

***In Situ* Investigation of Uranium and Technetium Reduction in Area 1**

Oregon State University

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University of Oklahoma:

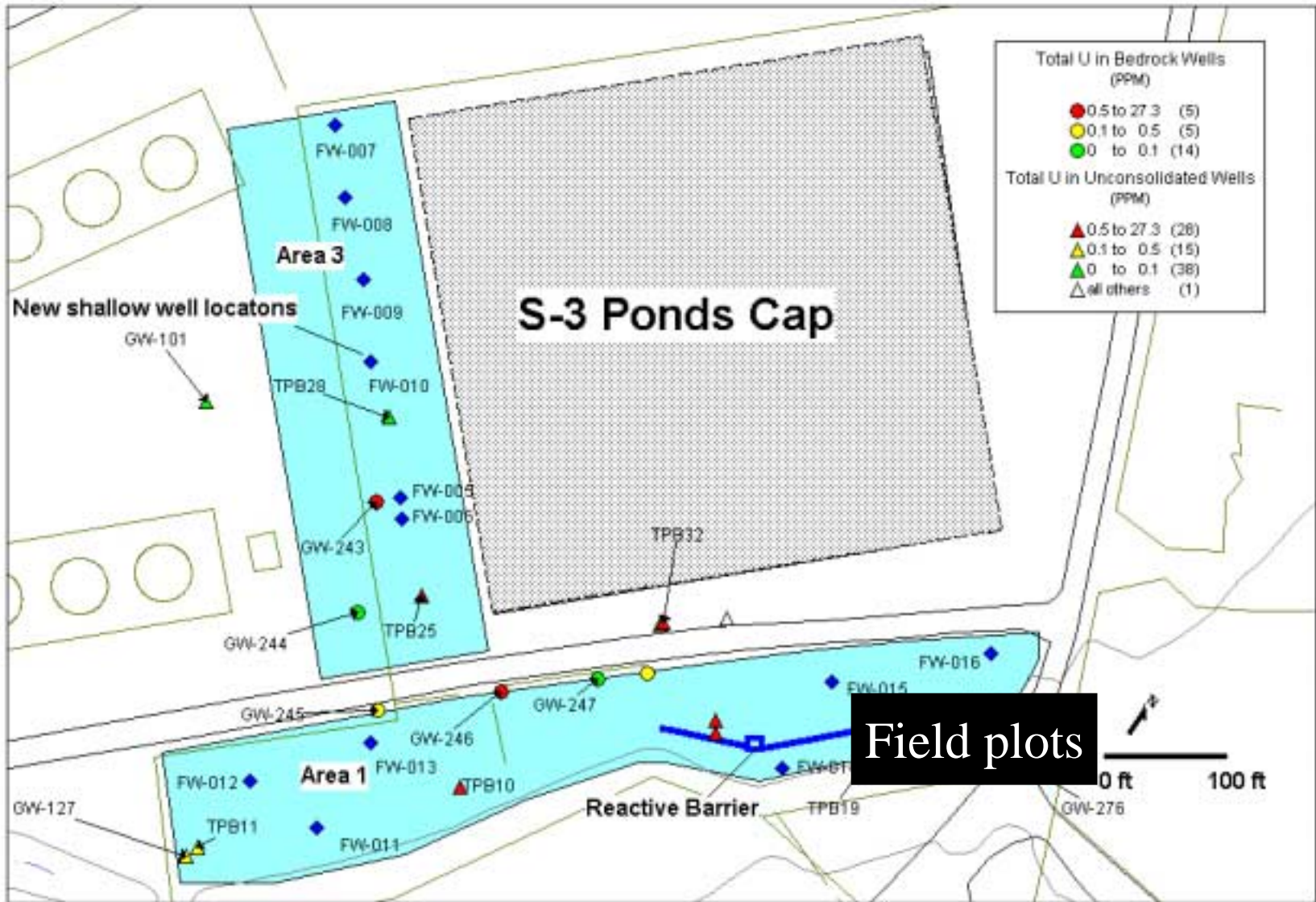
John Senko, Lee Krumholz, Dwayne Elias and Joe Suflita

FRC/ORNL

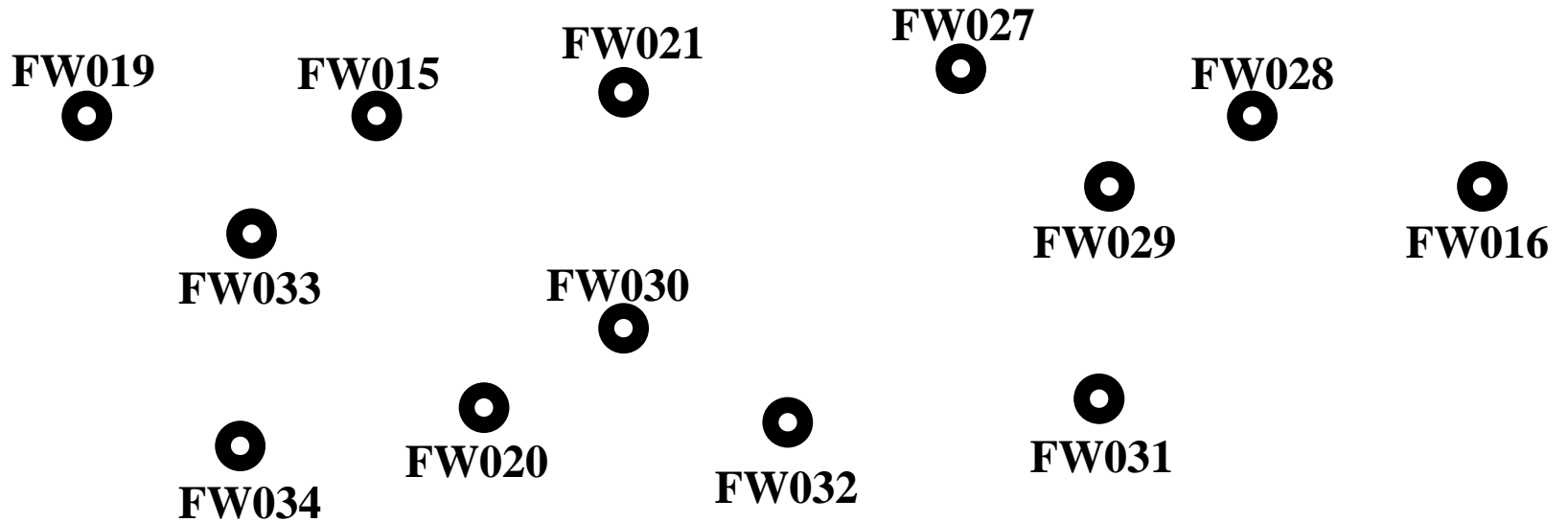
David Watson, Mary Anna Bogle, Barry Kinsall, Ken Lowe, Tonia Mehlhorn, and Norm Farrow

Research Hypotheses

- **Indigenous microorganisms with the capability to reduce uranium and technetium are present in the shallow aquifer at FRC Area 1**
- **Rates of uranium and technetium reduction are limited by the availability of suitable electron donors**
- **Injecting exogenous electron donor to stimulate denitrification, and iron reduction will increase rates of uranium and technetium reduction**



Wells in Area 1 Test Plot



5 m

Groundwater Geochemistry: Wells in Area 1 Test Plot

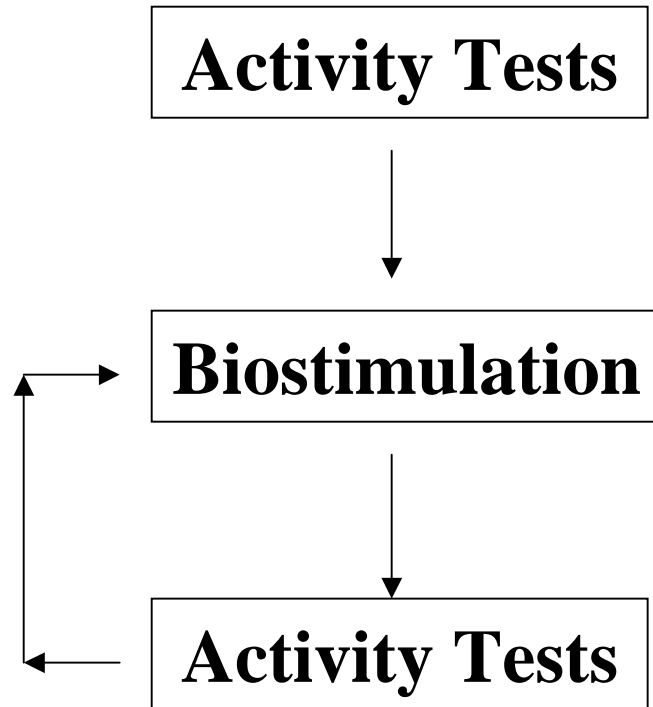
Well-ID	pH	Nitrate (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	Uranium (mg/L)	Technetium (pCi/L)
FW015	3.37	8305	215	760	7.7	18500
FW016	3.92	1016	18.4	276	0.61	
FW019	6.5	215	61	105	0.17	
FW020	4.62	76	102	20	0.02	
FW021	3.25	8463	41	281	1.38	30974
FW027	5.39	10401	3	281	0.029	26347
FW028	4.4	10367	5	145	0.55	12125
FW029	3.94	3870	219	170	1.68	12590
FW030	3.51	9007	3	247	1.53	21470
FW031	5.68	3890	7	71	0.011	2053
FW032	5.22	1460	1	87	0.008	1606
FW033	5.85	886	63	47	0.07	2237
FW034	6.79	48	72	22	0.12	66

