Coupled Transport and Biogeochemical Effects on Reduction of U (IV) and NO^{3-} as Co-contaminants in Natural Sediments and Soils

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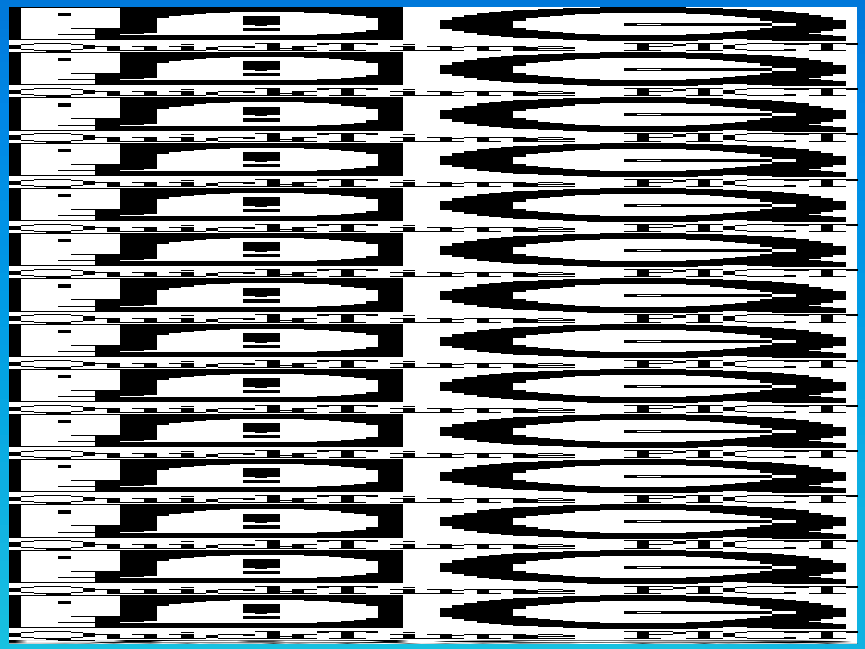
FRC Samples



1. Background Soil (Cores labeled FB602, FB603, FB604, and FB605), Groundwater (Containers labeled FW300-00730, FW300-00731)
2. Area 2 Soil (Cores labeled FB010, FB011, FB012, FB013, and FB014), Groundwater (Containers labeled TPB16-000732, TPB16-000733)
3. Area 3 Soil (Cores labeled FB006, FB007, FB008, and FB009), Groundwater (Containers labeled FW025-000728, FW025-00029)

Sample Preparation for Lab Studies

(1) Background Soil

Soil was passed though a 2 mm sieve. The fraction of particles <2.0 mm [~30% wt. of original sample] was used for batch experiments and for sediment characterization.

(2) Area 2 Soil (high uranium, low nitrate)

The majority of the work was performed inside a nitrogen purged glove bag or glove box to protect the microbial community and minimize the oxidation of any U(IV) to U(VI). Sieving and homogenizing the soil in its natural state was not possible because of the high clay content.

The soil was made into a slurry/solution using the Area 2 groundwater and passed through a 5.6 mm sieve [~25% wt. of original sample]. The mixed slurry was then poured into trays and placed inside a N2 glove box to evaporate the excess moisture. A strong desiccant was used to remove the moisture in the glove box. The sediment cakes were removed from the trays and again passed though the 5.6 mm sieve to re-homogenize and crumble back into a form appropriate for packing columns.

(3) Area 3 Soil (high nitrate, low uranium)

Soil was passed though a 2 mm sieve. The fraction of particles <2.0 mm [~45% wt. of original sample] was used for batch experiments and sediment characterization.

Table A: Soil Particle Size Analysis

	Moisture Content[1] (%)	Grain Density[2] ($g\ cm^{-3}$)	Sand[3] (%)	Silt[3] (%)	Clay[3] (%)
Background Soil	14.15 ± 1.4	2.86	54.7 ± 1.5	35.5 ± 1.1	9.9 ± .04
Area 2 Soil (<5.6 mm)	18.1	2.75	30.4 ± 7.8	41.1 ± 8.5	28.6 ± 0.7
Area 3 Soil (<2.0 mm)	12.28 ± 0.09	2.83 ± 0.08	51.5 ± 0.7	31.3 ± 0.2	17.4 ± 0.6

Methods:

[1]The moisture content reported was measured by drying a weighed amount of soil at 110°C overnight and re-weighing once the soil cooled down to RT (air dry).

