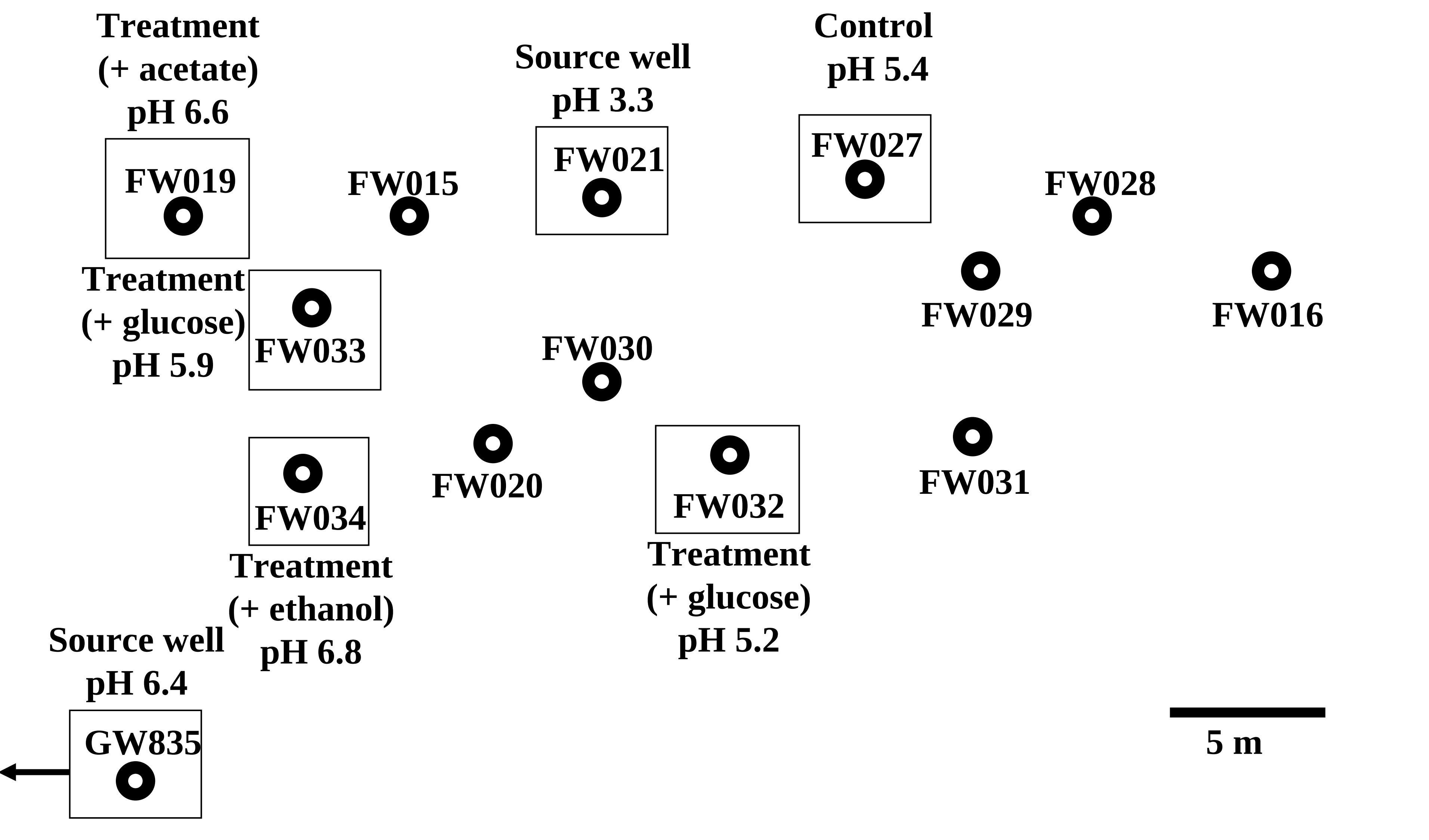
	GW835 (μM)	FW021 (μM)
pH	6.4	3.3
Tc (pM)	410	18000
U	5	6
Ag	1	0
Al	0	12000
As	1	0
Ba	0	10
Be	20	0
Bi	0	0
Br^-	150	0
Ca	3500	19000
Cd	0	4
Cl^-	650	7900
Co	1	46
Cr	1	0

	GW835 (μM)	FW021 (μM)
Cs	0	0
Cu	1	9
Fe	4	4
Ga	1	0
K	120	980
Mg	1100	8300
Mn	50	2500
Na	1100	23000
Ni	1	220
NO_3^-	1200	140000
Pb	0	0
Se	1	1
Sr	4	22
SO_4^{2-}	830	430
Zn	1	48

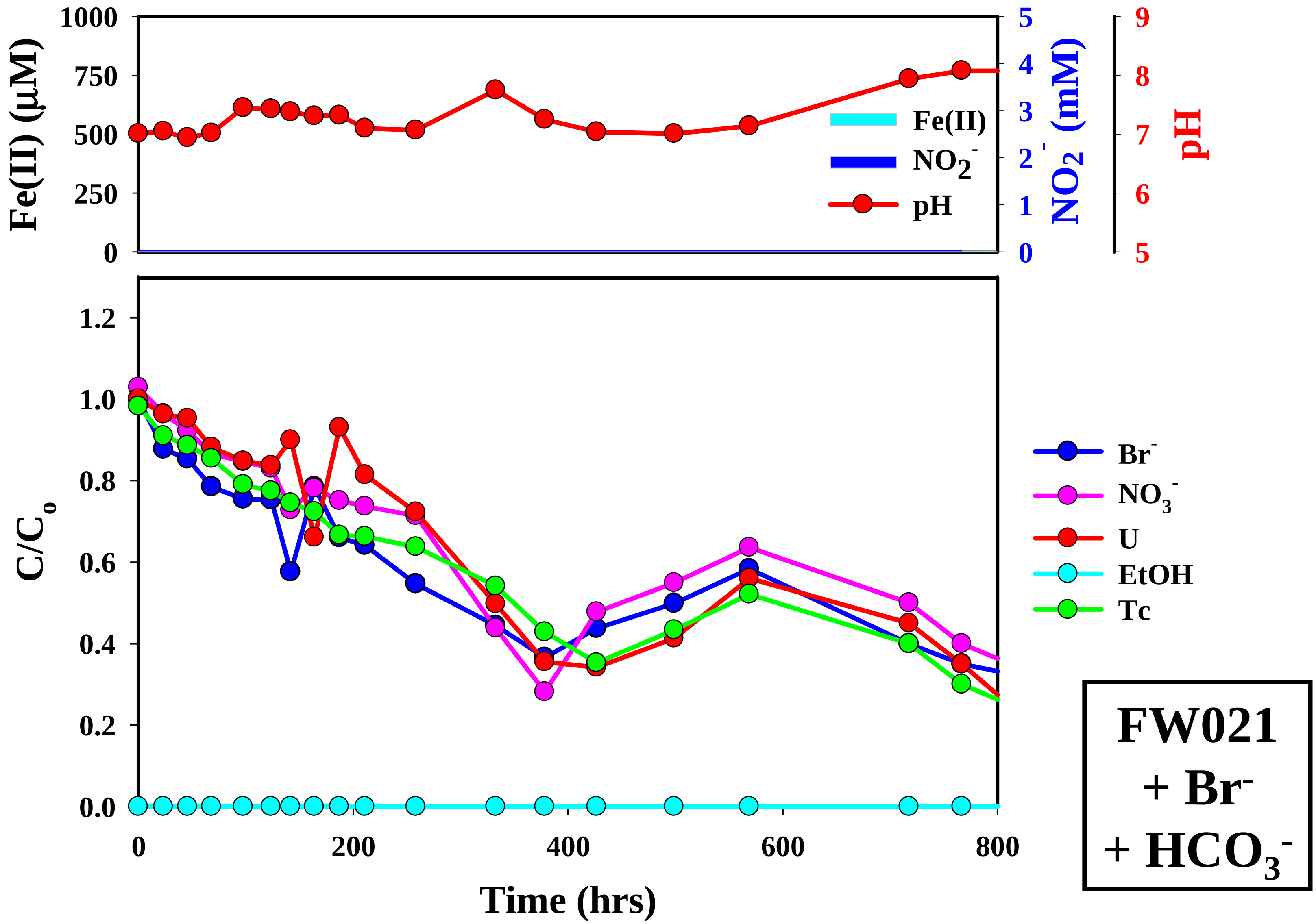
Push-Pull Test Overview

- **Phase I (42 tests)**
  - **Moderate pH (5.2 - 6.6) Area 1**
  - **Low vs high nitrate; + tracer; + HCO_3^-; +/- acetylene; +/- humics**
- **Phase II (16 tests)**
  - **Low pH (3.5 – 4.5) Area 1**
  - **Low vs high nitrate; + tracer; + HCO_3^-; +/- acetylene; +/- humics**
- **Phase III (25 tests)**
  - **moderate pH (5.5 – 6.8) Area 2**
  - **Low vs high nitrate; + tracer; + HCO_3^-; +/- sulfate; +/- humics**

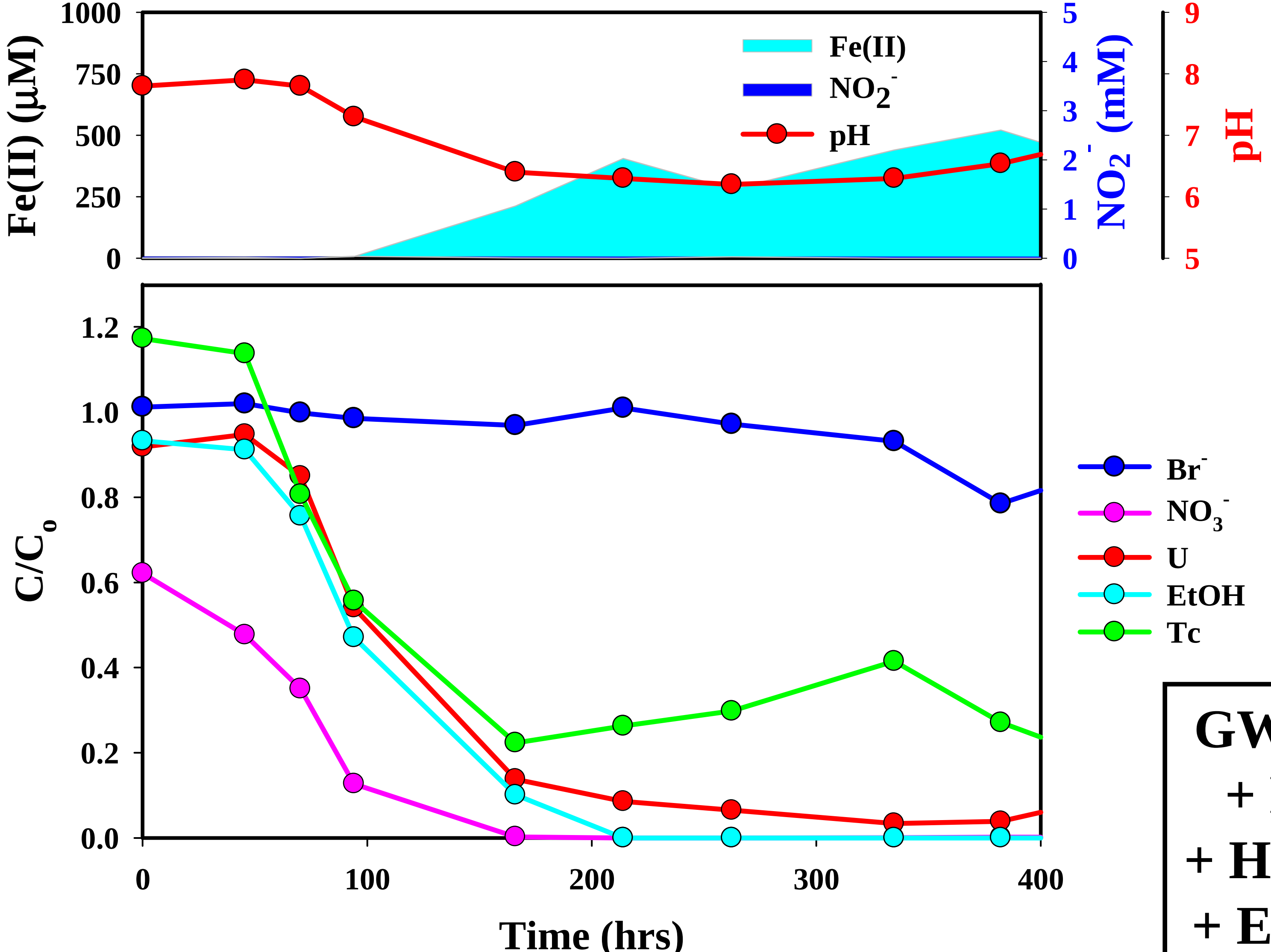
Field Manipulation Experiments: Phase I – Moderate pH (Area 1)



Control Wells (no added donor)