Temperature: 12-23°C; Dissolved oxygen: 1-5 mg/L

Laboratory Incubations

- In moderate pH sediments (pH 6.8), the addition of acetate, ethanol, or glucose stimulated complete reduction of NO_3^- within 10 days, with transient NO_2^- accumulation and U reduction
- In low pH sediments (pH 3.5), no donor utilization or denitrification activity was observed, even when sediments were neutralized with CaCO_3

Field Manipulation Experiments



Push-Pull Activity Tests

Treatment wells: Inject site groundwater with added tracer, bicarbonate, and selected electron donor

Control wells: Inject site groundwater with added tracer and bicarbonate only

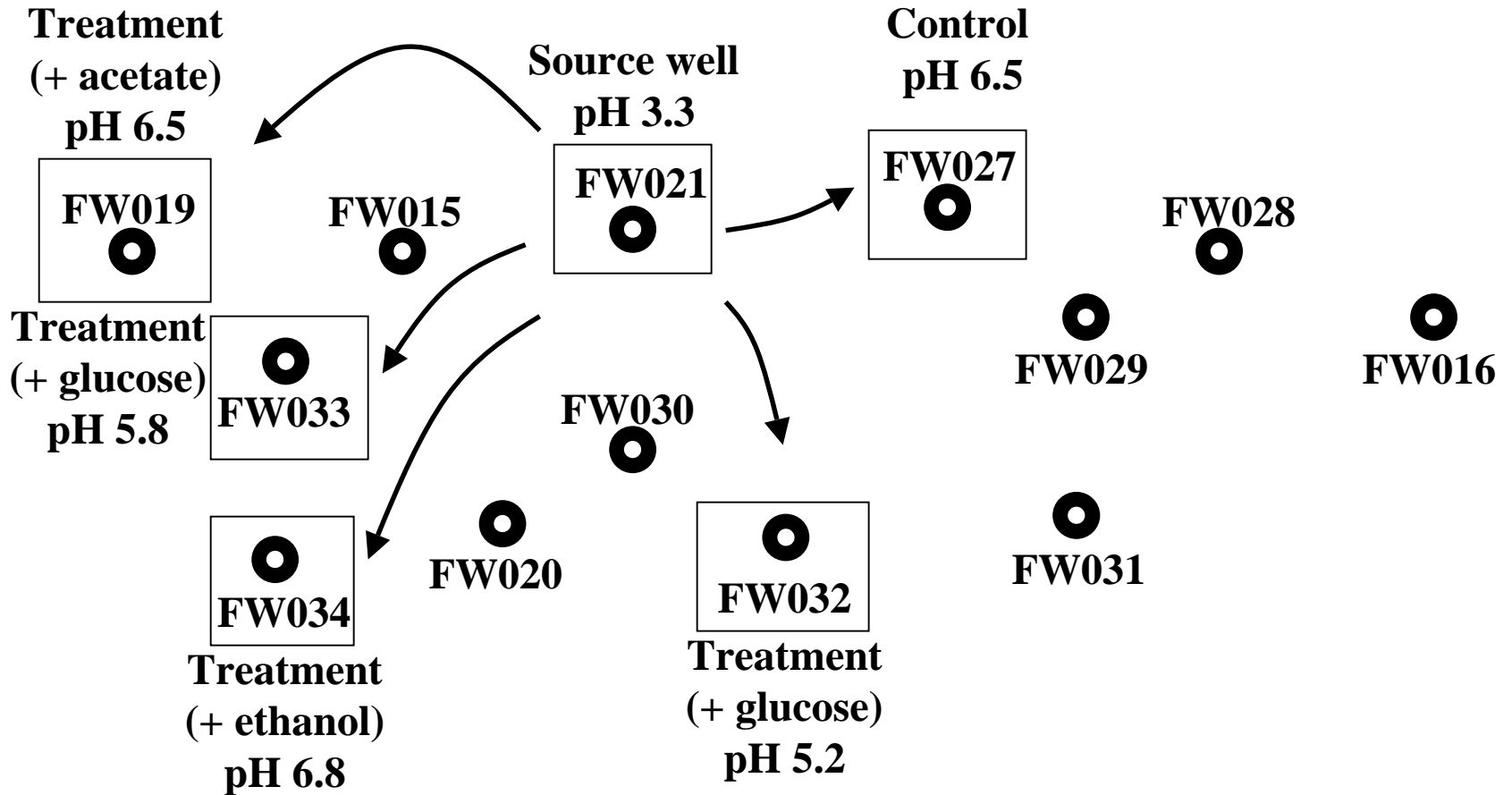
Biostimulation

Treatment wells only: Inject DI water with added tracer, bicarbonate, and donor

Geochemistry Data: Well FW021

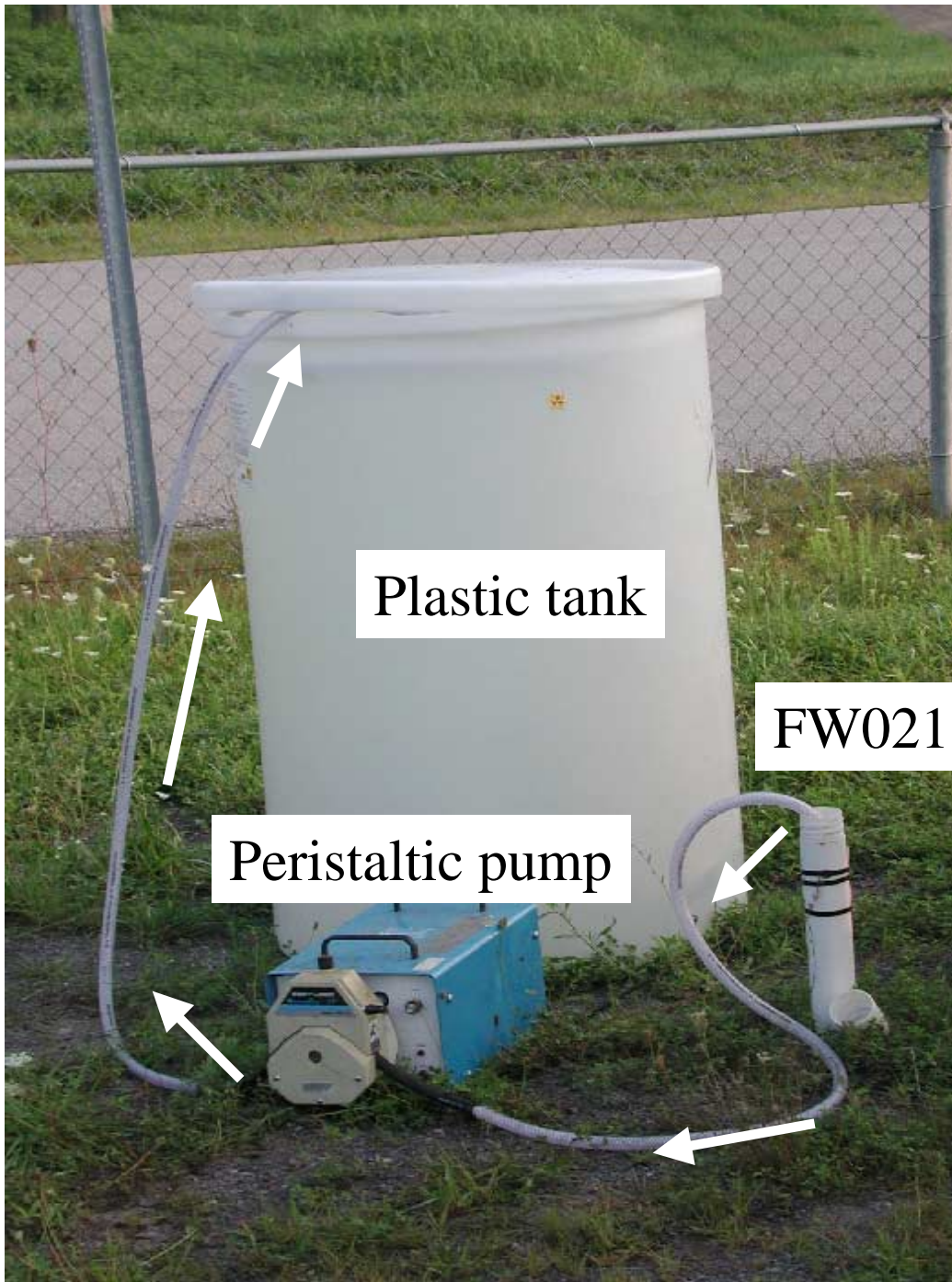
pH	3.25		Manganese	173	mg/L
Uranium	2	mg/L	Potassium	34	mg/L
Technetium	30974	pCi/L	Barium	23	mg/L
			Sulfate	17	mg/L
Nitrate	8463	mg/L	Nickel	10	mg/L
Calcium	1594	mg/L	Strontium	4	mg/L
Sodium	524	mg/L	Cobalt	1	mg/L
Magnesium	284	mg/L	Zinc	1	mg/L
Chlorine	271	mg/L	Gallium	1	mg/L
Aluminum	206	mg/L			