[2]Density was determined by water pycnometer.

[3]The hydrometer method was used to determine the soil particle size distribution.

Table B: pH and Electrical Conductivity Measurements[1]

	pH[2]	EC (mS/cm)[3]
Background Groundwater	7.14	0.313
Area 2 Groundwater	5.04	0.804
Area 3 Groundwater	6.92	55.40
Background Soil	7.52	0.420
Area 2 (<5.6 mm) Soil	7.92	1.029
Area 3 (<2.0 mm) Soil	6.48	0.948
Area 3 (<5.6 mm) Soil	5.78	1.499

Methods:

[1]1:1 soil extractions (24 hrs) of soil samples were used to make pH and EC measurements

[2] Corning electrode

[3] YSI 3253 cell

Table C: Uranium Concentration[1]

	U conc. (ppm)	
Background Groundwater	<0.03	<0.06[2]
Area 2 Groundwater	1.1	1.2[2]
Area 3 Groundwater	<0.03	0.54[2]
	Acid Digested	1:1 Extraction
	U conc. (ppm)	**U conc. (ppm)**
Background Soil	0.89	<0.03
Area 2 Soil	206 ± 7.02	1.06
Area 3 Soil (<2.0 mm)	12	0.43
Area 3 Soil (<5.6 mm)	25	<0.03

Method:

[1] KPA-11 (Kinetic Phosphorescence Analyzer, Chemchek Instruments)

[2] Liquid Scintillation

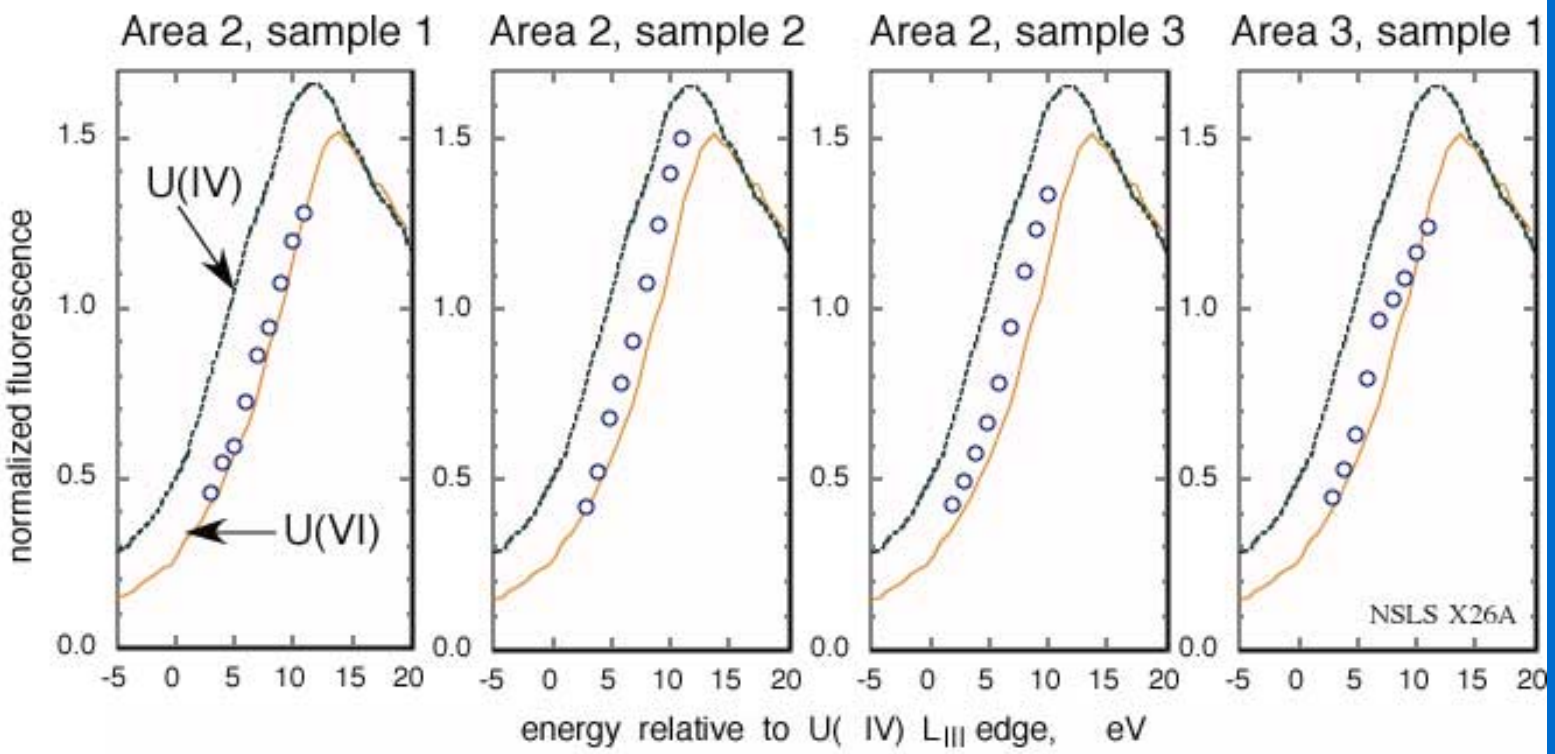
Table D: U(IV) and (U(VI) Fractions in Soils[1]