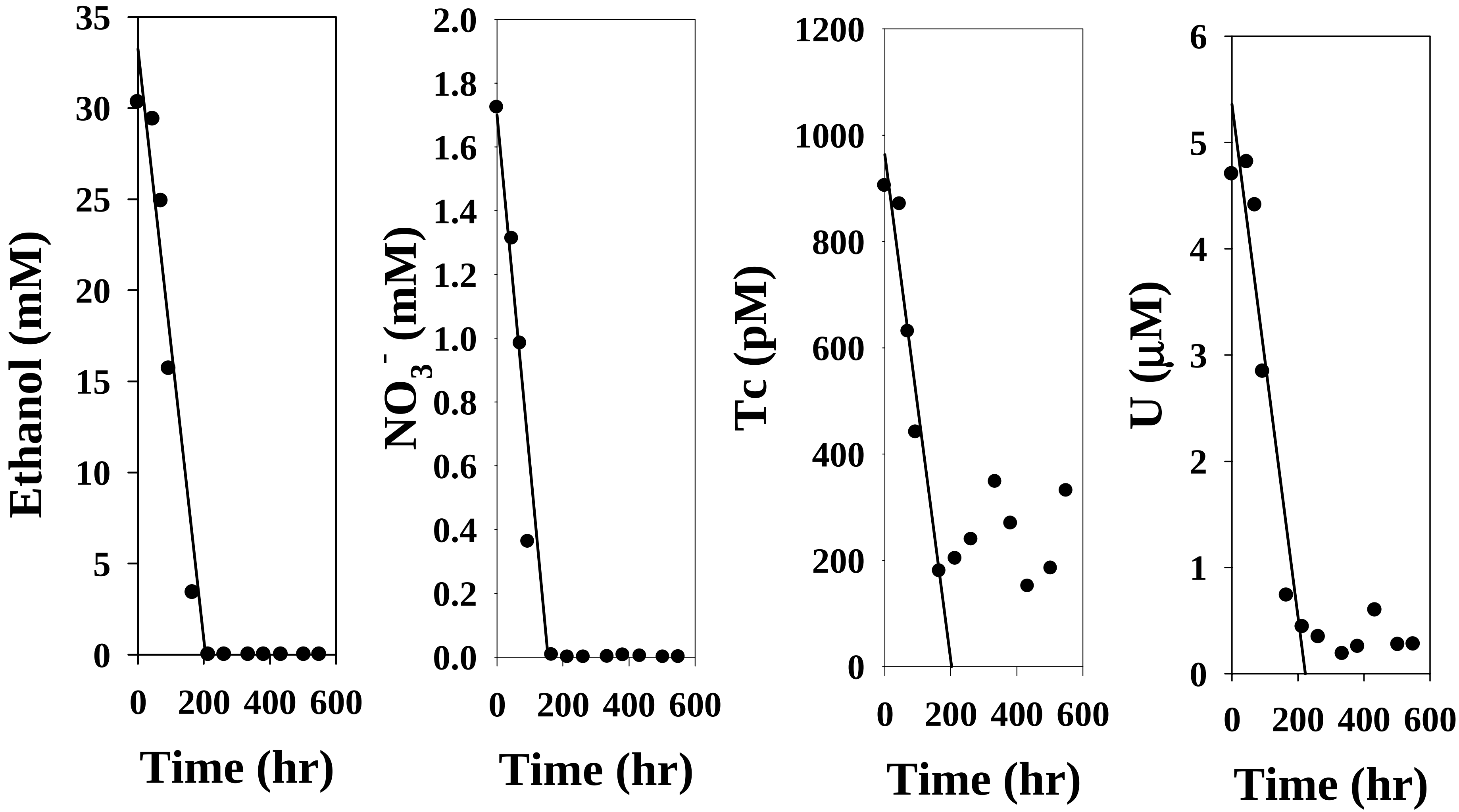


FW034 - 3 mM Nitrate

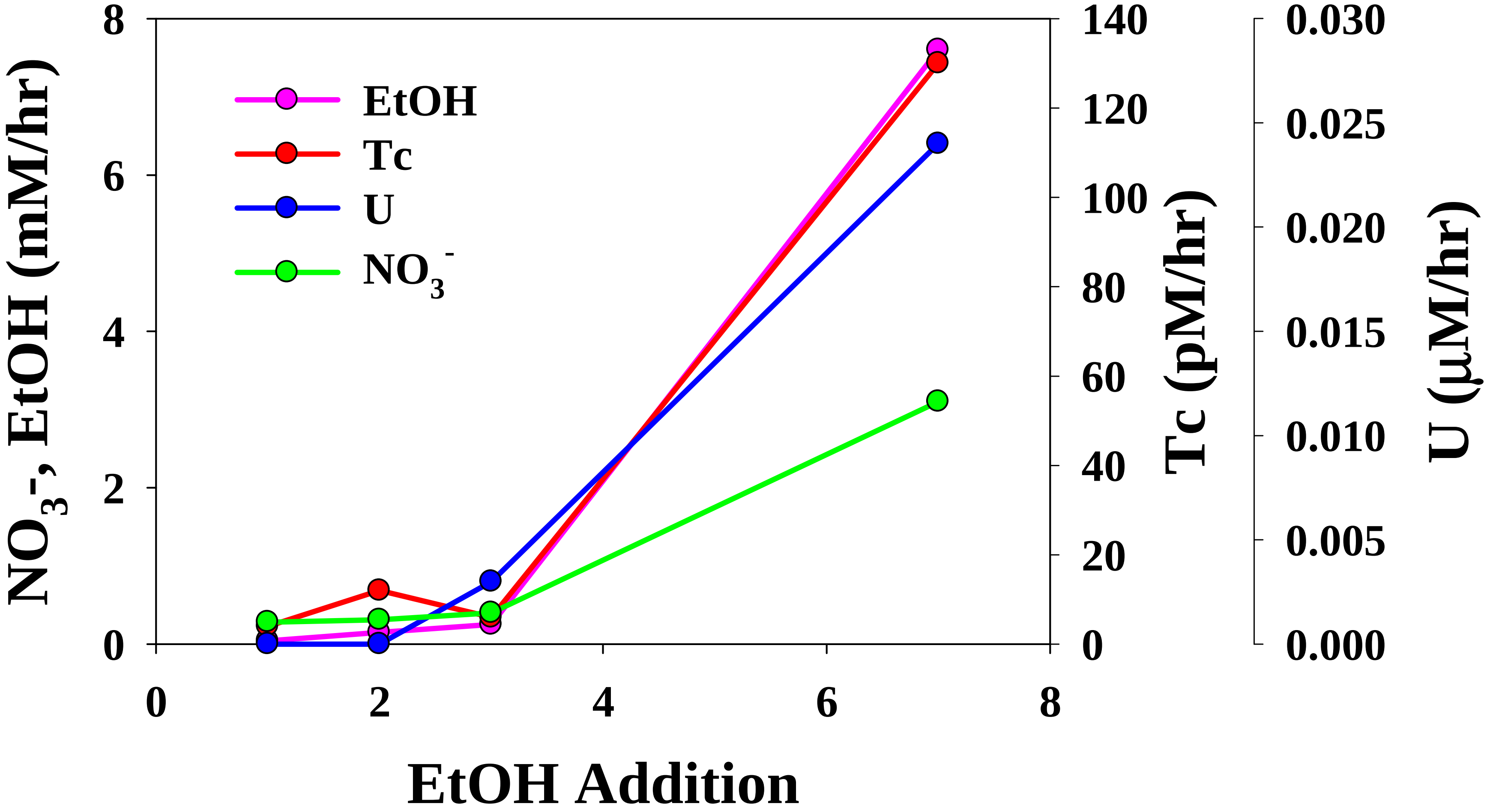


GW835
+ Br-
+ HCO_3^-
+ EtOH

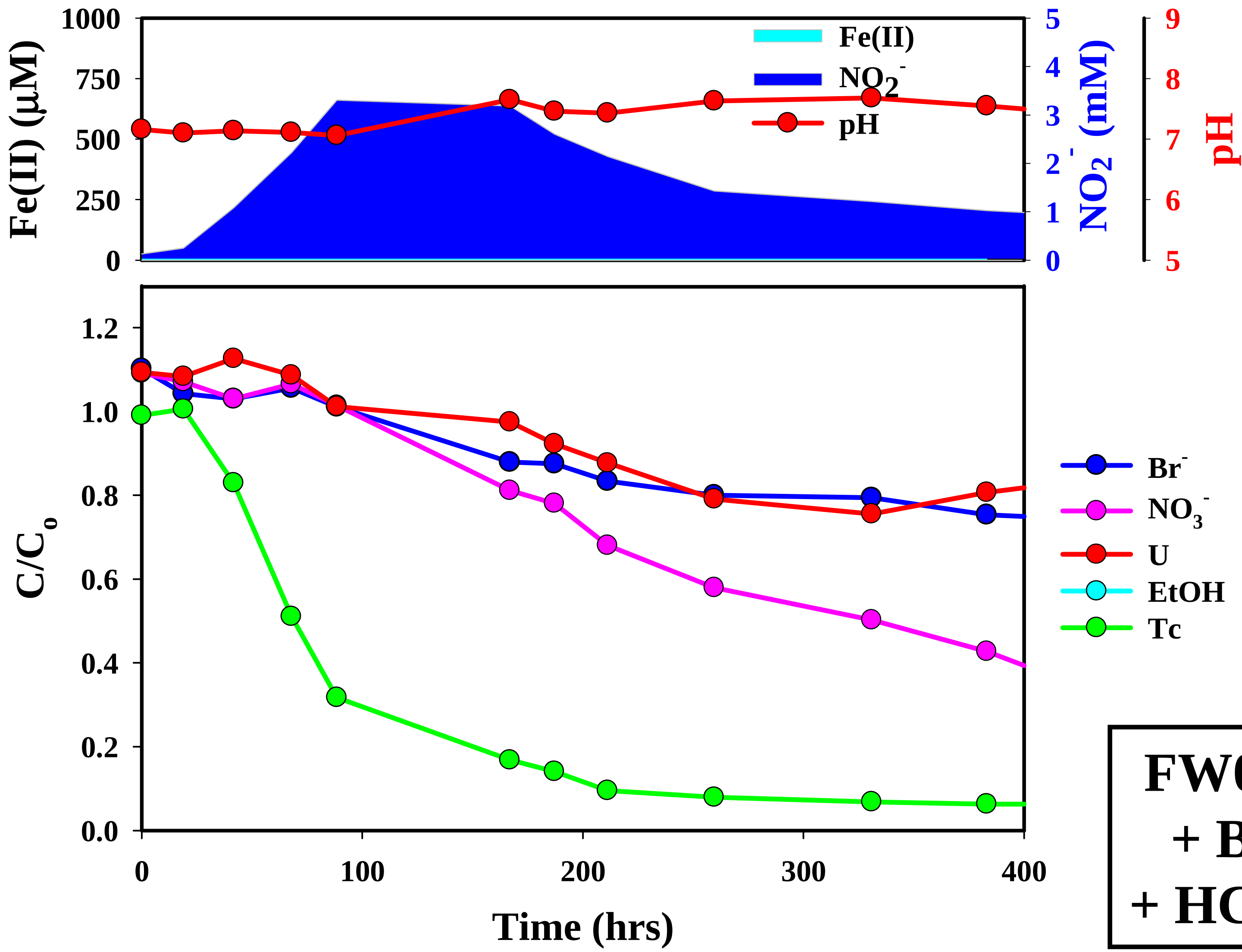
FW034 - 3 mM Nitrate



Effect of Successive Donor Additions on Microbial Activity – FW034

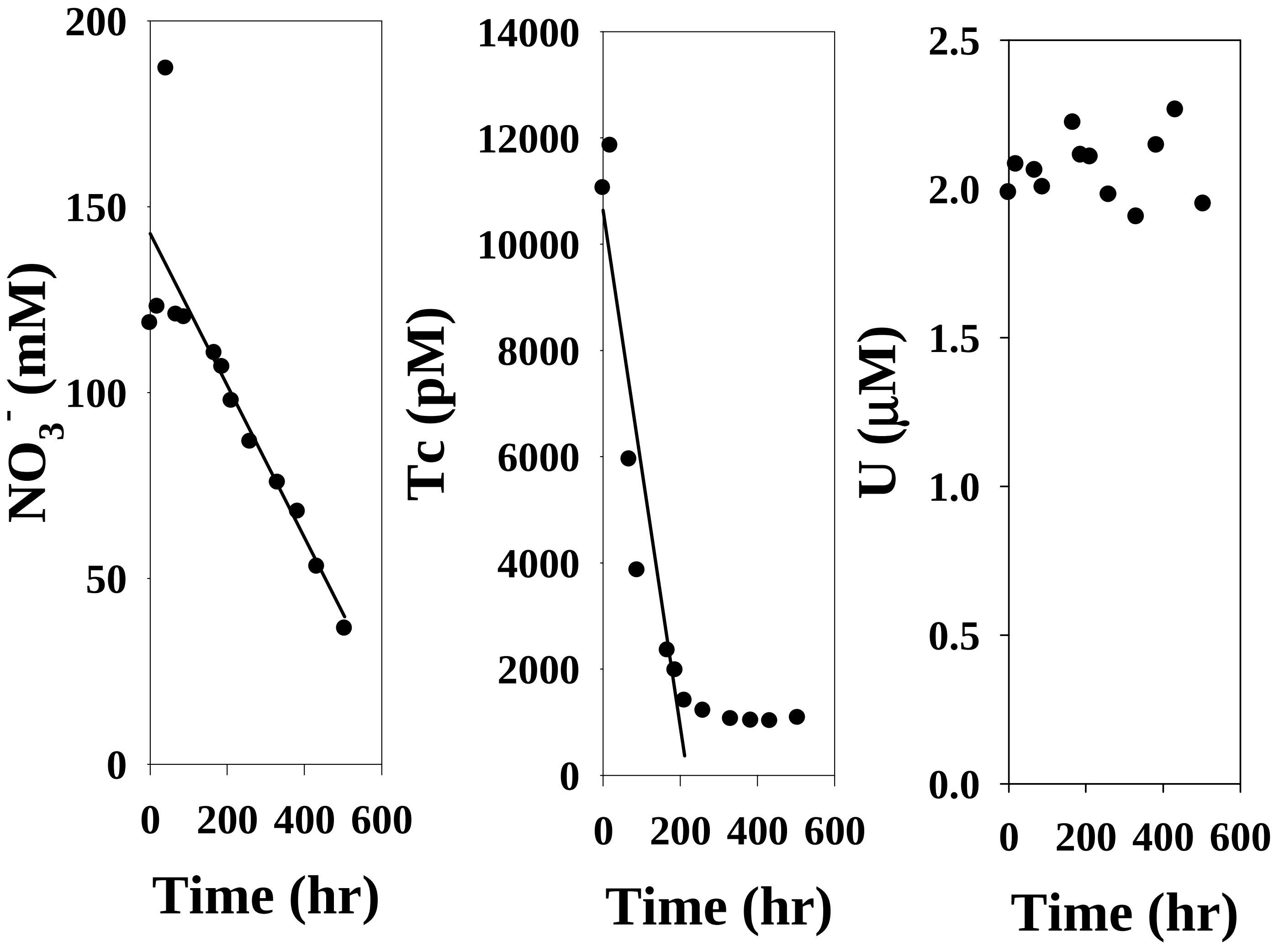


FW034 - 3 mM Nitrate
No Added Donor (After Biostimulation)

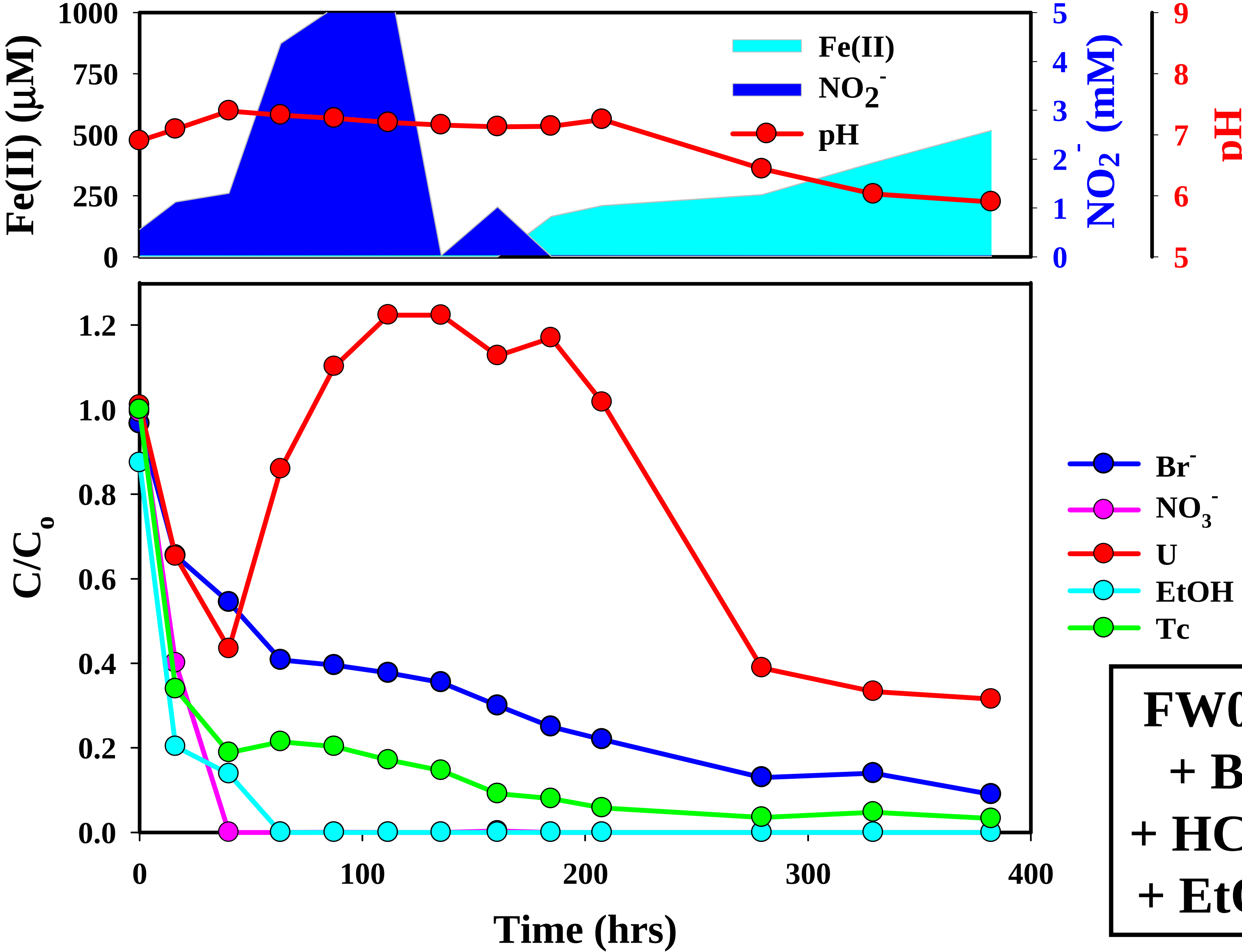


FW021
+ Br^-
+ HCO_3^-

FW034 - 3 mM Nitrate
No Added Donor (After Biostimulation)