Field Manipulation Experiments: Phase I – moderate pH



Push-Pull Activity Tests

Step 1.
Collect ~200 L
groundwater from
FW021



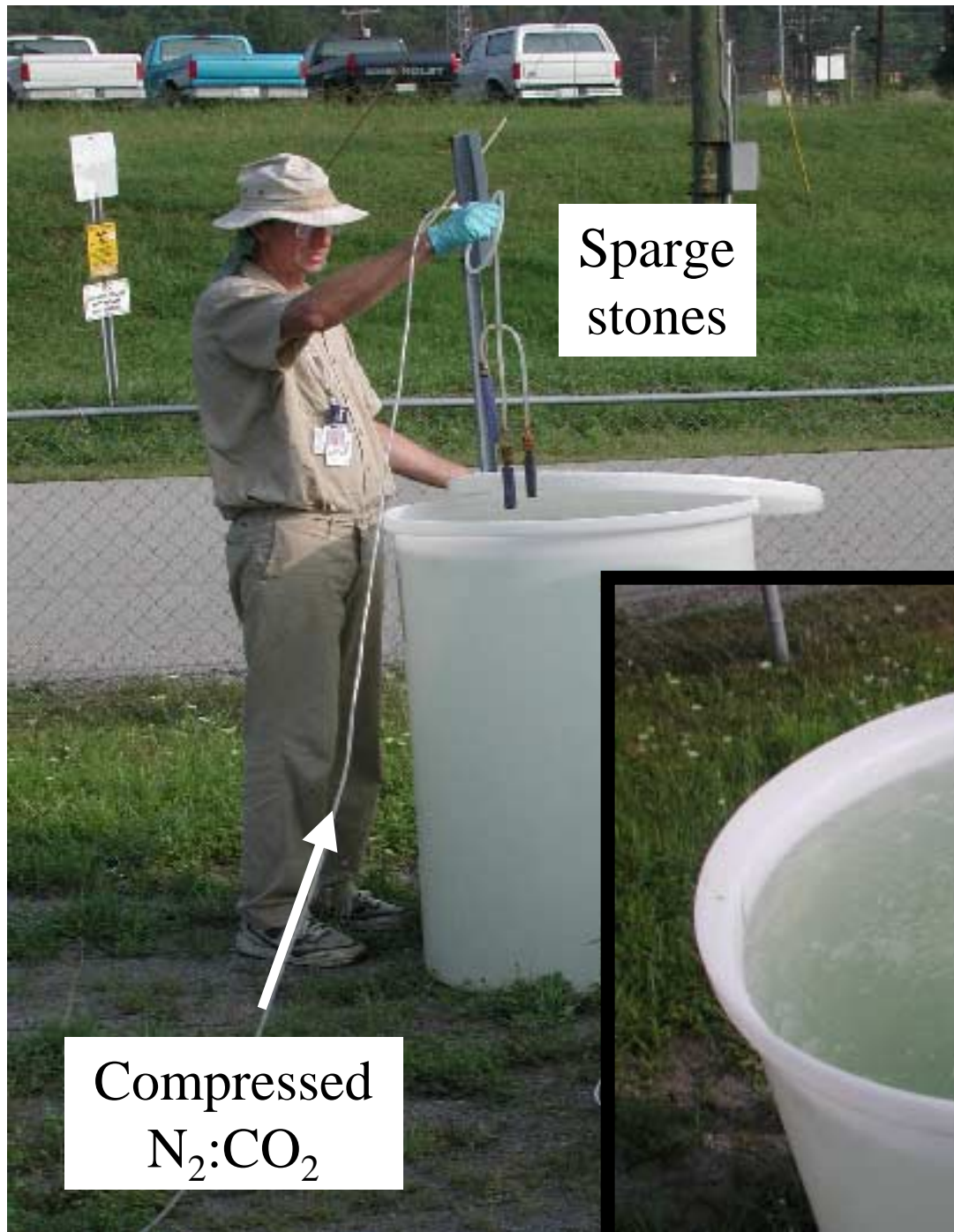
Test Solution Preparation



Step 2.

Add tracer and bicarbonate (all wells) and selected electron donor (treatment wells only)

**Observation:
precipitate formation**



Sparge
stones

Compressed
 $N_2:CO_2$

Step 3.
Mix with
 $N_2:CO_2$ gas
(80 %:20%)



Gas
bubbles



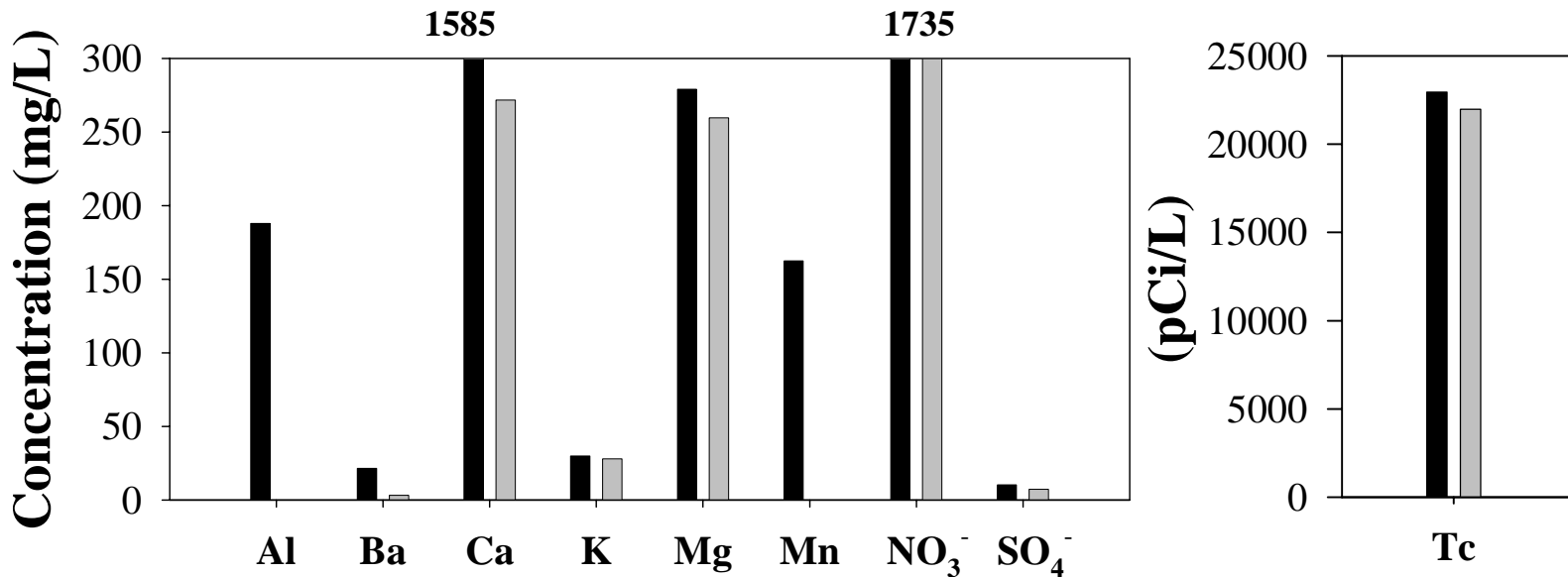
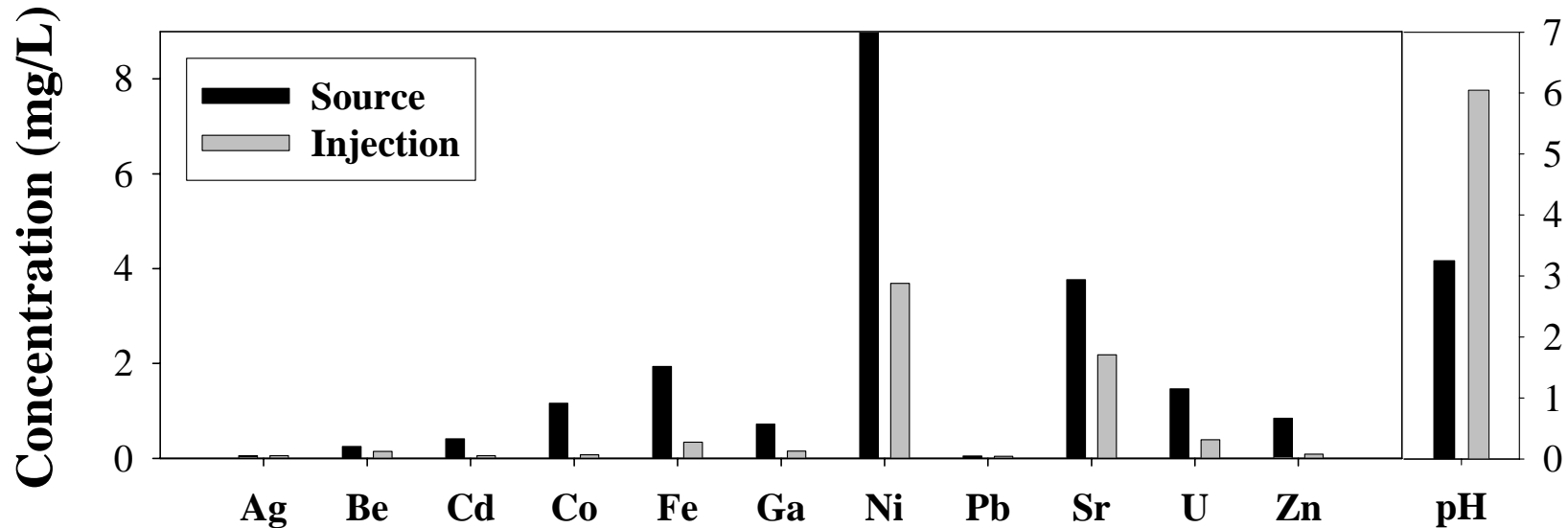
Syringe