Sample	U(IV) fraction	U(VI) fraction	uncertainty
Area 2, sample 1	0.10	0.90	±0.07
Area 2, sample 2	0.30	0.70	±0.14
Area 2, sample 3	0.31	0.69	±0.11
Area 2 Soil, average of 3	**0.24**	**0.76**	**±0.12**
Area 3 Soil, sample 1	**0.18**	**0.82**	**±0.17**

Method:

[1] Determined through synchrotron x-ray absorption spectroscopy at NSLS Beamline X26A, Brookhaven National Lab.

Oxidation State of Uranium in NABIR Oak Ridge Soils



Area 2, sample 1	Area 2, sample 2	Area 2, sample 3	Area 3, sample 1
U(VI) 90%	U(VI) 70%	U(VI) 69%	U(VI) 82%
U(IV) 10%	U(IV) 30%	U(IV) 31%	U(IV) 18%
uncert. 7%	uncert. 14%	uncert. 11%	uncert. 17%

Initial conditions for our latest experiments have uranium primarily in U(VI) forms.

Table E: Total NO_3^- + NO_2^- Analysis [1]

Groundwater	mg N/L
Background Groundwater	0.0683
Area 3 Groundwater	11737
Soil[2]	mg N/kg soil
Background Soil	0.408
Area 2 (<5.6 mm) soil	1.11
Area 3 (<2.0 mm) Soil	85
Area 3 (<5.6 mm) Soil	95

Methods:

[1] Lachat flow injection analyzer

[2] KCl extraction: 1:10 / soil: 2 M KCl

Table F: Native Organic and Inorganic Carbon Analysis [1]

	Organic Carbon (ppm)	Inorganic Carbon (ppm)	Total Carbon (ppm)
Background Groundwater	0.93	37.59	38.52
Area 3 Groundwater	3.48	3.34	6.82
Background Soil [2]	7.72	14.43	22.15
Area 2 (<5.6 mm) soil[2]	462.1	73.6	535.7
Area 3 (<2.0 mm) Soil[2]	4.53	0.21	4.74
Area 3 (<5.6 mm) Soil[2]	3.73	0.28	4.01

Method:

[1] Elemental Carbon Analyzer

[2] 1:10 soil extraction (1 hr) were used to measure Carbon in soils

Table G: $CaCO_3$ Analysis [1]

	$CaCO_3$ (wt.%)
Background Soil	0.85
Area 2 Soil	3.0
Area 3 (<2.0 mm) Soil	2.0

Method:

[1]Manometer method, soil was reacted with 2N HCl

Table H: X-Ray Fluorescence Analysis

Major Elements	Concentrations in dried powder (wt. %)		
	Background Soil	**Area 3 Soil**	**Area 2 Soil**
SiO_2	61.09 ± 0.17	53.15 ± 1.27	64.00 ± 0.15
TiO_2	0.75 ± 0.01	0.72 ± 0.01	0.81 ± 0.00
Al_2O_3	17.96 ± 0.12	17.69 ± .26	17.10 ± .08
Fe as Fe_2O_3	6.27 ± 0.03	8.44 ± 0.38	6.27 ± 0.04
MnO	0.26 ± 0.00	0.37 ± 0.05	0.10 ± 0.00
MgO	2.09 ± 0.00	2.07 ± 0.11	1.7 ± 0.01
CaO	1.14 ± 0.00	3.81 ± 1.30	0.49 ± 0.00
Na_2O	0.81 ± 0.05	.37 ± 0.07	0.34 ± 0.07
K_2O	4.80 ± 0.02	5.06 ± 0.17	3.48 ± 0.06
P_2O_5	0.13 ± 0.00	0.08 ± 0.01	0.09 ± 0.01
SO_3	<0.04	<0.04	<0.04
Loss on Ignition	4.63 ± 0	7.87 ± 0.86	5.59 ± 0.41

*note: CO_2 included in loss on ignition

Trace Elements	Concentrations in dried powder (mg/kg soil)		
	Background Soil	**Area 2 Soil**	**Area 3 Soil**
Pb	13	33 ± 1	16 ± 1
Nb	14	3 ± 0	12 ± 0
Zr	251	155 ± 1	251 ± 1
Y	22	22 ± 1	30 ± 0
Sr	67	92 ± 1	66 ± 1
Rb	134	131 ± 2	114 ± 0

Microbiological Analyses

Background Sediment	1.3×10^4 cells/g
Area 2 Sediment	$< 10^4$ cells/g
Area 3 Sediment	3×10^4 cells/g

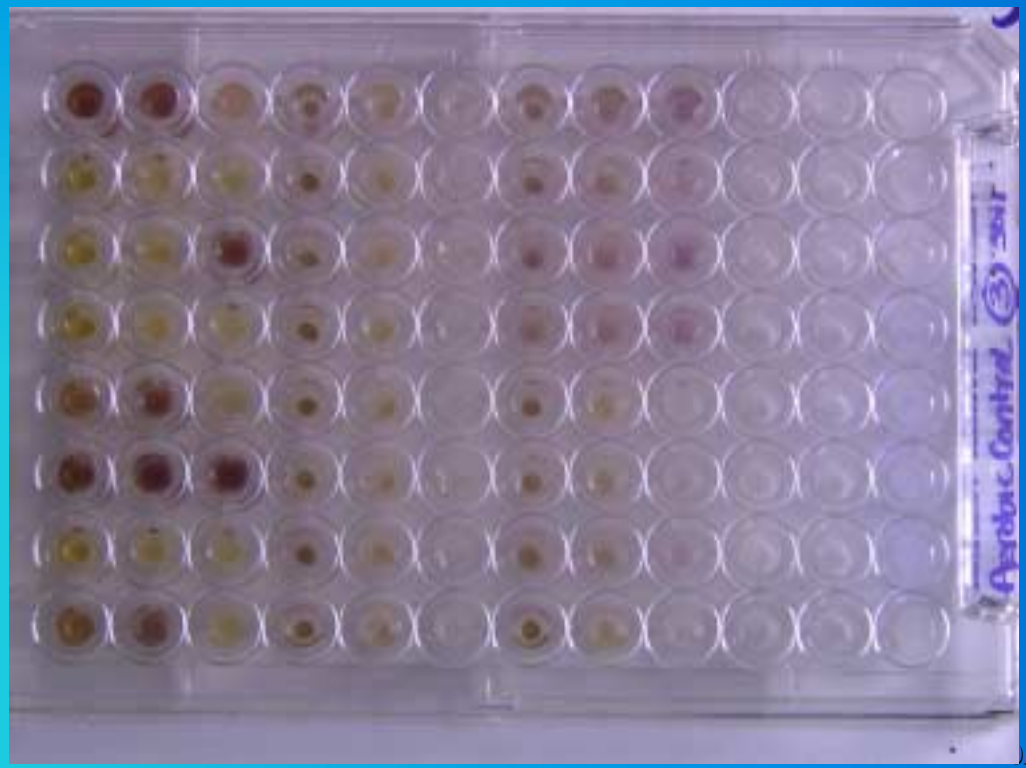
Non Detectable: dehydrogenase, phosphatase

Biolog Enrichments: Analysis incomplete

DNA Community Analysis: in progress

Biolog Enrichments (Single ED)