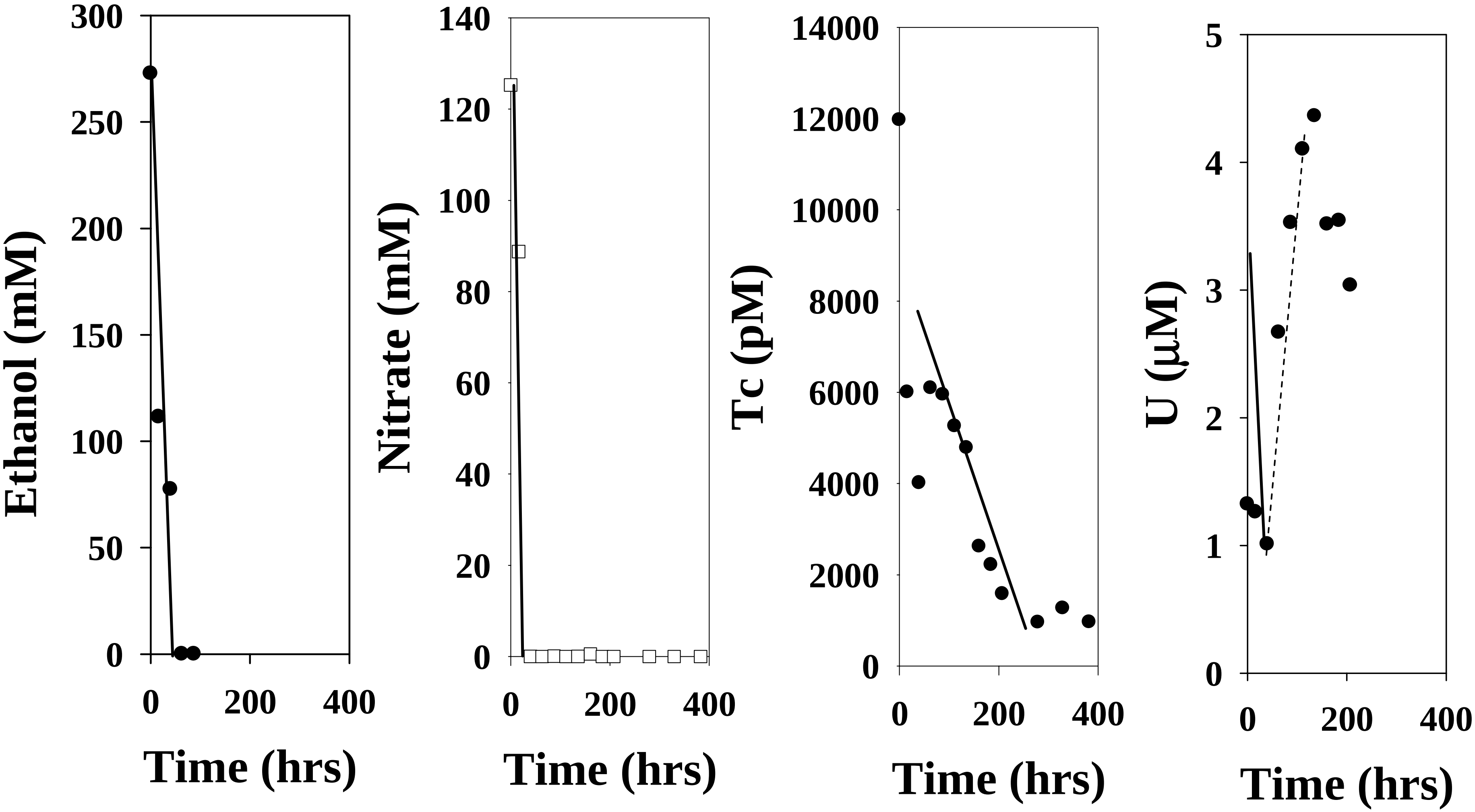


FW034 – 120 mM Nitrate

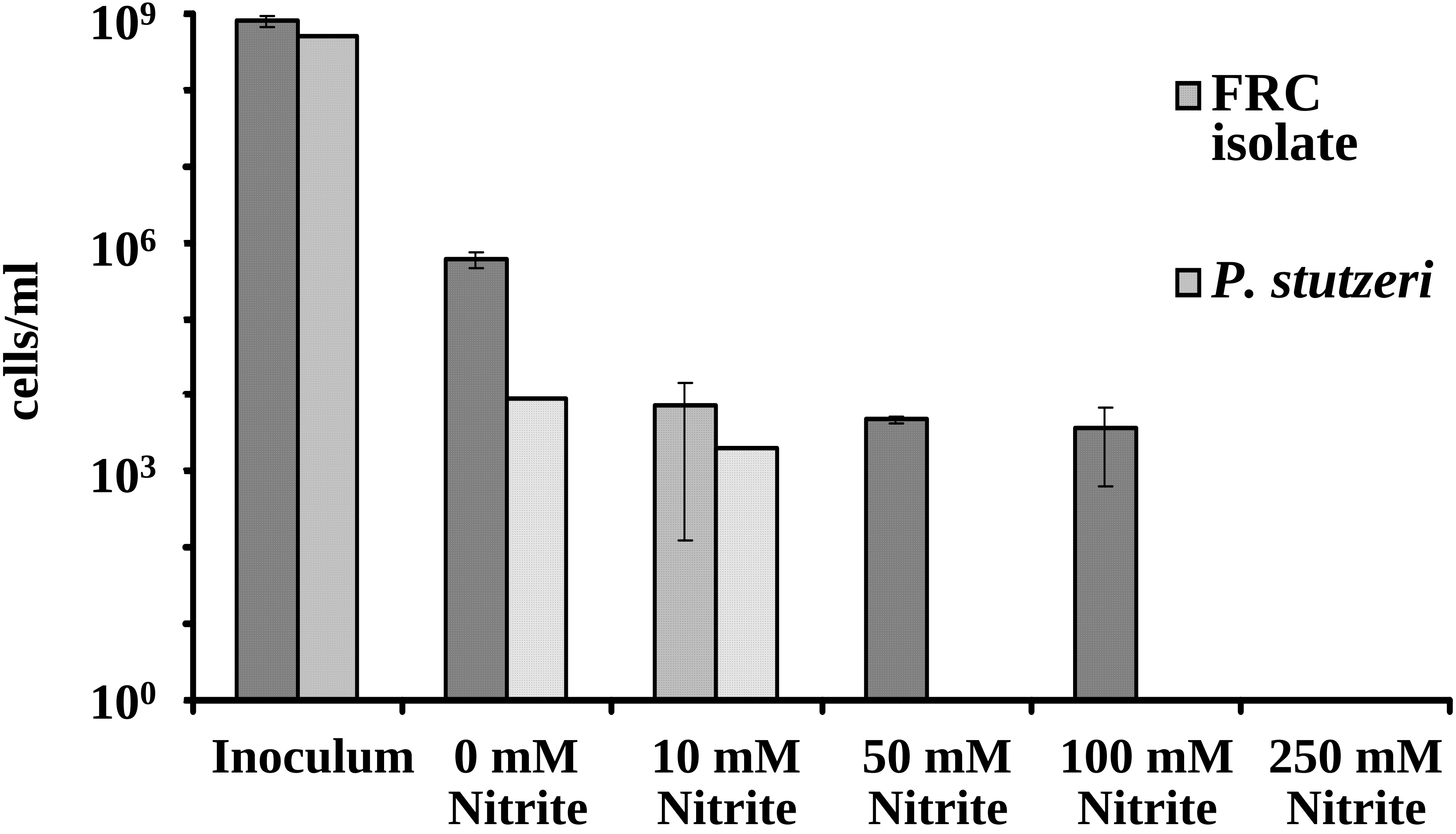


FW021
+ Br^-
+ HCO_3^-
+ EtOH

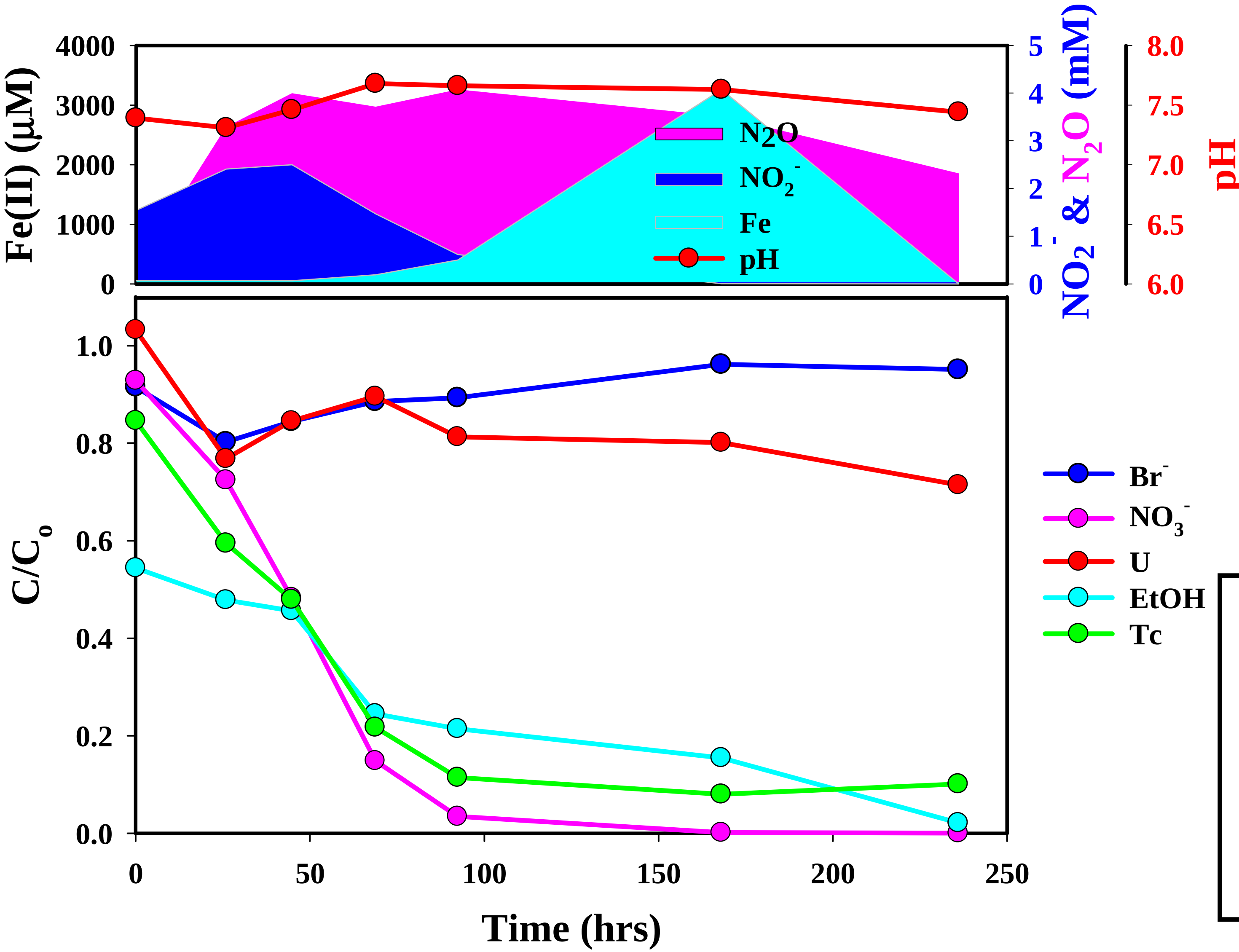
FW034 – 120 mM Nitrate



Effect of Nitrite on Survival in Laboratory Incubations

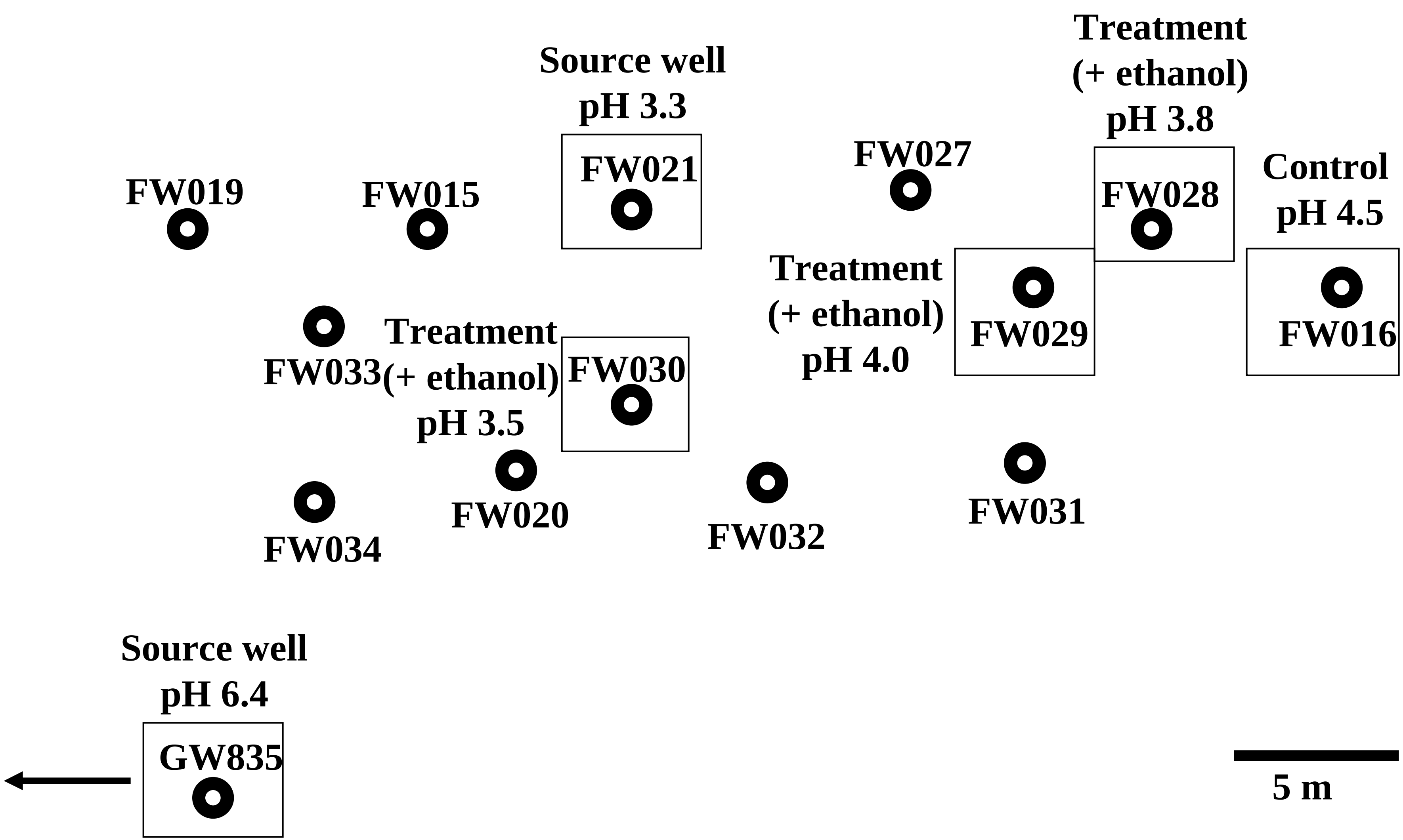


FW034 – 120 mM Nitrate
Acetylene Block Experiment

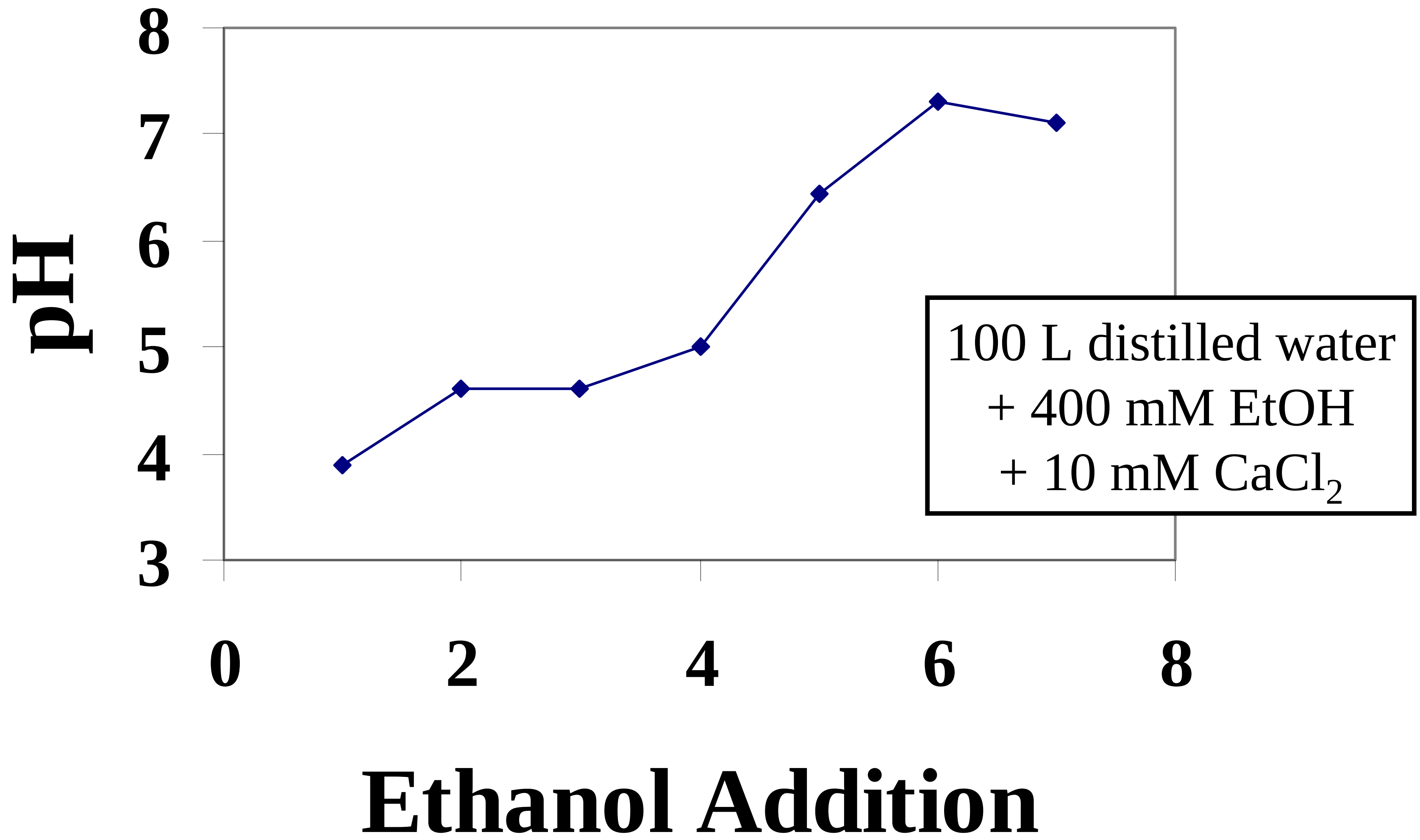


FW021
+ Br^-
+ HCO_3^-
+ EtOH
+ C_2H_2

Field Manipulation Experiments: Phase II – Low pH (Area 1)