Step 4.
Sample composition
of test solution
before- and after-
mixing



Filtering
samples

Test Solution Composition



Precipitate Formation

Raising pH of acidic groundwater generates large quantities of solids, which could clog pore space

Ex. ~ 100-200 pore volumes

One alternative would be to raise pH in porous treatment zone (reactive barrier) upgradient of electron donor addition

Test 24
(mg/L)

Ca	1314
Al	188
Mn	162
Mg	19
Ba	18
Ni	5
SO₄²⁻	3
K	2
Sr	2
Co	1
U	1
Zn	1
Total	1718

Step 5.
Test Solution Injection (“Push”)



**The
“Dosatron”**

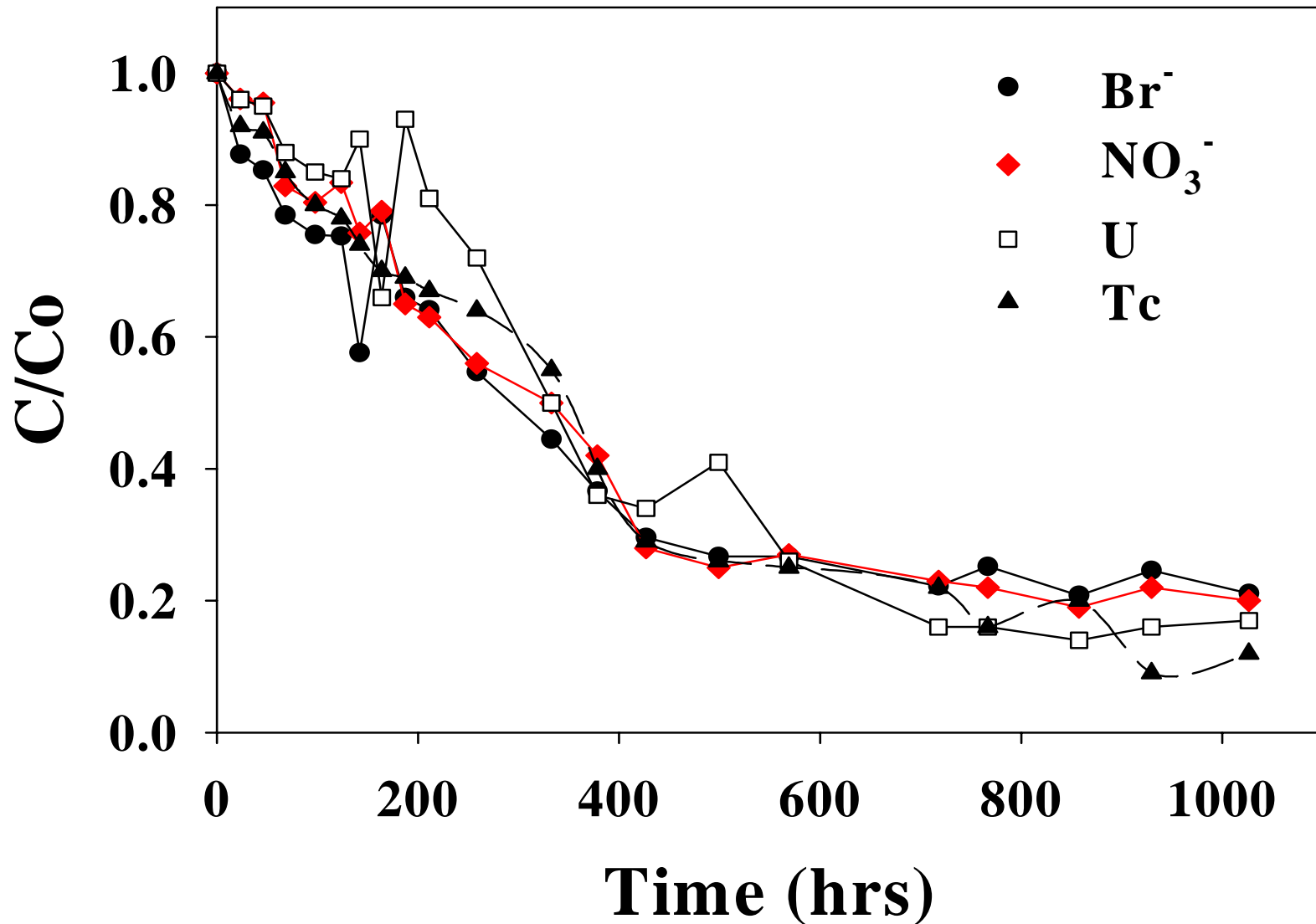
Step 6. Periodic Sampling

- **Samples of injected test solution/groundwater mixture collected from injection well and analyzed for:**
 - **Inorganic anions, donor and products (IC)**
 - **Uranium (KPA) Technetium (LSC)**
 - **Elemental composition (ICP)**
 - **Total iron pH**