Area sampled	GW/soil	anoxic/oxic	La	Ac	Py	Bu	Pr	TSB	HRC
bkgd	GW	anoxic	3	2	2	3	3	3	3
bkgd	Sediment	anoxic	3	3	3	3	3	3	3
2	GW	anoxic	3	2	3	2	2	3	3
2	Sediment	anoxic	3	3	3	3	3	3	3
3	GW	anoxic	0	0	0	0	0	0	0
3	Sediment	anoxic	3	3	3	0	0	3	3



Biolog Enrichments

Area sampled	GW/soil	anoxic/oxic	La/FeIII	Ac/FeIII	Py/FeIII	Bu/FeIII	Pr/FeIII	TSB/FeIII	HRC/FeIII
bkgd	GW	anoxic	0	0	0	0	0	0	0
bkgd	Sediment	anoxic	0	0	0	0	2	2	0
bkgd	GW	oxic	3	0	0	0	0	3	3
bkgd	Sediment	oxic	3	0	3	3	3	3	3
2	GW	anoxic	0	0	0	0	0	0	0
2	Sediment	anoxic	0	0	0	0	0	2	0
2	GW	oxic	0	0	0	0	0	0	0
2	Sediment	oxic	0	0	0	0	0	3	0
3	GW	anoxic	0	0	0	0	0	0	0
3	Sediment	anoxic	0	0	0	0	0	0	0
3	GW	oxic	0	0	0	0	0	0	0
3	Sediment	oxic	3	0	3	0	0	3	3

Area sampled	GW/soil	anoxic/oxic	La/NO3	Ac/NO3	Py/NO3	Bu/NO3	Pr/NO3	TSB/NO3	HRC/NO3
bkgd	GW	anoxic	0	0	0	0	0	0	0
bkgd	Sediment	anoxic	0	0	0	0	0	0	0
bkgd	GW	oxic	0	0	0	0	0	0	0
bkgd	Sediment	oxic	0	0	0	0	0	0	0
2	GW	anoxic	0	0	0	0	0	0	0
2	Sediment	anoxic	0	0	0	0	0	0	0
2	GW	oxic	0	0	1	0	0	0	0
2	Sediment	oxic	1	0	0	1	1	0	0
3	GW	anoxic	0	0	0	0	0	0	0
3	Sediment	anoxic	0	0	0	0	0	0	0
3	GW	oxic	0	0	0	0	0	0	0
3	Sediment	oxic	0	1	0	3	1	1	1

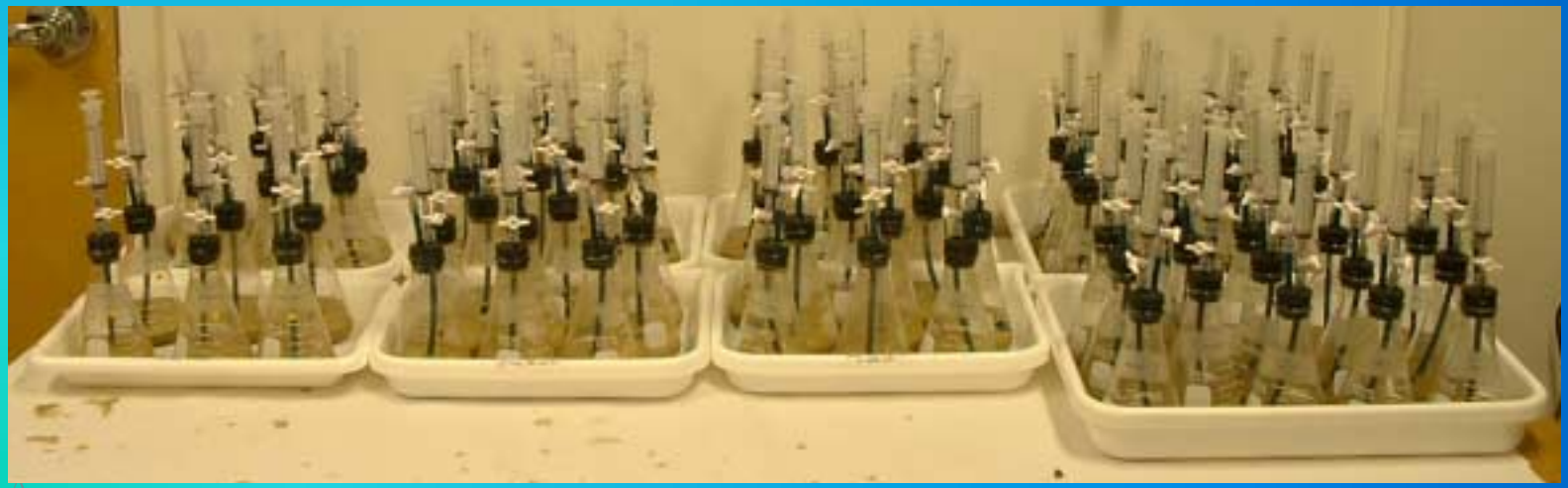
Biolog Enrichments cont.