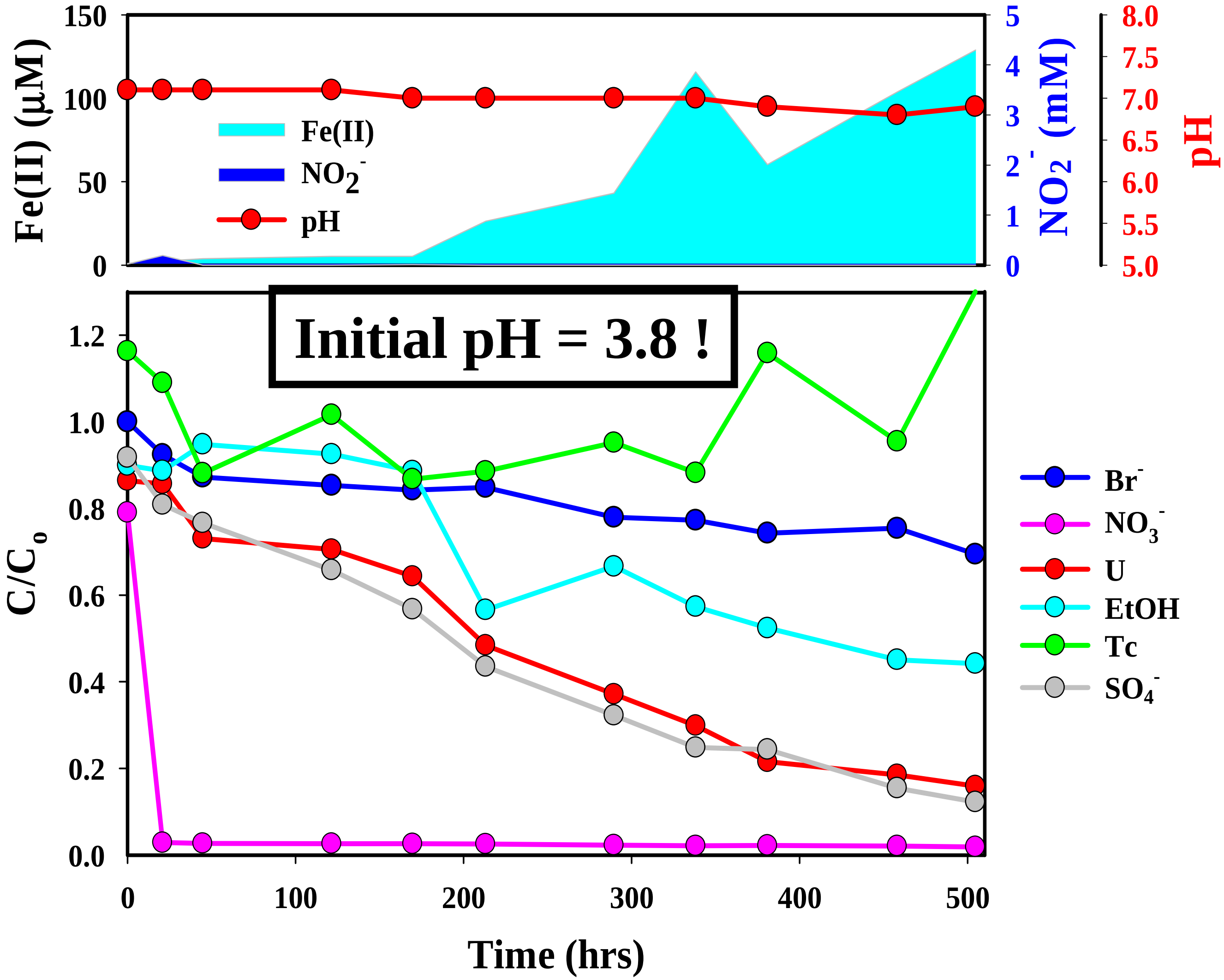
Effect of Biostimulation on pH FW028



Optimum pH for Growth of Nitrate Reducers – FRC Isolates

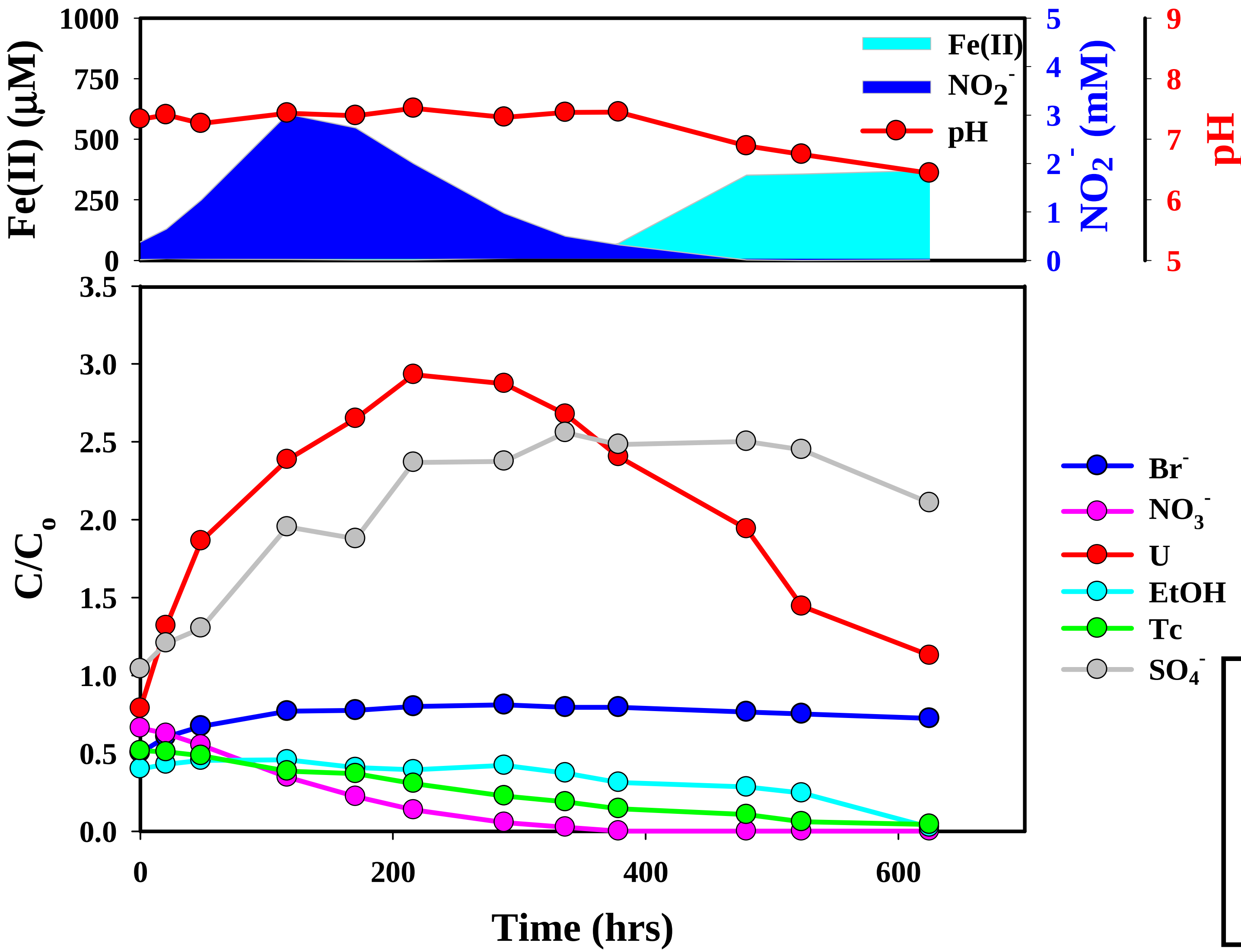
Isolate	pH range	Optimum pH
FW033#1	6.5 - 8.0	8.0
FW033#3	5.5 - 7.5	7.0
FW032#1	5.5 - 7.5	6.5
FW032#2	4.5 - 8.0	6.5
FW032#3	6.0 - 8.0	7.0

FW028 – 3 mM Nitrate After Biostimulation



GW835
+ Br^-
+ HCO_3^-
+ EtOH

FW028 – 120 mM Nitrate
After Biostimulation

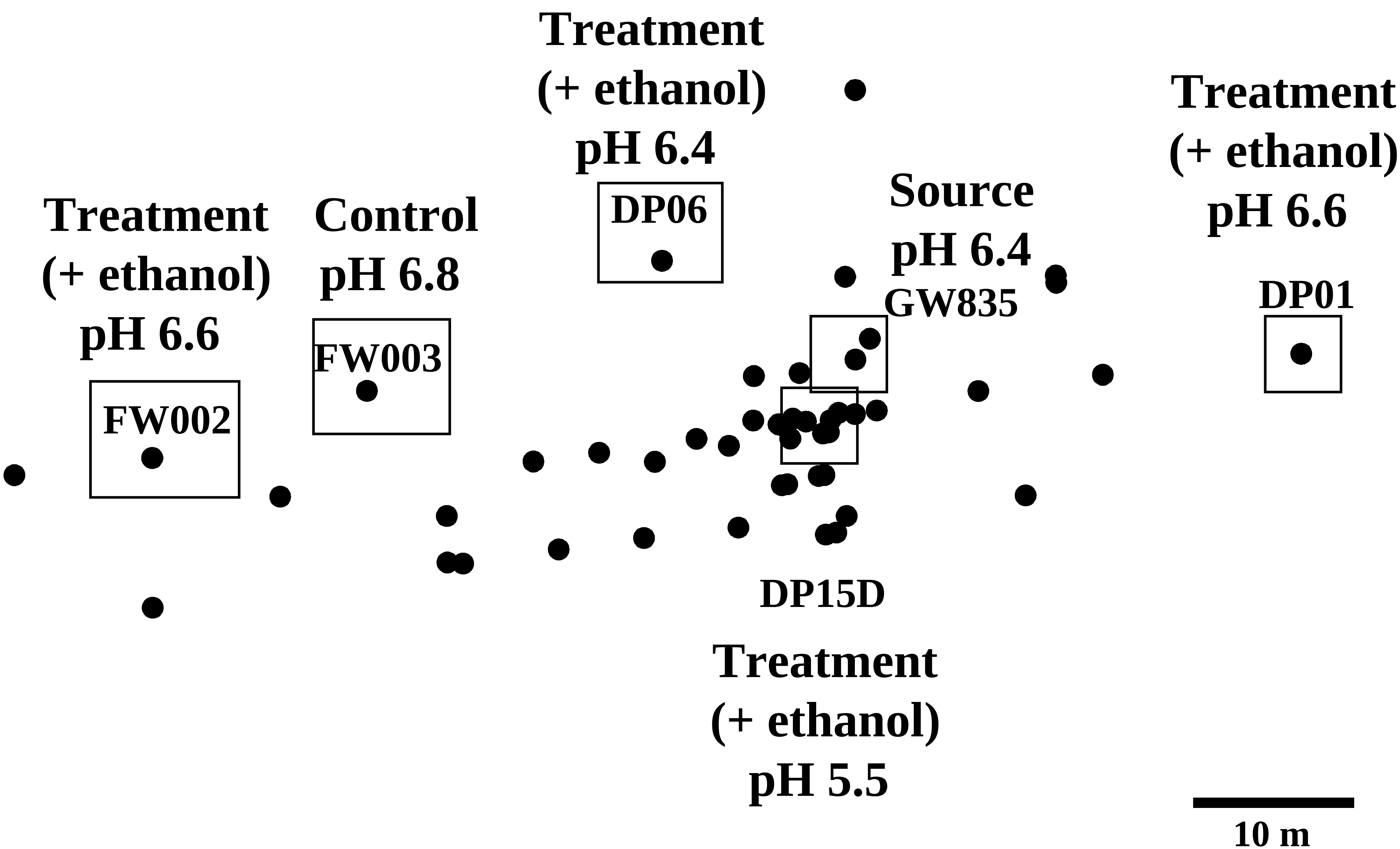


FW021
+ Br^-
+ HCO_3^-
+ EtOH

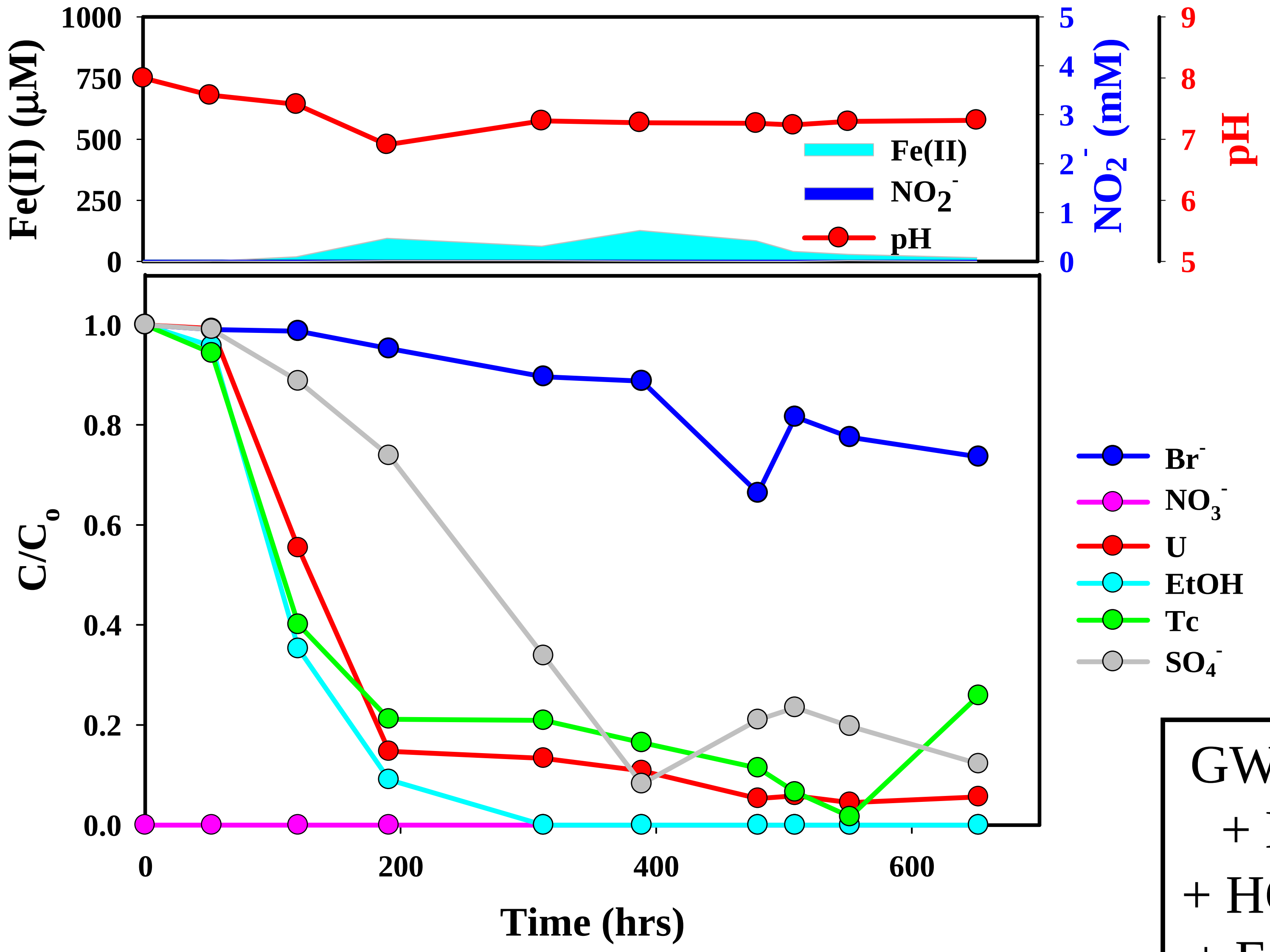
Effect of Low pH on Microbial Activity

- **Microbial activity was stimulated in low pH (< 4) sediments with *neutralized* groundwater (no added bicarbonate)**
- **Little microbial activity observed in laboratory microcosm studies or field push-pull tests conducted with FW021 (pH ~ 3.4) groundwater without added bicarbonate**
- **One explanation may be Al and/or Ni toxicity**