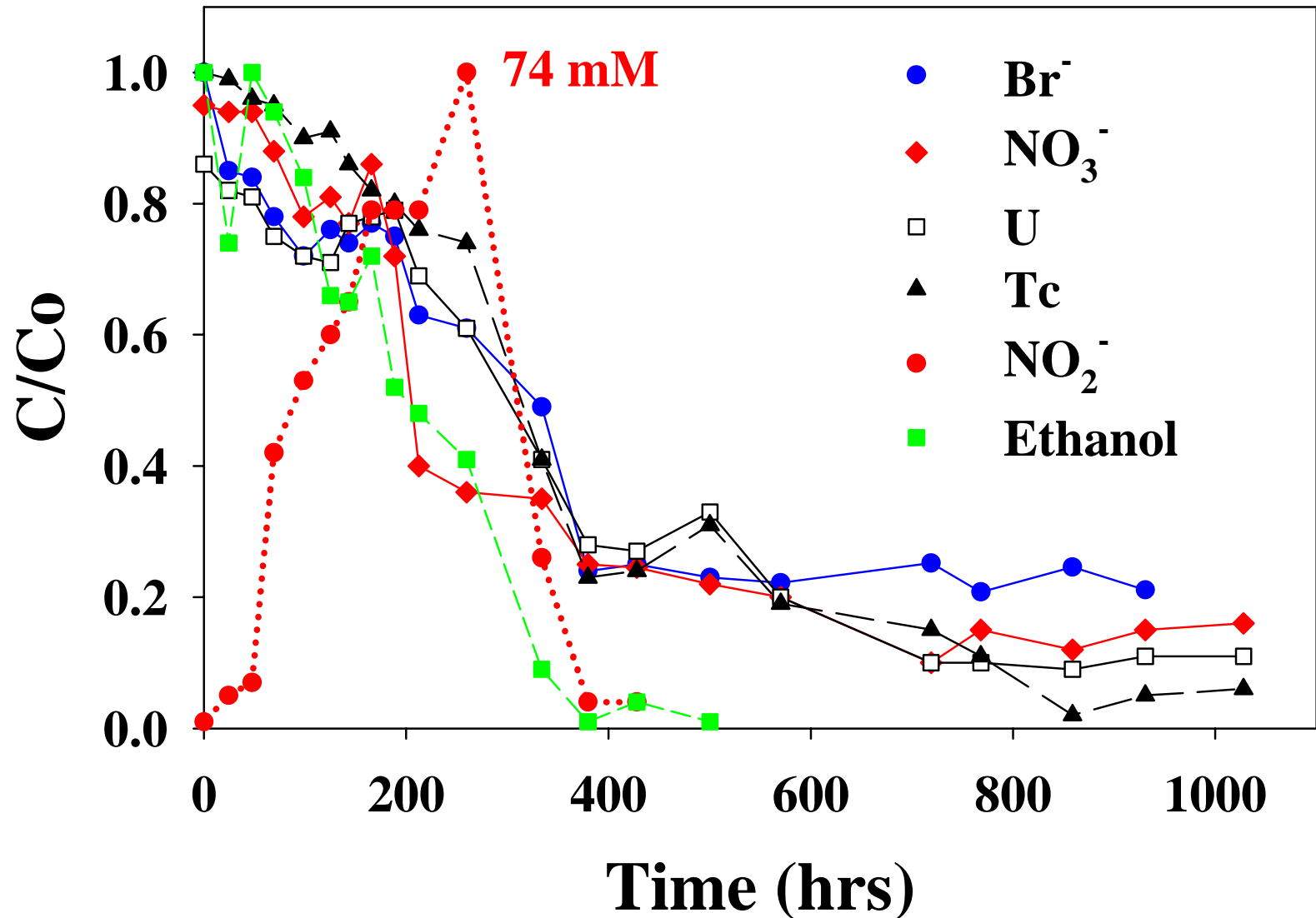
Field Manipulation Experiments

Well	Test	Donor	Donor utiliz. ?	Rate (mM/hr)	Nitrate rem. ?	Rate mM/hr	Nitrite prod. ?	Max C. (mM)	Tc rem. ?	Rate (pCi/L/hr)	U rem. ?	Rate (uM/hr)
FW031	18, 24	control	-	-	NO	-	NO	-	NO	-	NO	-
FW027	20, 26	control	-	-	NO	-	NO	-	NO	-	NO	-
FW019	13	control	-	-	NO	-	NO	-	NO	-	NO	-
FW019	15	acetate	YES	0.14	YES	0.13	YES	76	NO	-	NO	-
	21	acetate	YES	0.40	YES	0.36	YES	8	YES	151	NO	-
	27, 31, 35	acetate	Biostimulation									
	39	acetate	YES		YES	0.50	YES	2	YES	16	NO	-
FW034	16	ethanol	YES	0.11	YES	0.64	YES	4	NO	-	NO	-
	22	ethanol	YES	0.25	YES	0.39	YES	12	YES	200	YES	0.003
	28, 32, 36	ethanol	Biostimulation									
	40	ethanol	YES		YES	3.16	YES	4	YES	68	YES	0.003
FW033	17	glucose	YES	0.08	YES	0.76	YES	61	YES	17	NO	-
	23	glucose	YES	0.16	YES	0.59	YES	31	YES	62	NO	-
	29, 34, 38	glucose	Biostimulation									
	41	glucose	YES		YES	3.16	YES	23	YES	228	YES	0.019
FW032	19	glucose	YES	0.02	NO	-	NO	-	NO	-	NO	-
	25	glucose	YES	0.11	YES	0.44	YES	9	YES	244	YES	0.001
	30, 33, 37	glucose	Biostimulation									
	42	glucose	YES		YES	0.51	YES	4	YES	800	YES	0.015

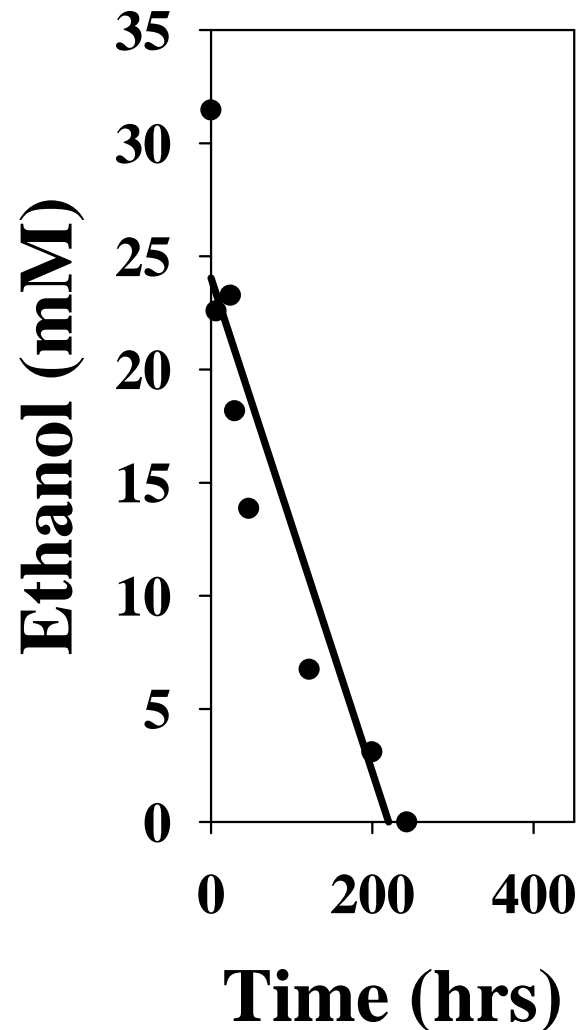
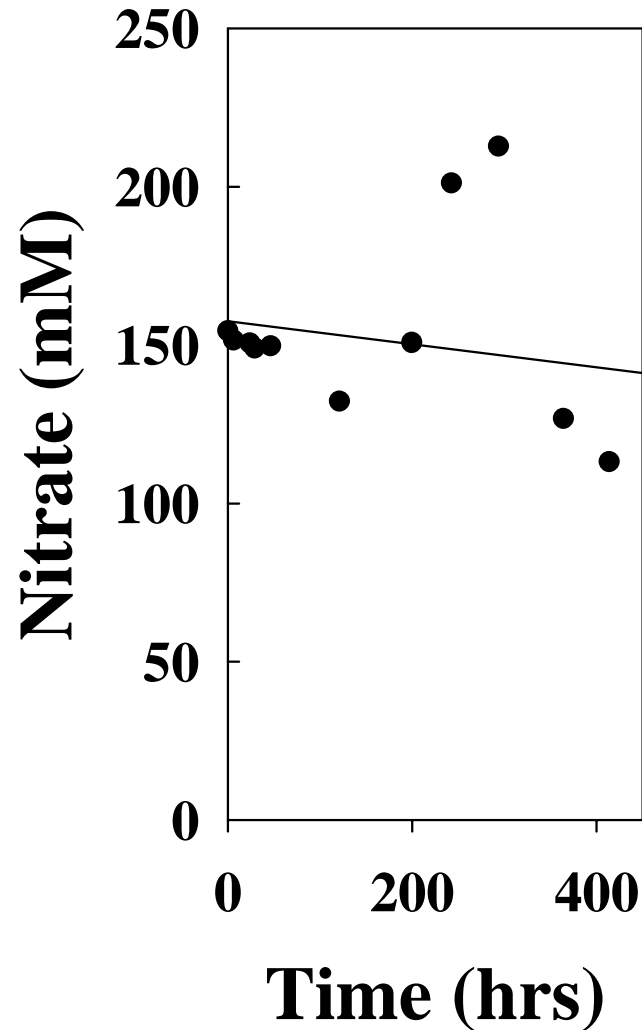
Results: Control Wells (no added donor)