Area sampled	GW/soil	anoxic/oxic	La/U(VI)	Ac/U(VI)	Py/U(VI)	Bu/U(VI)	Pr/U(VI)	TSB/U(VI)	HRC/U(VI)
bkgd	GW	anoxic	3	3	3	3	3	3	3
bkgd	Sediment	anoxic	3	3	3	3	0	3	3
bkgd	GW	oxic	2	2	2	2	2	1	2
bkgd	Sediment	oxic	0	0	0	0	0	0	0
2	GW	anoxic	3	3	3	3	3	3	3
2	Sediment	anoxic	3	3	3	3	3	3	3
2	GW	oxic	1	1	1	2	2	0	0
2	Sediment	oxic	2	1	2	2	2	1	0
3	GW	anoxic	0	0	0	0	0	0	0
3	Sediment	anoxic	3	3	3	1	2	3	3
3	GW	oxic	0	0	0	0	0	0	0
3	Sediment	oxic	1	0	1	3	2	0	0

Molecular community analysis is being done for the positive enrichments: TRFLP, clone library, Q-PCR with probes for N and Fe reducers

Part I. Effects of pH and carbon on bioreduction of NO3- and U6+ (FRC Area 3 sediment and groundwater high in nitrate)

- **Progress to Date: Laboratory incubations are currently in progress investigating rates of NO3- U6+ reduction in response to organic carbon amendments. Due to the carbon concentration required to complete denitrification we are investigating the efficacy of a commercially available slow releasing polylactate form of carbon (Regenesis HRC) in addition to a rapid release version of the same product (Regenesis HRC Prime). We are following microbial activity through analysis of gas headspace CO_2, CH_4, N_2O and H_2. Upon complete reduction of NO3- and U6+ we will destructively sample sediment/solution and extract DNA in order to determine changes in microbial community composition in response to each treatment.**



Form of Carbon added (10,000 ppm)	Carbon Release Rate	Buffered to pH	% NO_3^- remaining after 11 weeks Ψ	Predicted time for complete nitrate reduction
Regenesis HRC Prime	Fast	6.0/	16.91	13-14 weeks
Regenesis HRC Prime	Fast	4.8/	18.73	14-15 weeks
Regenesis HRC Prime	Fast	2.2*	23.70	14-15 weeks
Regenesis HRC	Slow	6.0/	30.77	16-17 weeks
Regenesis HRC	Slow	4.8*	19.02	14-15 weeks
Regenesis HRC	Slow	2.2Φ	26.07	15-16 weeks
No added Carbon	N/A	6.0/	52.53	23-24 weeks
No added Carbon	N/A	4.8*	59.33	27-28 weeks