Field Manipulation Experiments: Phase III – Moderate pH (Area 2)

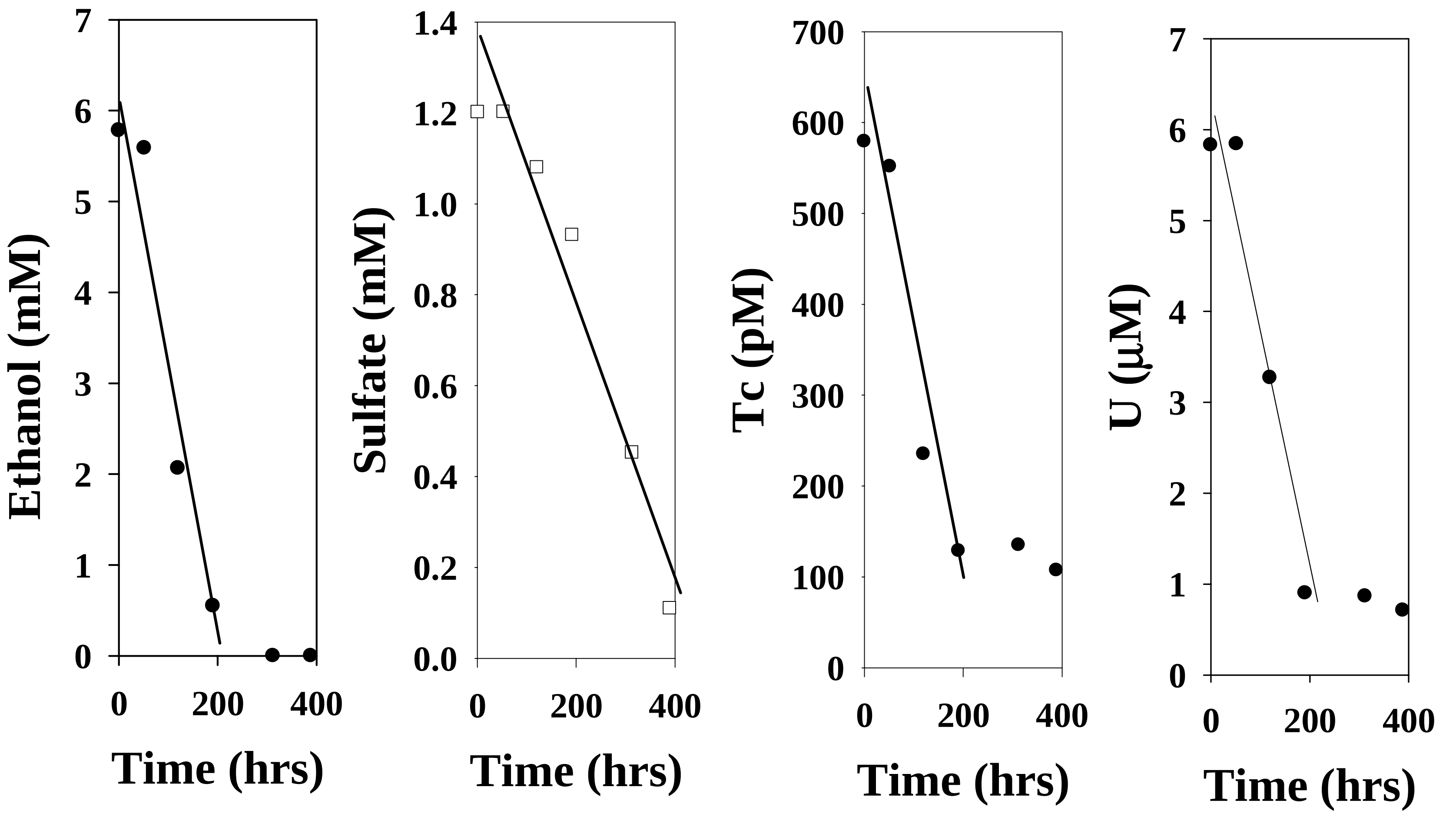


DP06 – 3 mM Nitrate



GW835
+ Br^-
+ HCO_3^-
+ EtOH

Results: DP06 – 3 mM Nitrate



Summary of Push-Pull Tests (95 tests)

- **Indigenous microorganisms in the shallow aquifer in Areas 1 and 2 have the capability:**
  - **To utilize ethanol, glucose, and acetate**
  - **To reduce nitrate to nitrite via denitrification**
  - **To reduce sulfate and Fe(III)**
  - **To immobilize Tc and U**
- **Biostimulation by successive donor additions increases pH and microbial activity**
- **Biostimulation initiated ethanol utilization and nitrate and Tc reduction in low pH (< 4) environments**

Summary (Continued)

- **Push-pull tests are able to quantify in situ microbial activity:**

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

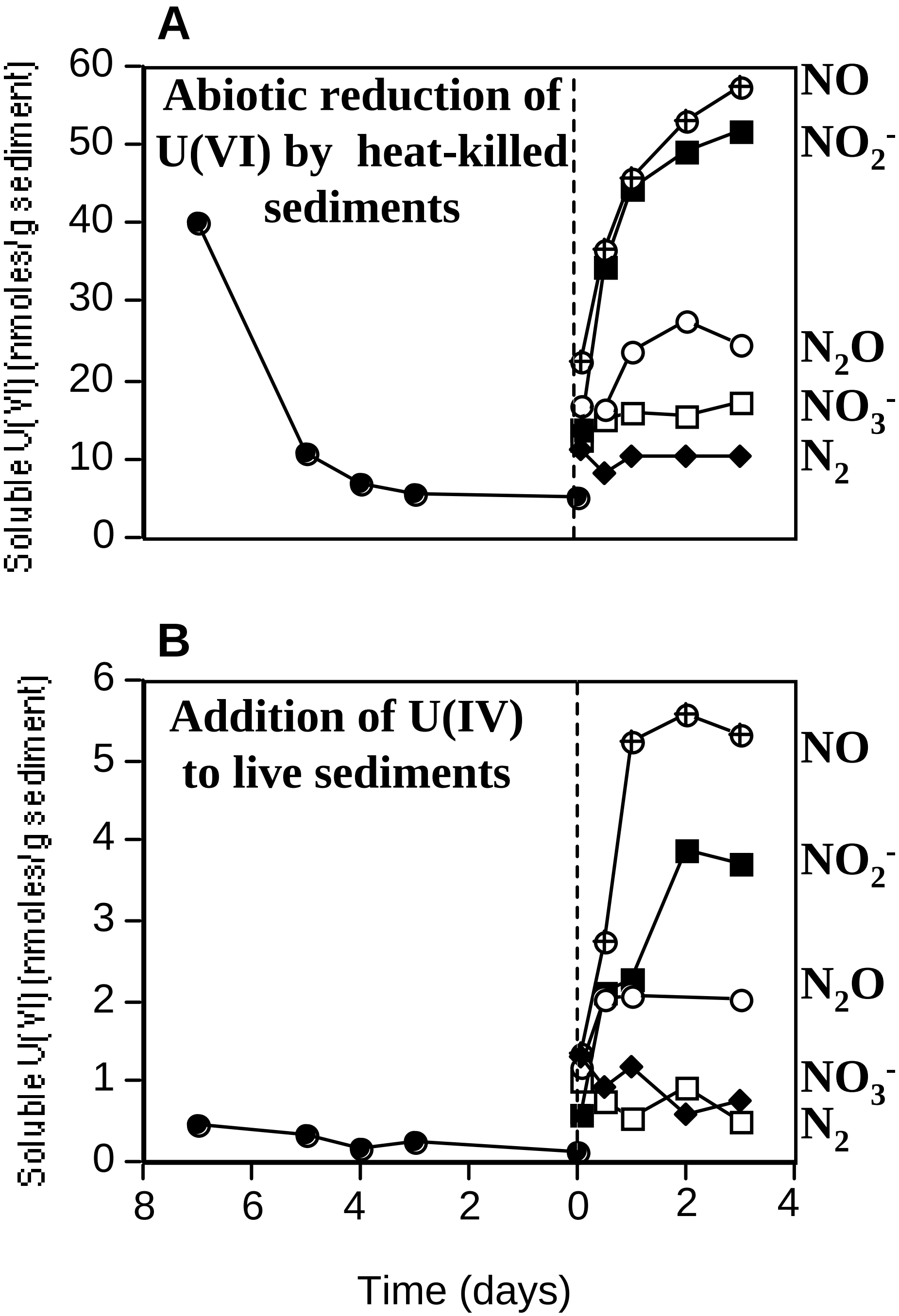
Activity (after biostimulation)

Initial pH	EtOH (mM/hr)	NO_3^- (mM/hr)	SO_4^{2-} (mM/hr)	U(VI) (μM/hr)	U(IV) (μM/hr)	Tc(VII) (pM/hr)
3.3 – 3.9	0.3 – 1.0	0.1 – 0.4	0 – 0.01	$10^{-4} – 10^{-3}$	$10^{-3} – 10^{-2}$	4 – 30
5.2 – 5.6	0.3 – 4.0	0.3 – 4.0	0 – 0.01	$10^{-4} – 10^{-3}$	$10^{-3} – 10^{-2}$	10 – 150
5.6 – 7.2	0.1 – 2.0	0.1 – 2.0	0 – 0.03	$10^{-4} – 10^{-3}$	$10^{-3} – 10^{-2}$	4 - 10

Some Additional Comments

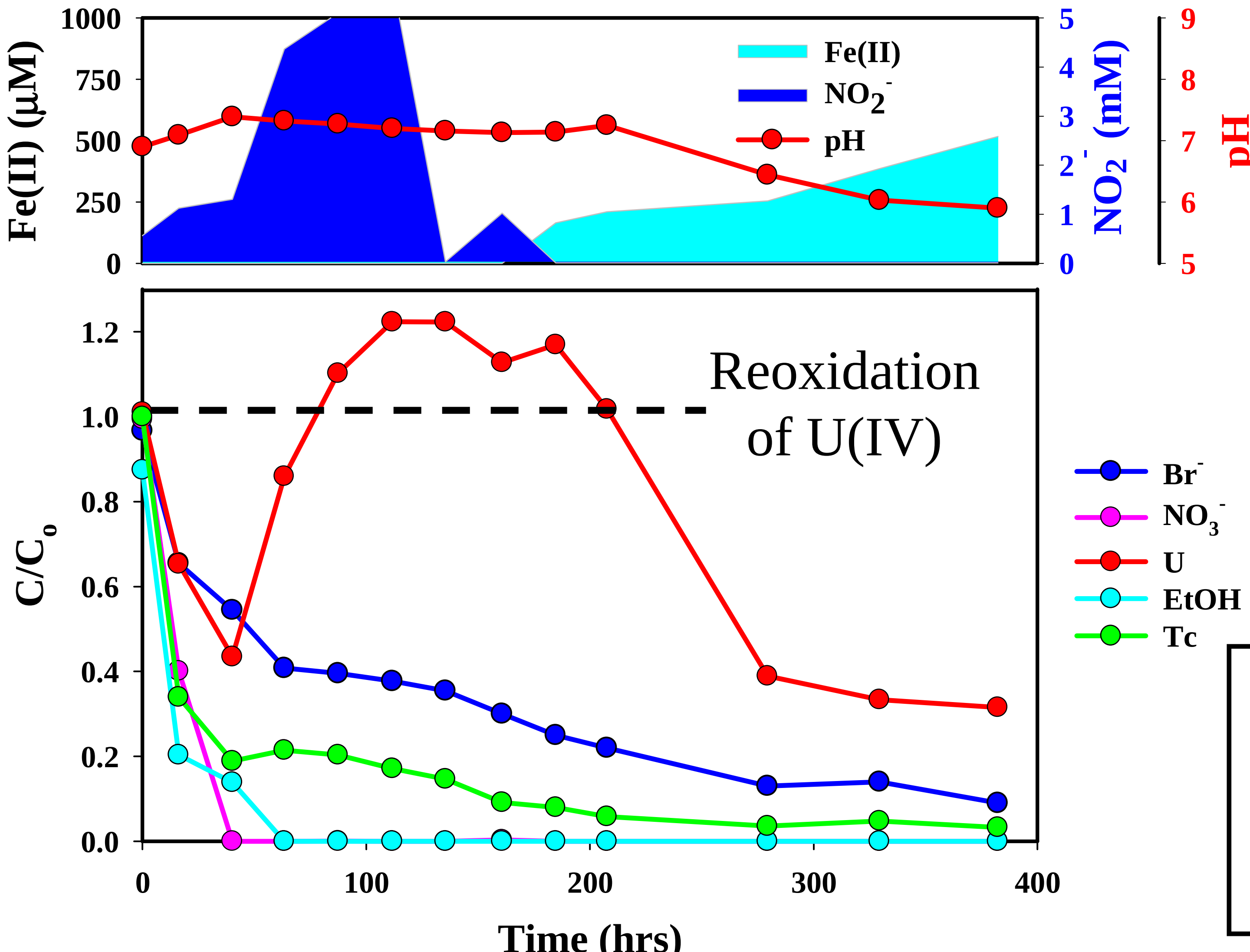
- **Desired metabolic capability is widespread and it may be relatively easy to create subsurface conditions that favor U and Tc reduction**
- **However, in high nitrate environments, nitrate and denitrification intermediates will rapidly oxidize U(IV)**
- **pH increases resulting from biostimulation will result in formation of U(VI)-containing solids**
- **Clogging of aquifer by precipitates, biomass, and (perhaps) N_2 gas is possible in the long-term**

Nitrate and Denitrification Intermediates Can Rapidly Oxidize U(IV)