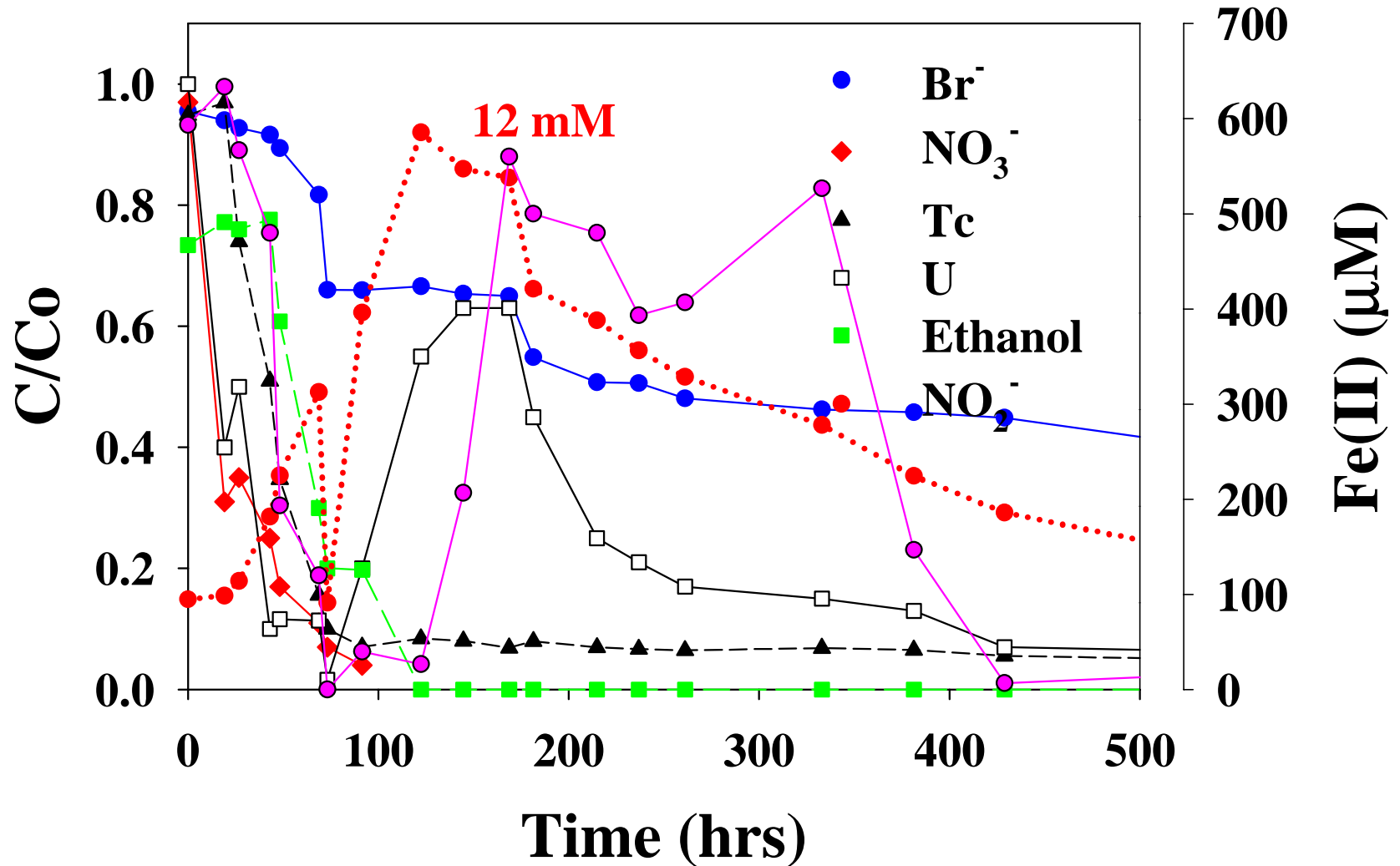
Results: FW034 - 1st ethanol addition



Results: FW034 - 1st ethanol addition



Results: FW034 – 2nd ethanol addition



Ferrous Iron Production



Injection

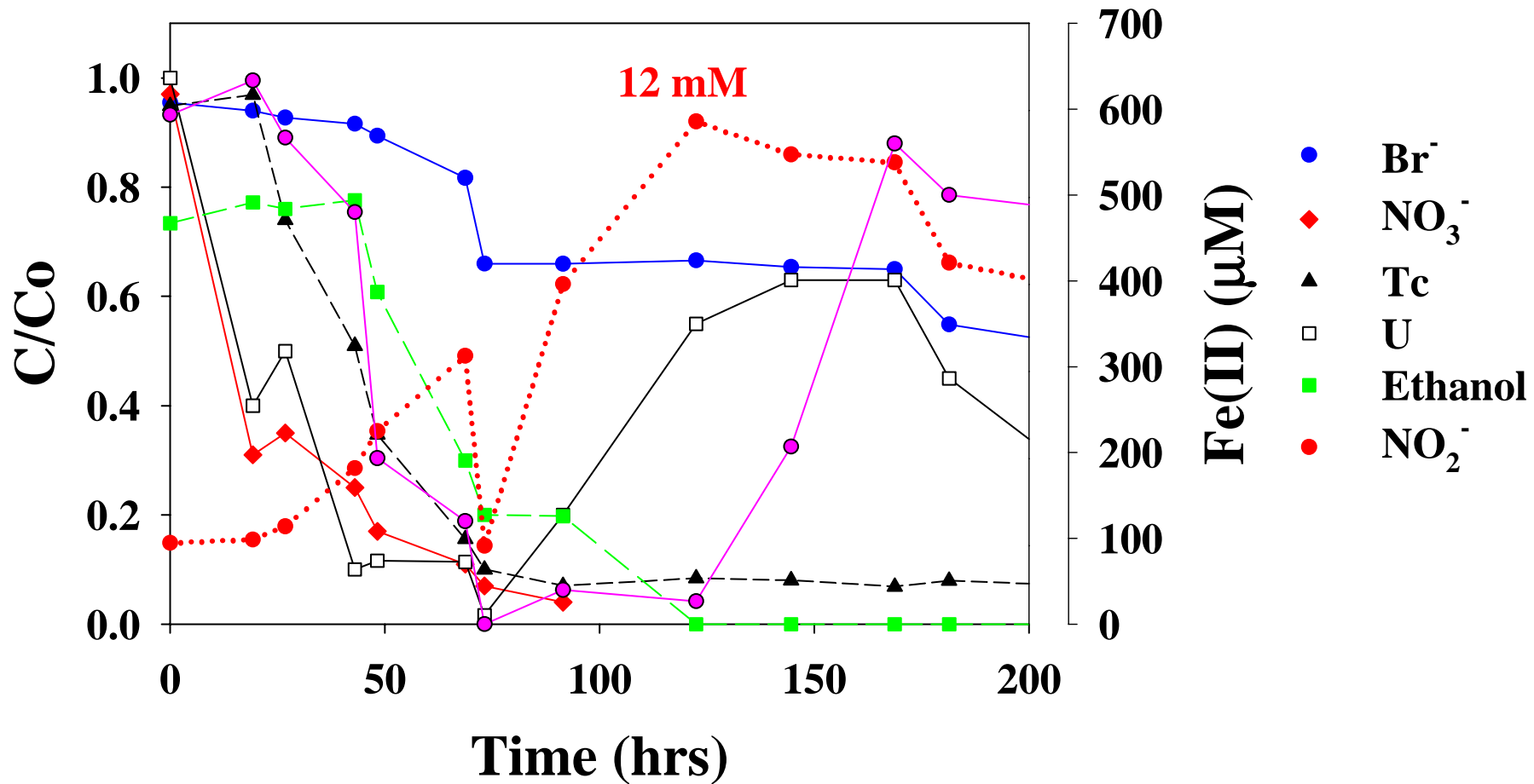


Early extraction

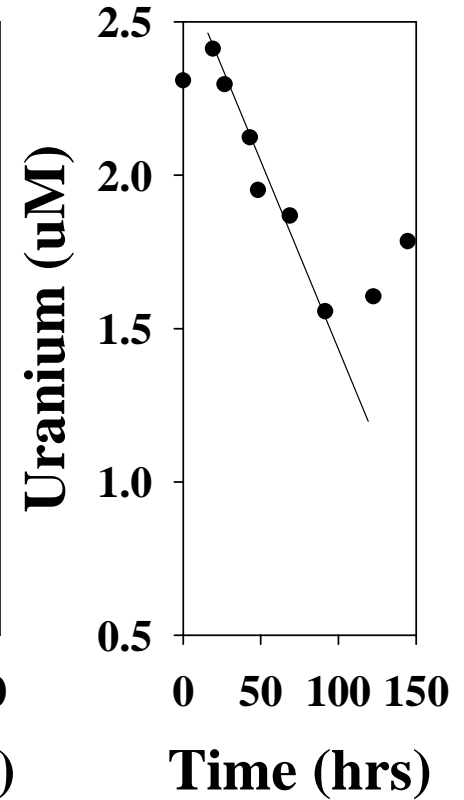
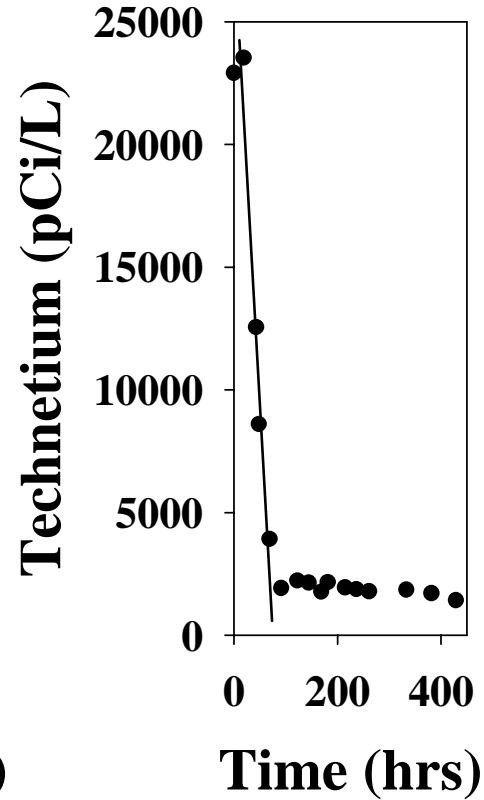
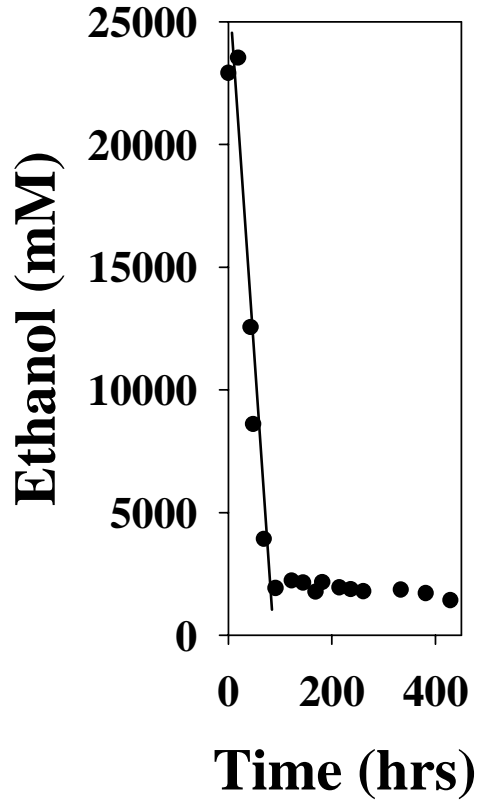
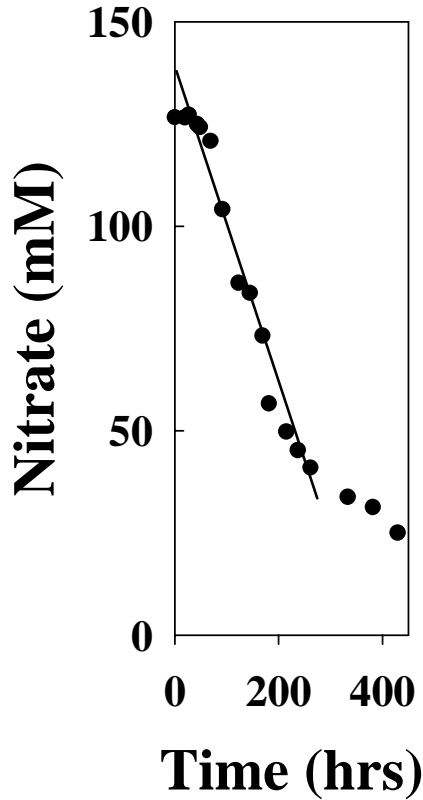