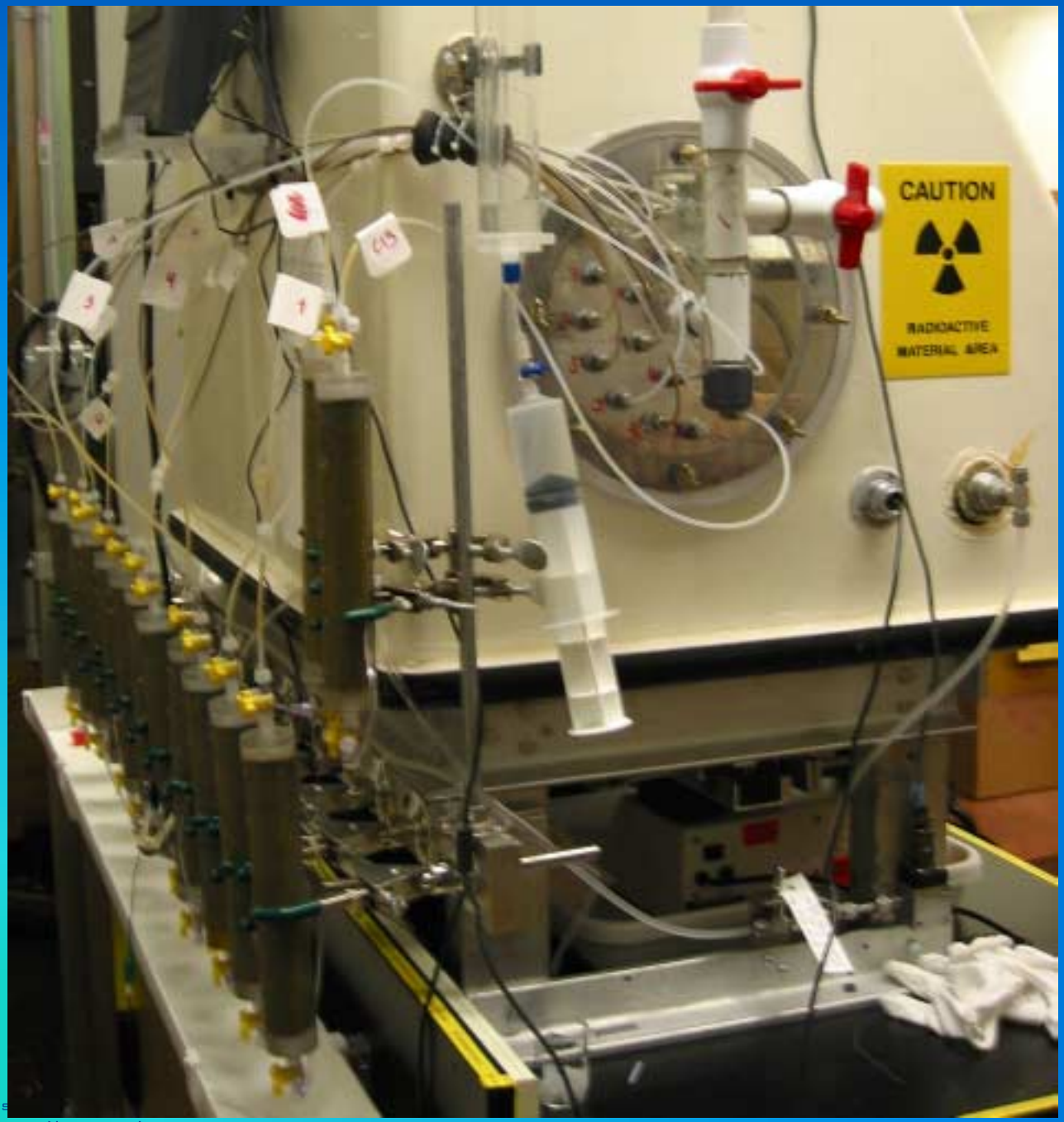
/ pH increased by adding 1M KOH
* Unbuffered pH of solution after carbon addition
Φ pH decreased by adding 1M HCl
Ψ Initial nitrate concentration of groundwater from Area 3 was 56,000 ppm.

Part 2. Diffusion-limited U6+ biogeochemical transformation (FRC background area sediments)

- Progress to Date: Column experiments of 2 types are in progress. The first type examines the U contamination process, with U6+ diffusion into soil columns at different levels of initial organic carbon and microbial activity. The second set of experiments focus on bioremediation of previously contaminated sediments, with organic carbon solutions diffusing into U6-spiked columns. Measurements include U oxidation state determination by micro-XANES spectroscopy, soluble U (kinetic phosphorimetry) redox potential profiling, microbial activity, and microbial community analysis.

Part 3. U4+ reoxidation in subsurface environments that revert to oxygenated conditions (FRC Area 2 sediments)

- **Progress to date: These experiments are designed to evaluate the long-term stability of previously bioreduced U. In step 1 of this experiment, FRC Area 2 sediments containing 200 ppm U, initially primarily as U6+ were packed into columns and infused with lactate solutions to accelerate reduction. Supporting measurements include analyses of U concentrations in effluents, in-situ determination of sediment U6+ : U4+, redox potential profiling, and pore water chemical analyses. This step is nearing completion. In following steps, columns will be exposed to oxygenated waters under flow-through or diffusion conditions, with sediment and solution U6+ concentrations monitored to determine reoxidation rates.**


CAUTION
RADIOACTIVE
MATERIAL AREA