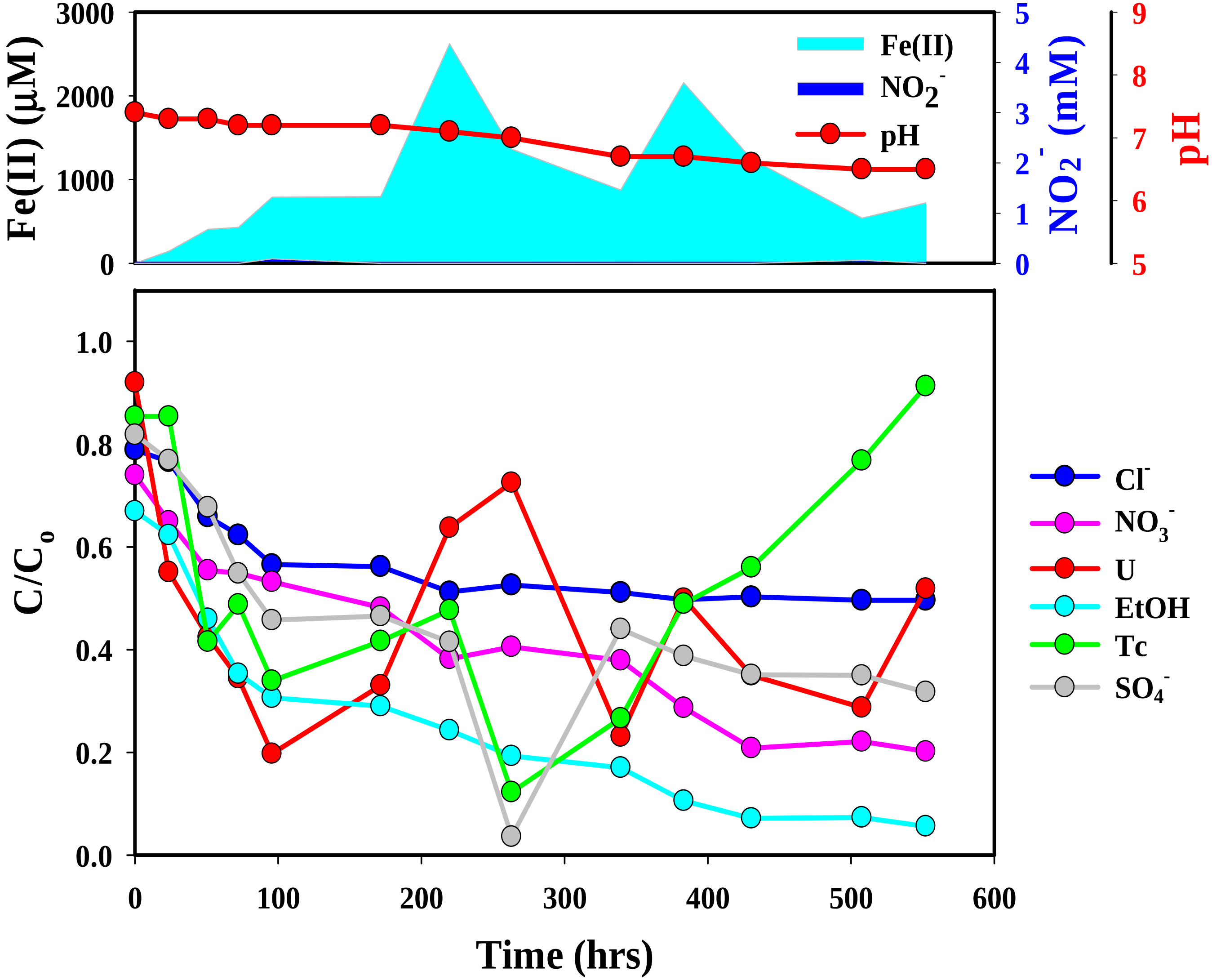
Laboratory incubations

In Situ Reoxidation of U(IV)
FW034 - 120 mM Nitrate



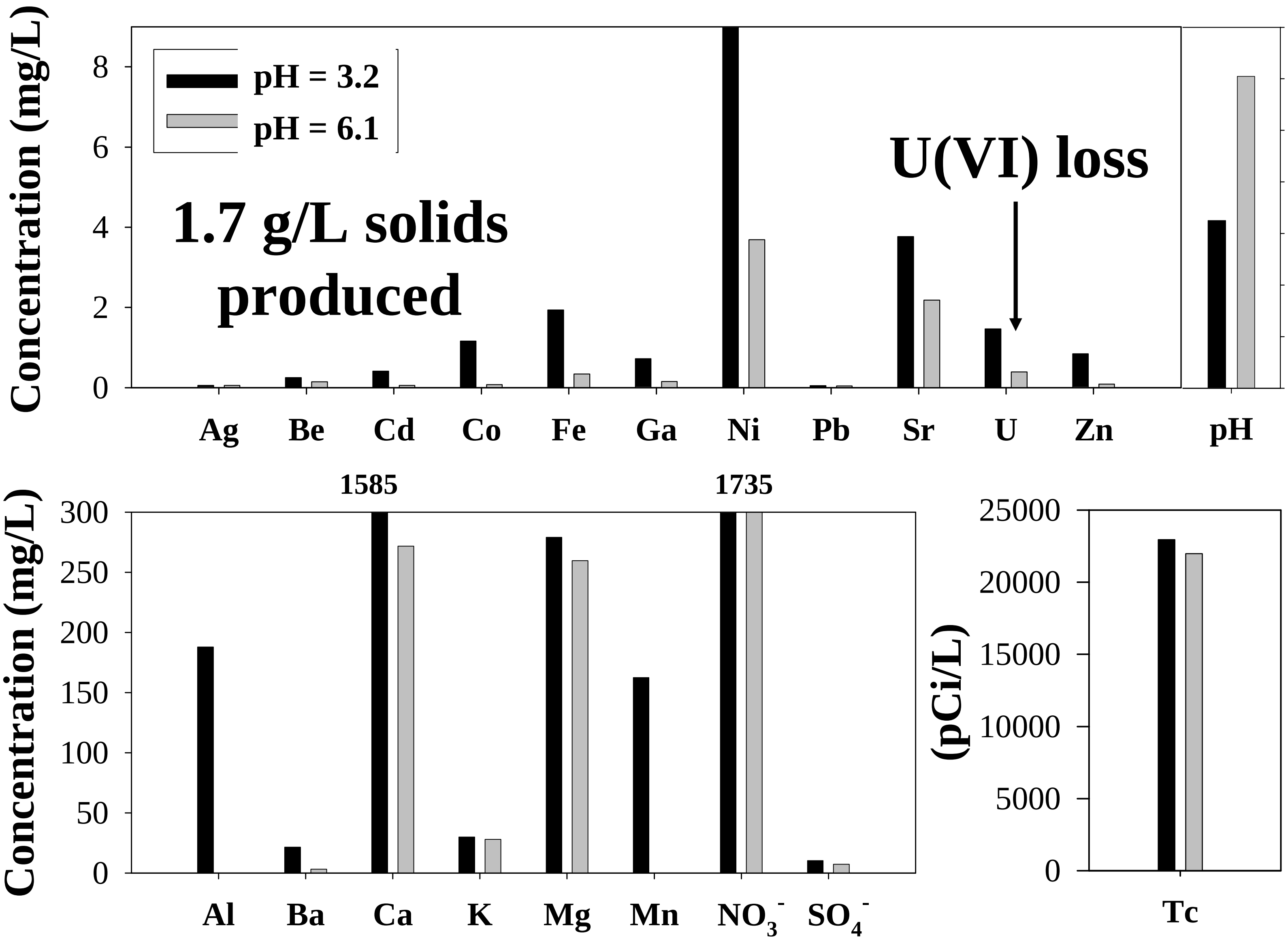
FW021
+ Br^-
+ HCO_3^-
+ EtOH

In Situ Reoxidation of U(IV)
DP-15D – 20 mM Nitrate



GW835
+ Cl^-
+ HCO_3^-
+ EtOH
+ NO_3^-

Precipitate Formation with Increasing pH



Current Research Strategy

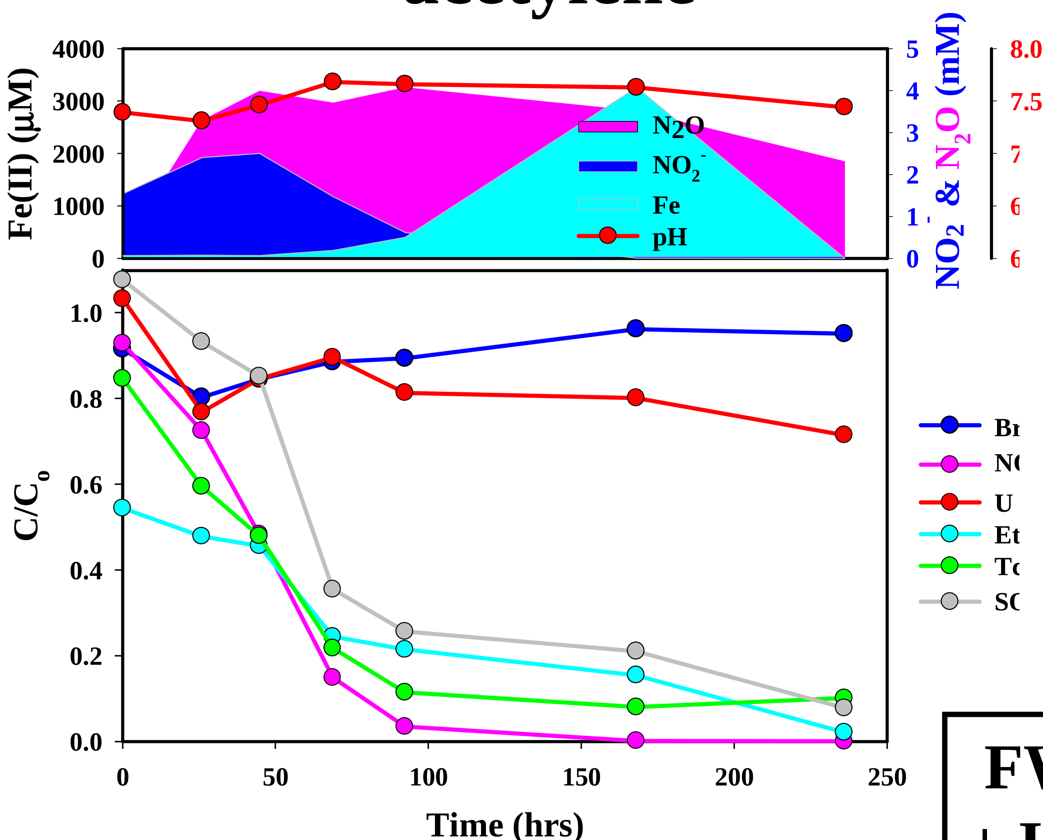
- **Continued laboratory and in situ testing to obtain rates of U(VI) reduction and U(IV) oxidation under defined conditions**
  - **Stimulating microbial activity with low pH water**
  - **Strategies for reducing rates of U(IV) oxidation (amendments with sulfate, acetylene, humics, etc.)**
- **Intermediate-scale laboratory experiments to investigate coupled biogeochemical reactions and transport**
  - **Model groundwater flow path**
  - **Platform for testing numerical models**
  - **Source of biostimulated groundwater and sediment**

Current Research Strategy (cont.)

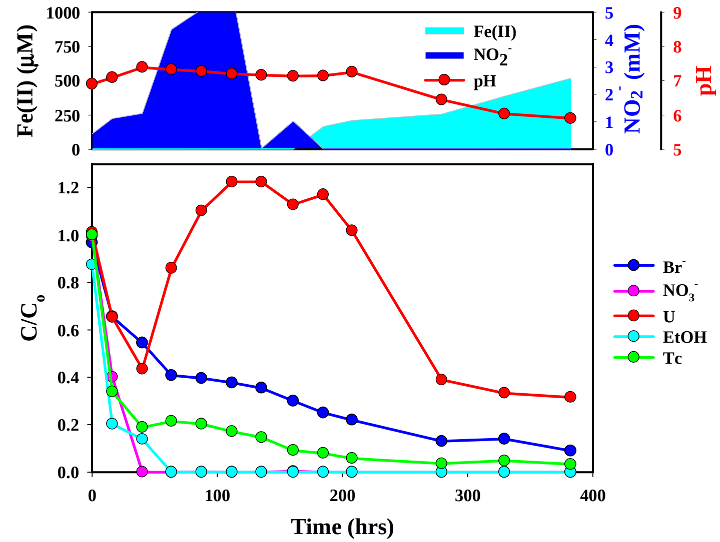
- **Push-pull tests with chemical monitoring for reaction-path calculations**
  - **Charge-balanced anion/cation/pH, U and Tc**
  - **First set of experiments completed, laboratory analyses in process**
- **Near-well estimation of aquifer heterogeneity**
  - **Multilevel samplers installed in three closely-spaced wells**
  - **Small-scale vertical heterogeneity in water composition will be monitored during series of push-pull tests**

Can Acetylene Inhibit Microbial Oxidation of U(IV) ?

+ acetylene



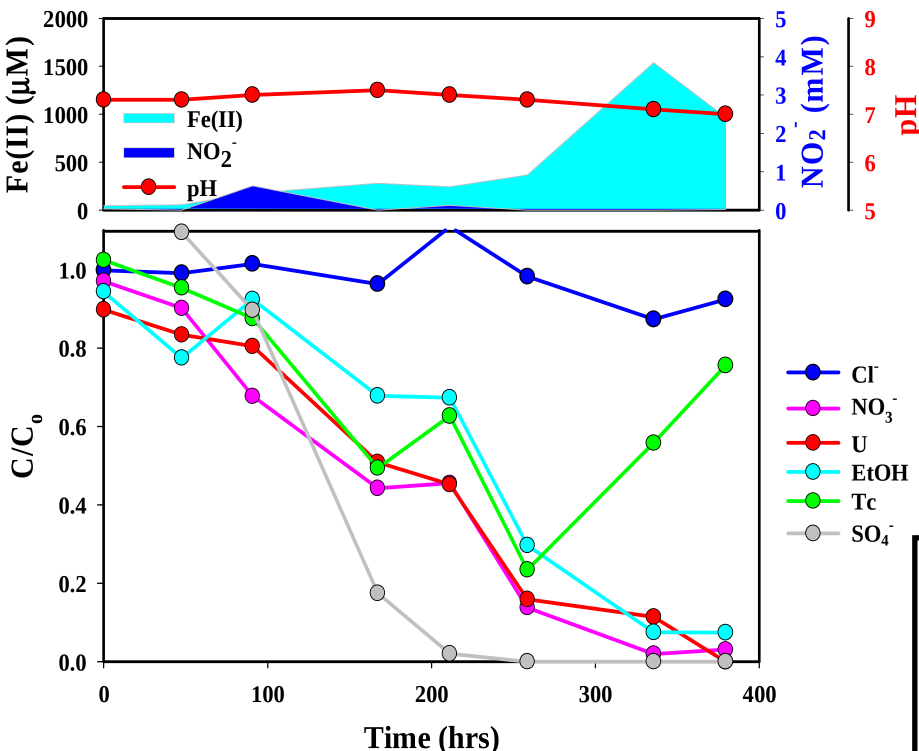
- acetylene



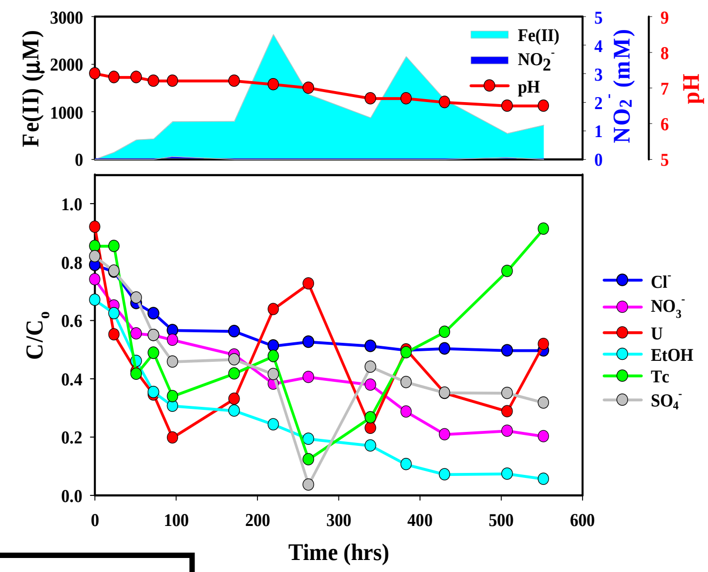
FW021
+ HCO_3^-
+ EtOH

Can Sulfide Mitigate U(IV) Oxidation by Denitrification Intermediates ?