Late extraction

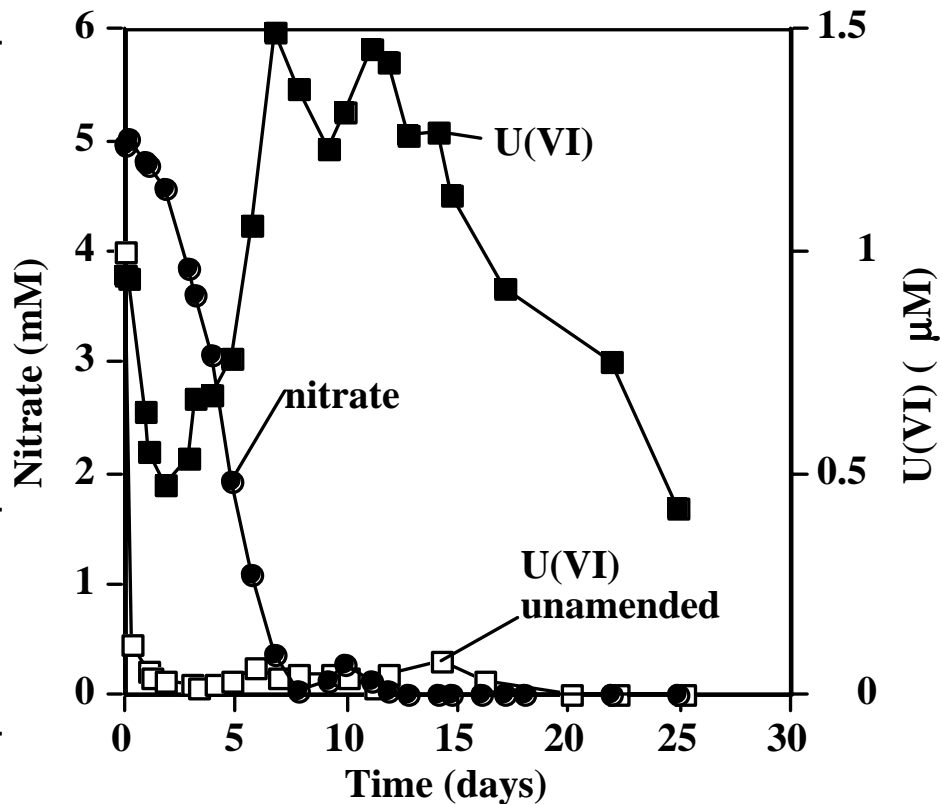
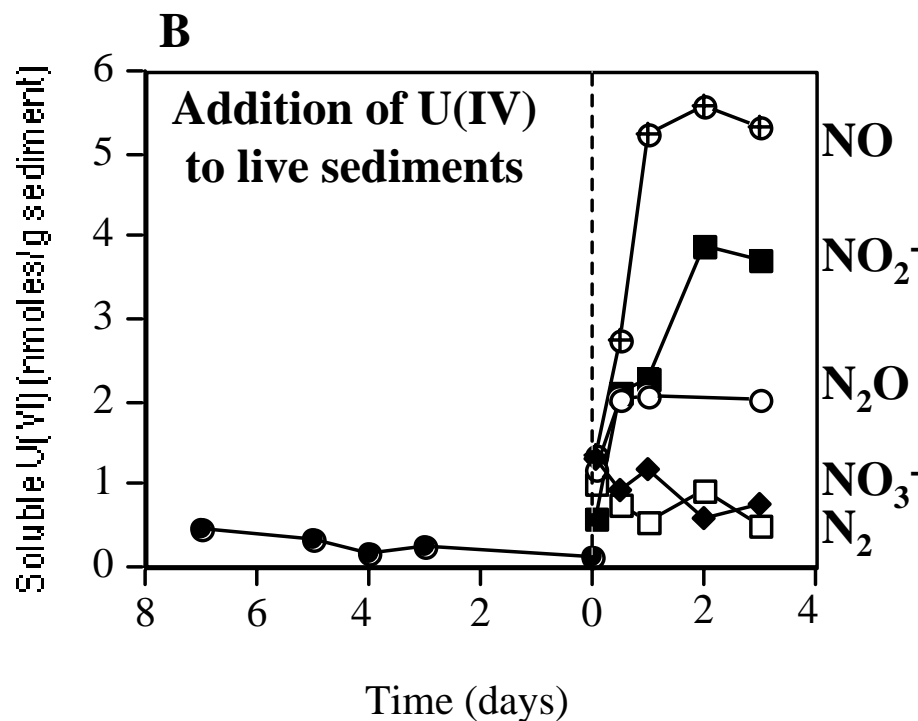
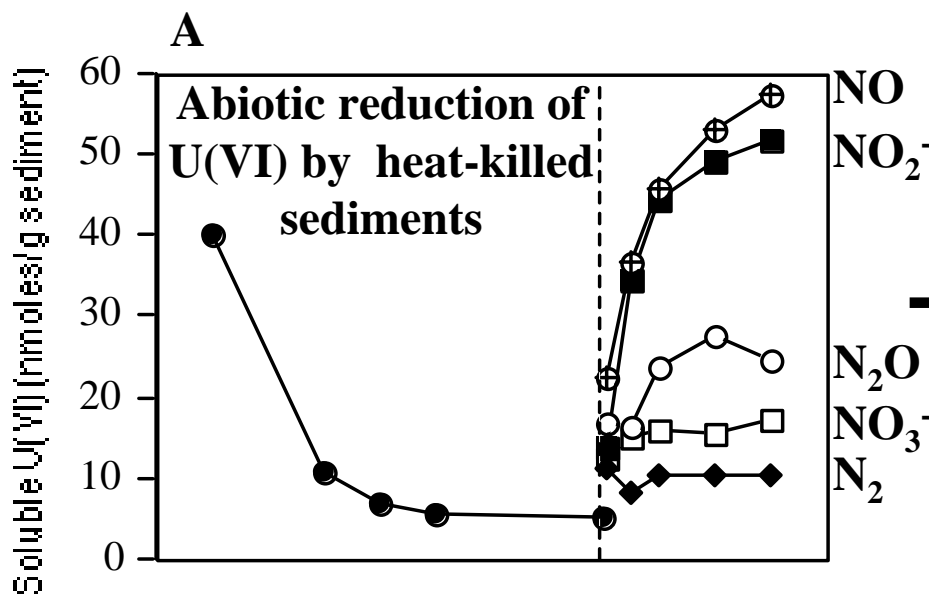
Results: FW034 – 2nd ethanol addition