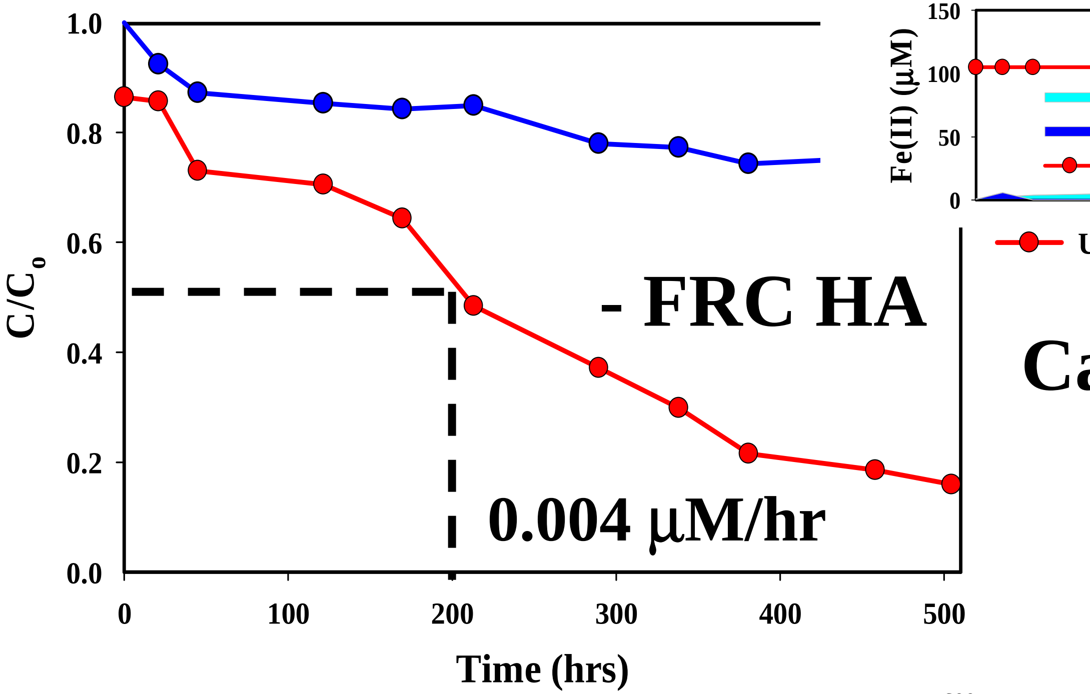
+ 20 mM nitrate following + 20 mM sulfate

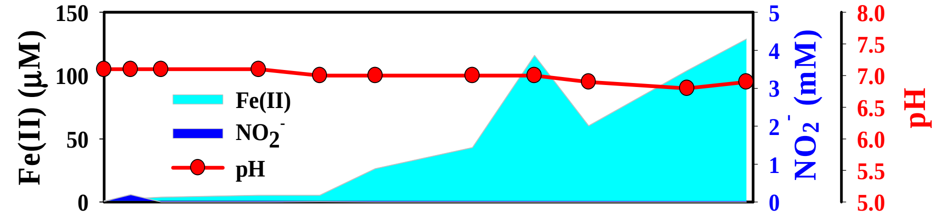


+ 20 mM nitrate - added sulfate

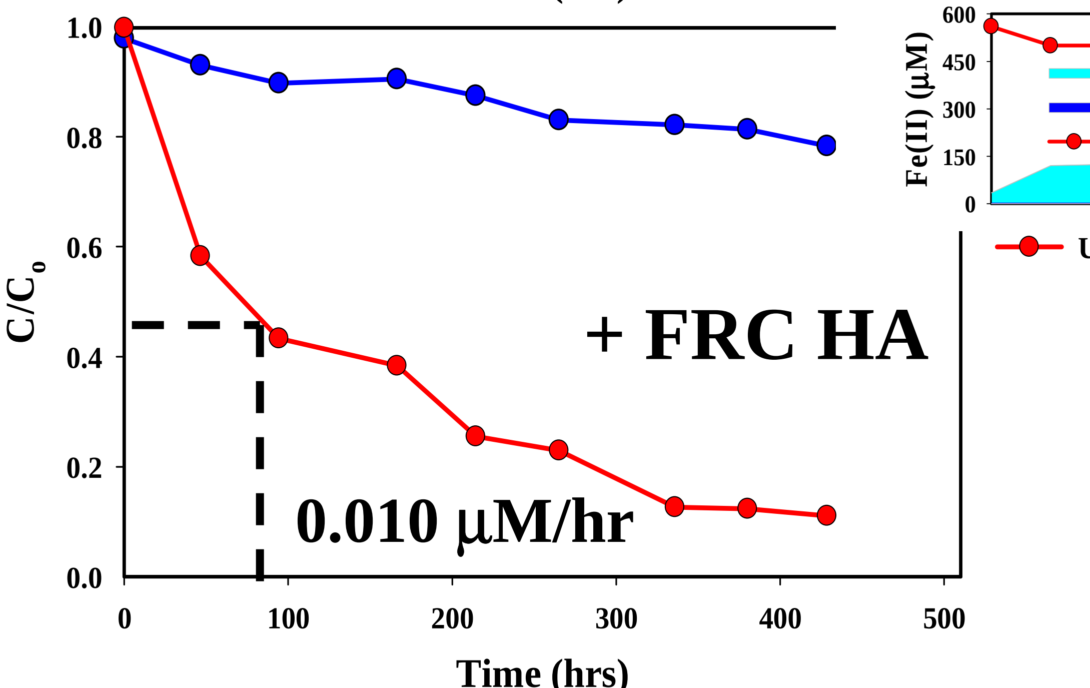


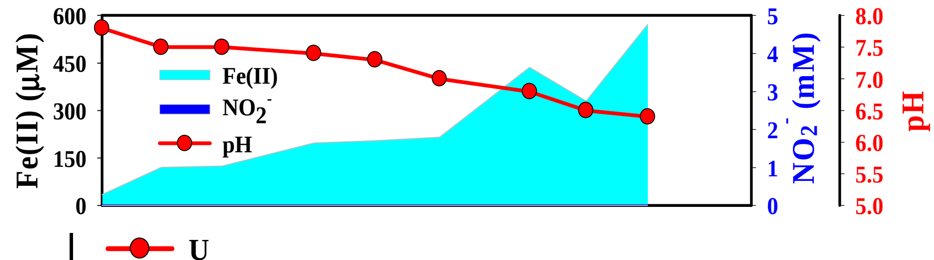
GW835
+ HCO_3^-
+ EtOH



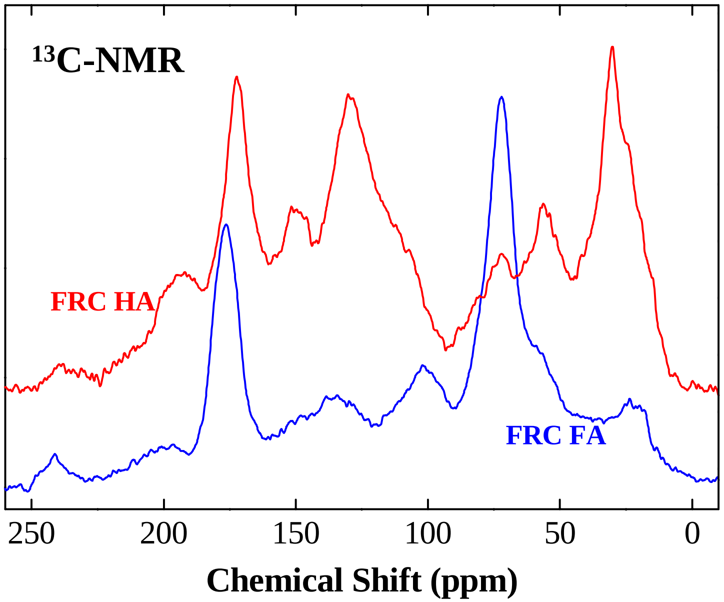


Can Added Humic Acids Increase Rates of Bioreduction ?



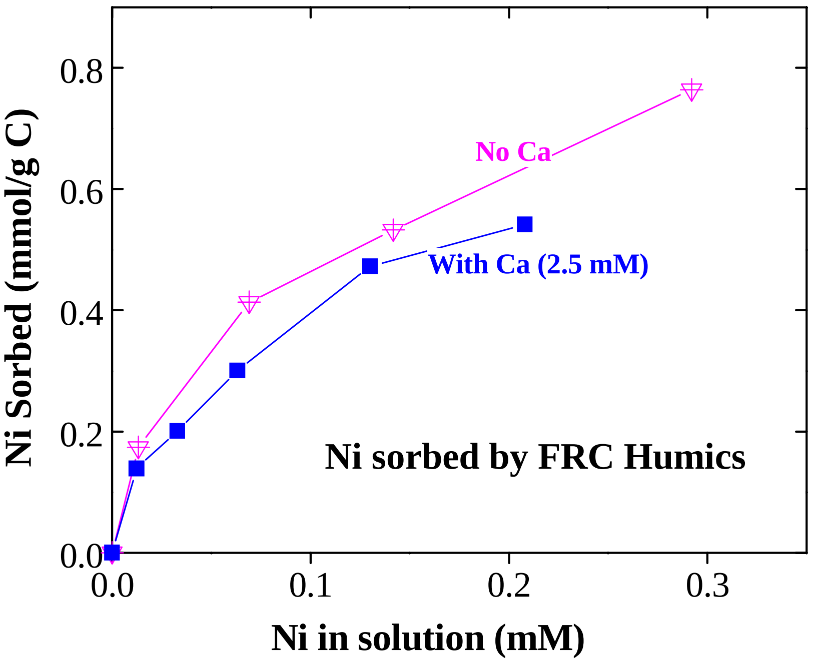


GW835
+ HCO_3^-
+ EtOH

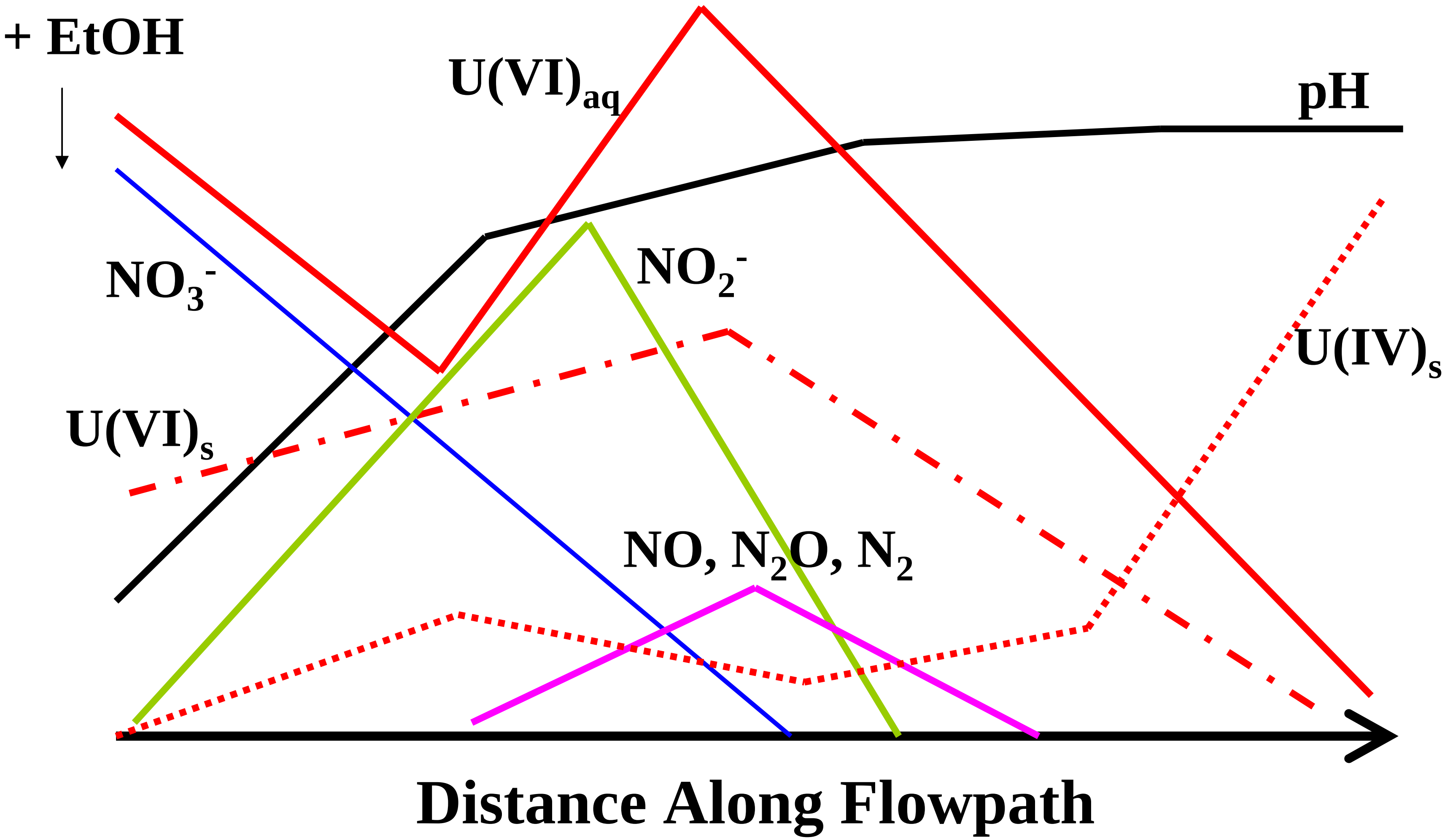


- **FRC humic acid enriched with aromatics and quinone moieties.**
- **FRC fulvic acid depleted with aromatics, but enriched with carboxyl and hydroxyl moieties.**

- **FRC humics sorb and complex with Ni, Al, and other heavy metals.**



Coupling Transport with Bioimmobilization



Small-Scale Laboratory Models

FW021
pH = 3.3
NO_3^- = 120 mM
U(VI) = 6 μM
Tc = 18000 pM
+ Al, Ni, etc.

→ **Crushed limestone column** →

pH = 6.1
NO_3^- = 120 mM
U(VI) = 5 μM
Tc = 18000 pM
- Al, Ni, etc.

System operated for 100 pore volumes

↓ **Limestone/sediment chamber + EtOH** ↓

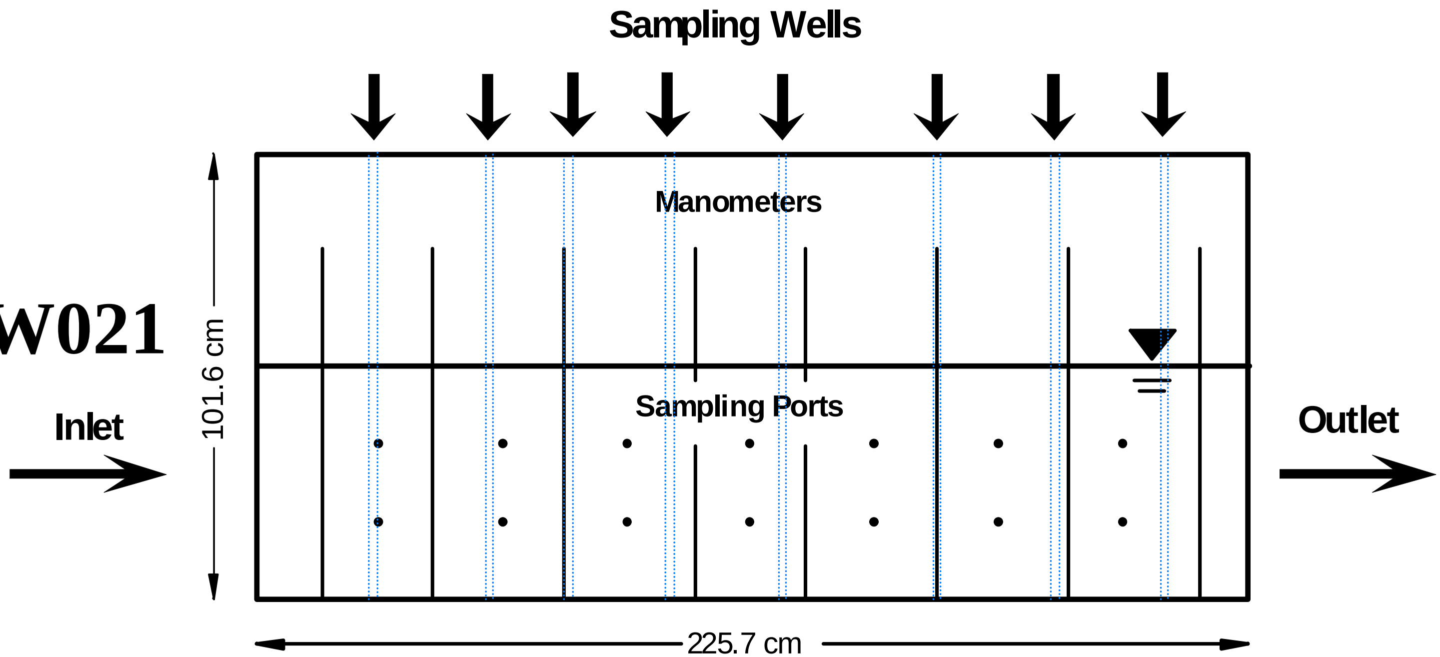
pH = 6.4
NO_3^- = 2 mM
U(VI) = 5 μM
Tc = 18000 pM
(~ GW835)

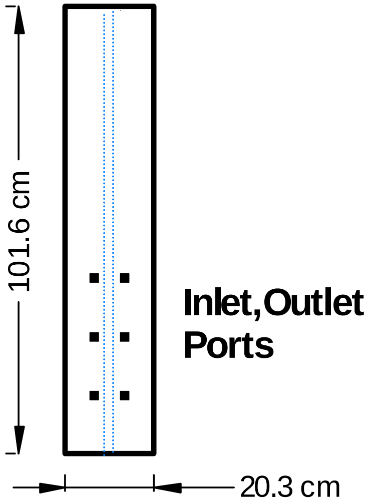
← **Limestone/sediment Column + EtOH** ←

pH = 6.6
NO_3^- = 0
U(VI) ~ 0
Tc ~ 0

Intermediate-Scale Physical Model – Area 1

FW021





320 L Total volume

128 L pore volume

700 kg limestone

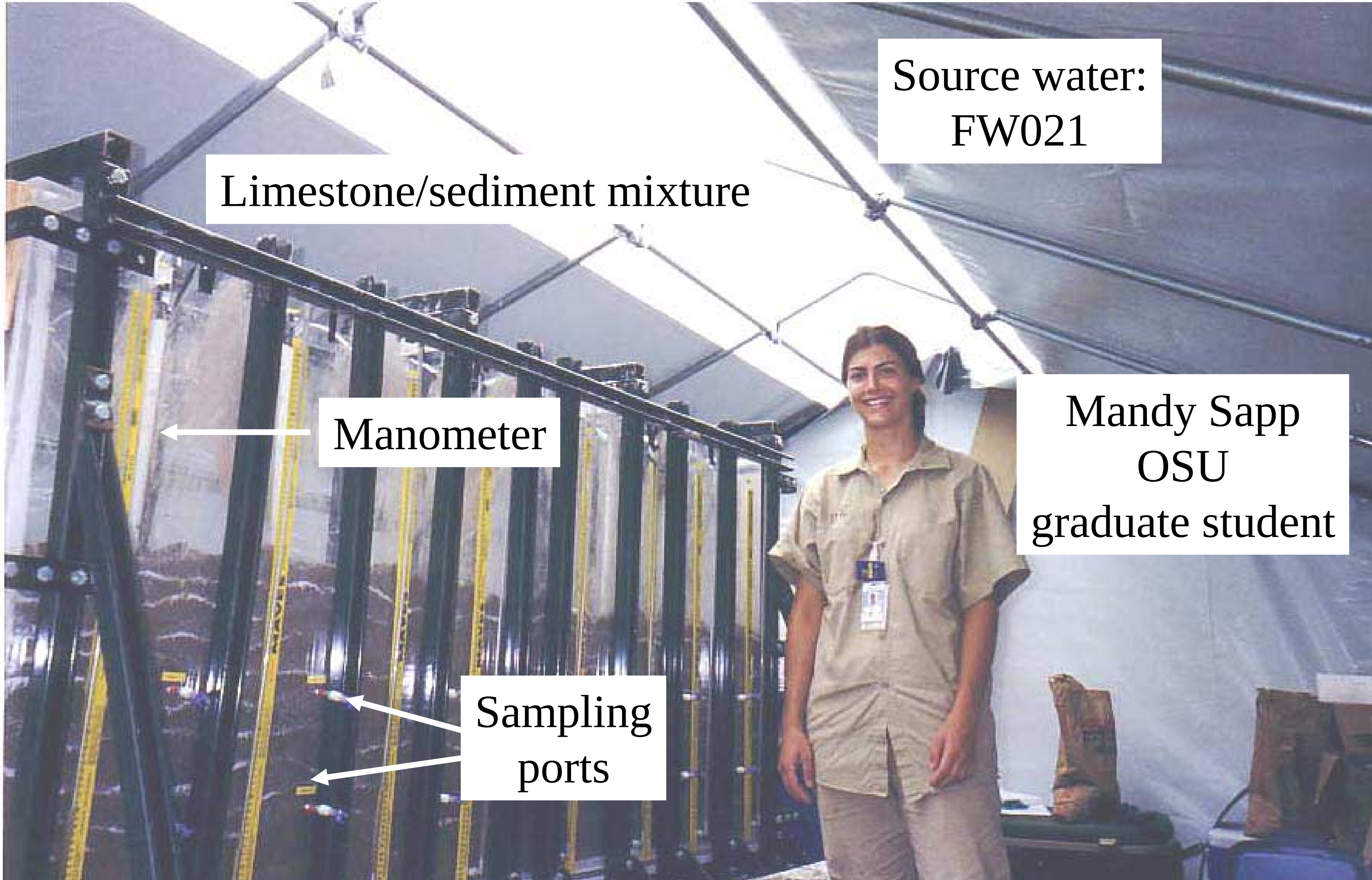
18 kg sediment

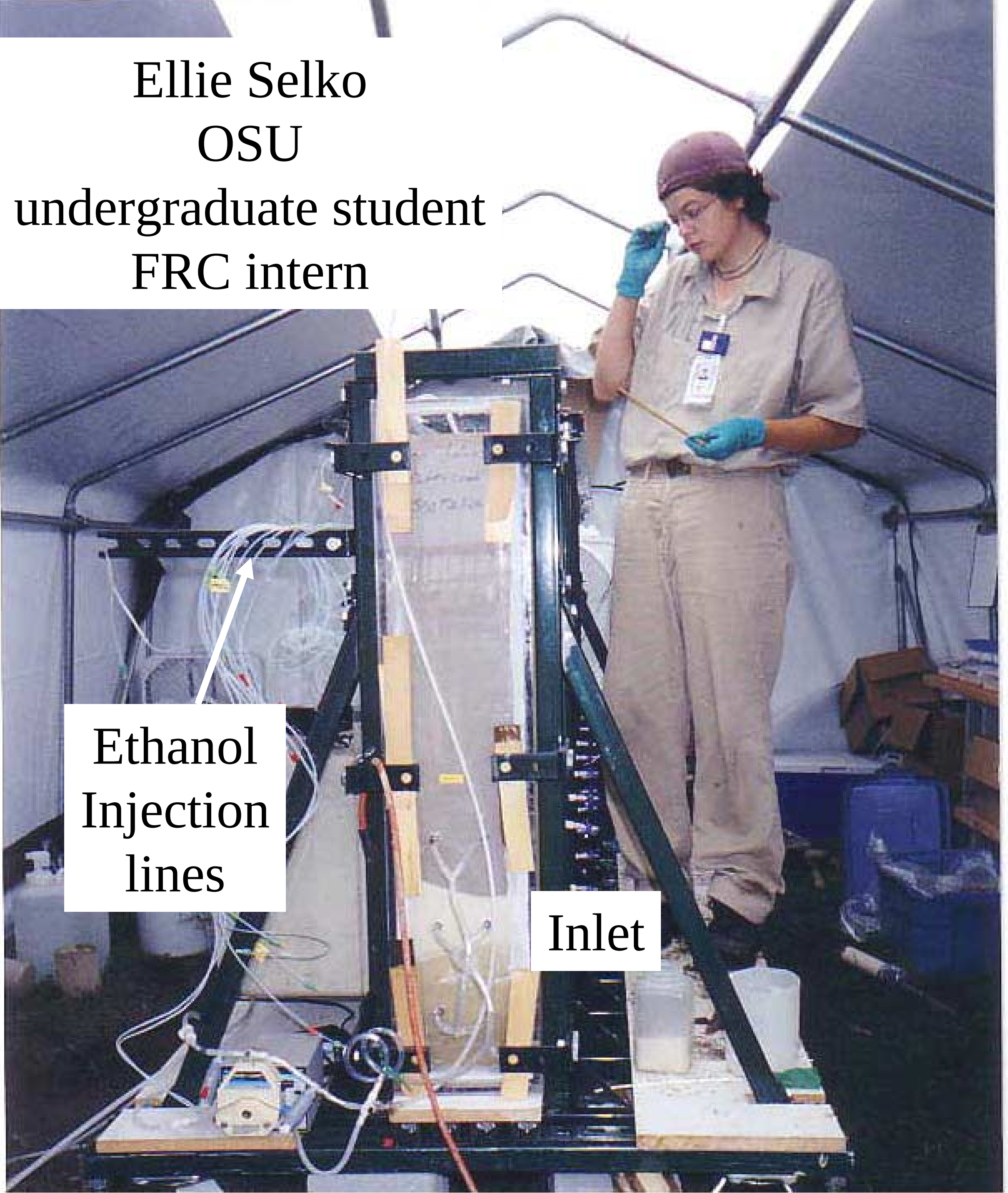
<u>Current flow rate</u>

=3.7 mL/min = 5.3 L/day

=0.04 pore volumes/day

Intermediate-Scale Physical Model – Area 1



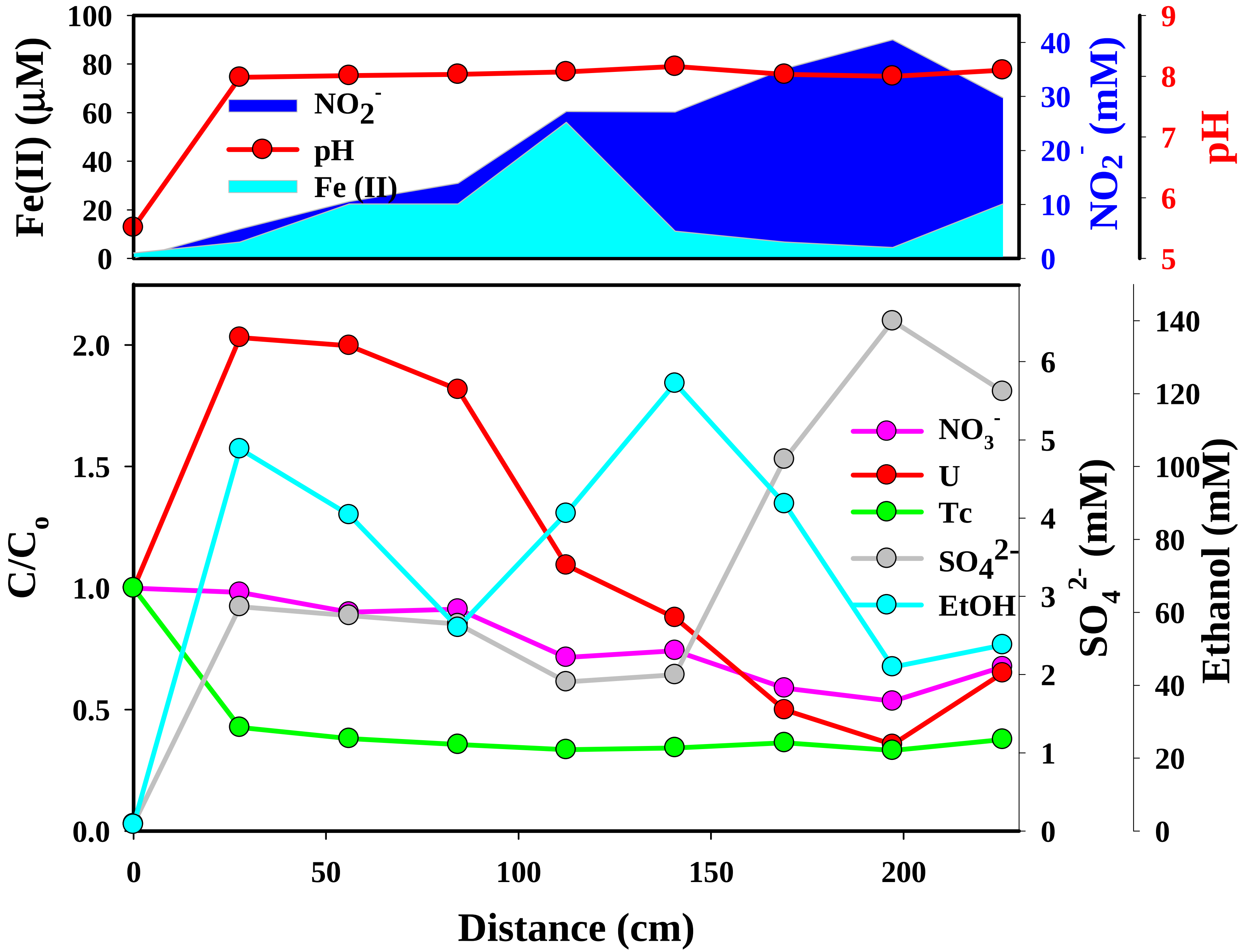


Constant inflow, increasing in steps

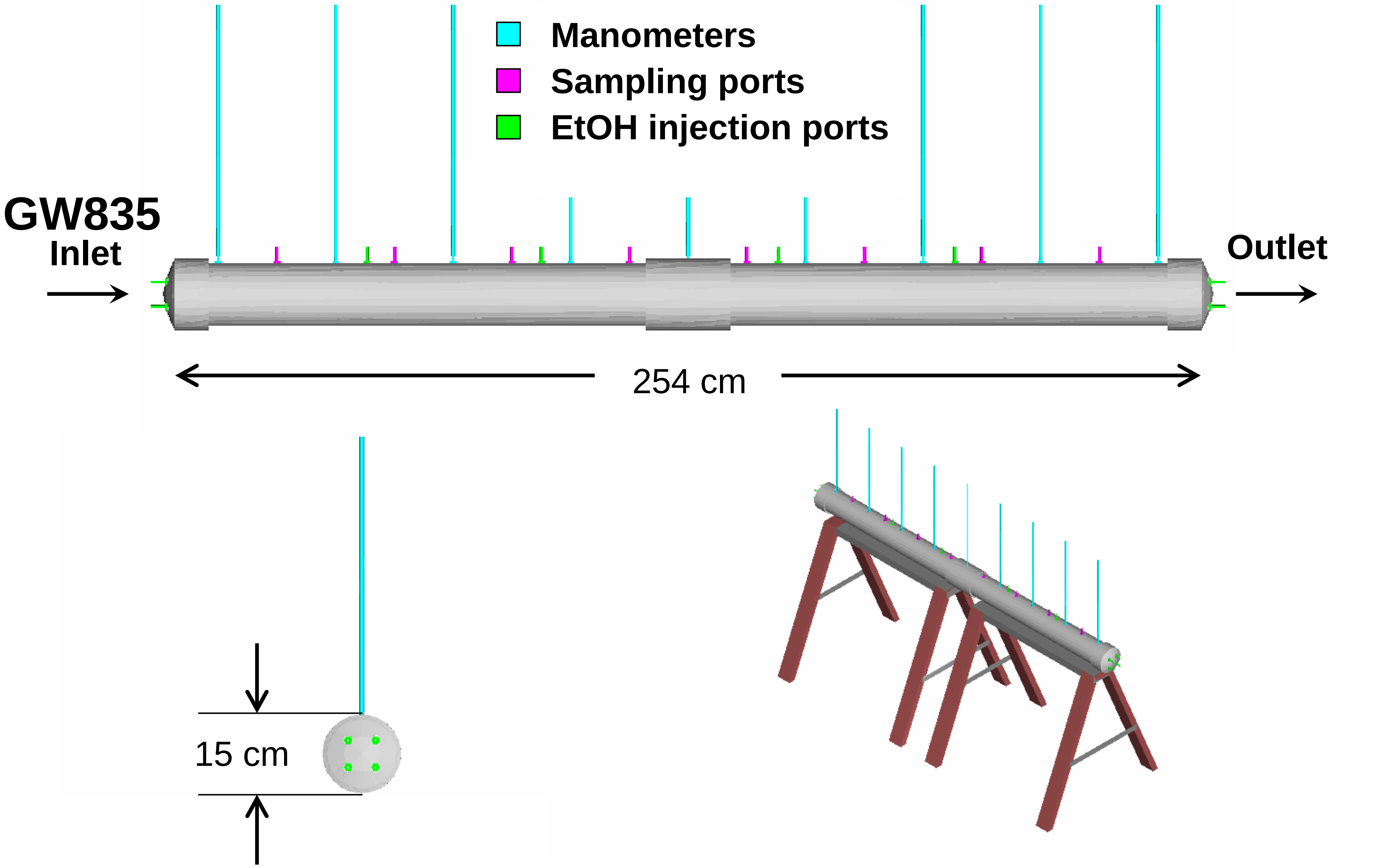
Daily injections of neat ethanol in six locations

Monitoring wells located along model centerline provide access to saturated zone

Example Data: Day 26 ~ 1 pore volume



Intermediate-Scale Physical Model – Area 2



Intermediate-Scale Physical Model – Area 2

Collaboration Opportunities

- **Field push-pull tests in Area 1 and Area 2**
  - **General purpose, field-testing platform**
  - **Numerical modeling**
  - **Microbial community dynamics**
  - **Sediment biogeochemistry (post-test sampling)**
- **Intermediate-scale physical models**
  - **Numerical modeling**
  - **Microbial community dynamics**
  - **Sediment biogeochemistry (destructive sampling will produce ~ kg size samples)**

Groundwater Remediation
Michael (age 6)