Results: FW034 – 2nd ethanol addition



Remobilization of Uranium

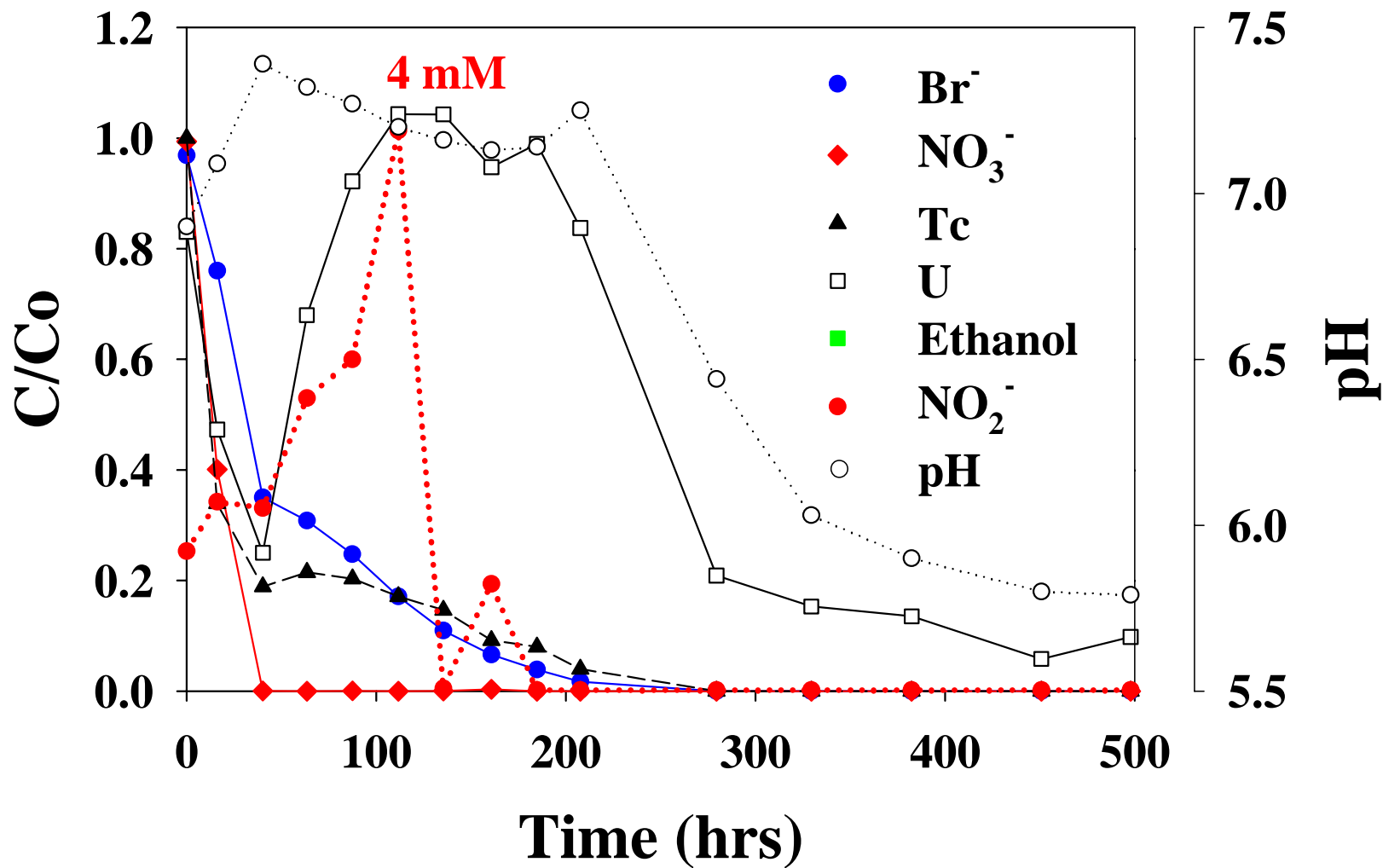


Biostimulation

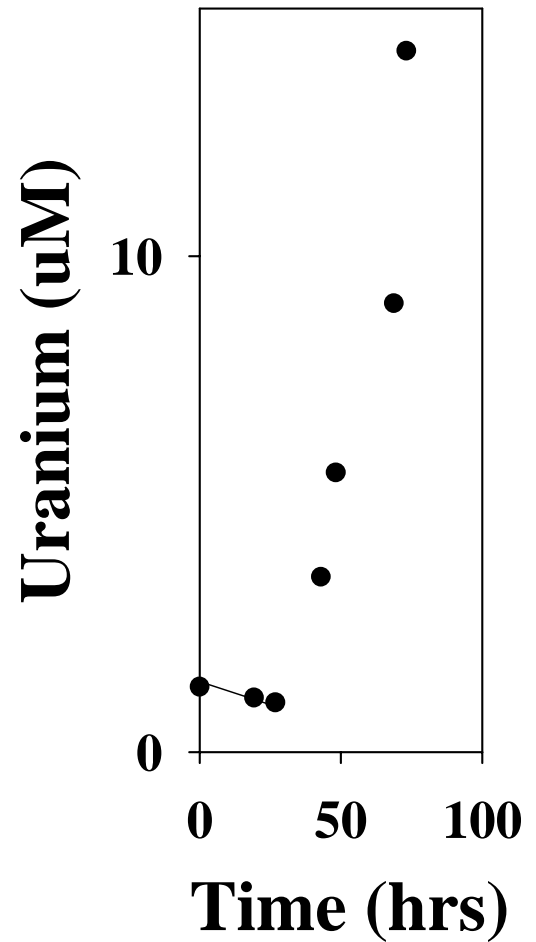
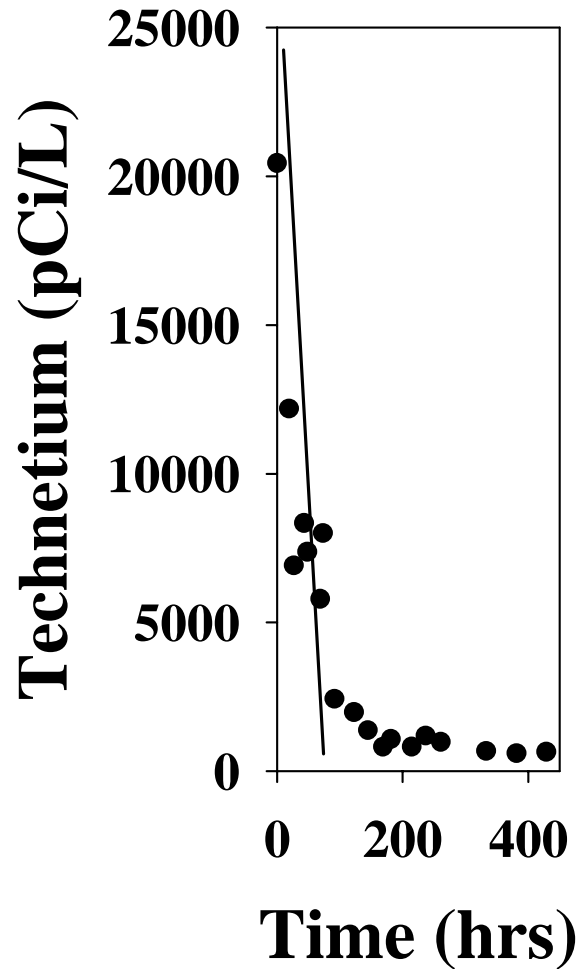
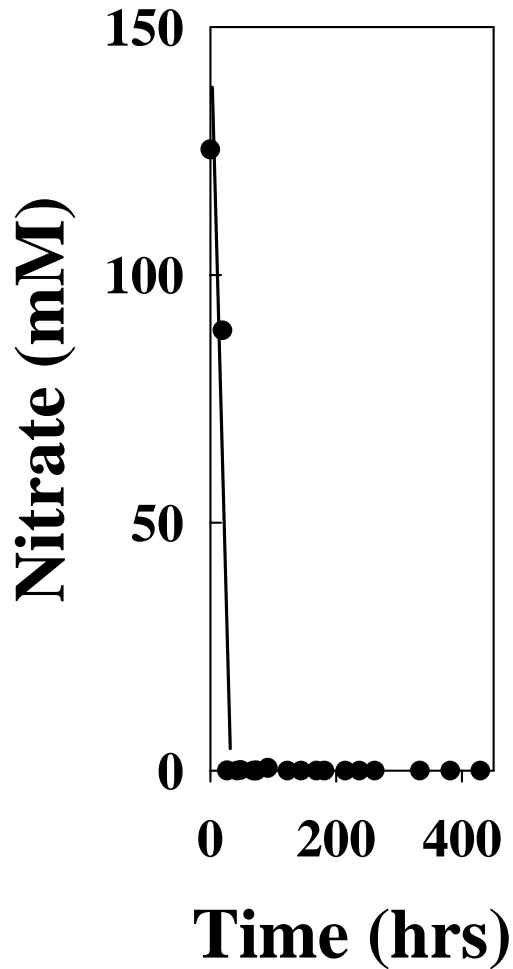
To increase microbial activity a series of sequential electron donor additions was conducted

FW019	Acetate x 3
FW034	Ethanol x 3
FW033	Glucose x 3
FW032	Glucose x 3

Results: FW034 – 7th ethanol addition



Results: FW034 – 7th ethanol addition



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	30, 33, 37	glucose	Biostimulation									
	42	glucose	YES		YES	0.51	YES	4	YES	800	YES	0.015

Summary: Phase I – Moderate pH

- **Injected acetate, glucose, or ethanol was rapidly utilized in all cases.**
- **Sequential donor additions resulted in:**
 - **Increased rates of donor utilization**
 - **Increased rates of denitrification**
 - **Increased production of ferrous iron**
 - **Increased rates of technetium immobilization**
 - **Increased rates of uranium immobilization**
- **Denitrification intermediates may have resulted in remobilization of previously immobilized uranium but not technetium (?)**