Factors controlling in situ uranium and technetium bioreduction at the NABIR Field Research Center

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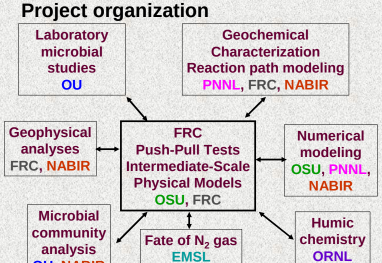
Introduction

Research hypotheses

- Indigenous microorganisms in the shallow aquifer at the FRC have the capability to reduce U(VI) and Tc(VII) but rates are limited by:
  - scarce electron donors,
  - low pH and high Al^{3+}, Ni^{2+}, Ca^{2+} concentrations.
- U(VI) and Tc(VII) reduction rates can be increased by:
  - successive donor additions,
  - raising pH to precipitate metals,
  - adding humics to complex metals and serve as electron shuttles.
- U(IV) but not Tc(IV) is readily oxidized and mobilized by high (> 20 mM) NO_3^-:
  - NO_3^- and denitrification intermediates oxidize Fe(II) to Fe(III) and this oxidizes U(IV),
  - oxidation rates are comparable to reduction rates,
  - oxidation rates are reduced in the presence of sulfides.
- U(VI) and Tc(VII) reduction can be achieved in a sequential permeable reactive barrier containing three zones:
  - pH adjustment,
  - denitrification and Tc(VII) reduction,
  - U(VI) reduction.

Project organization



Recent Publications

- Istok, J.D., J.S. Senko, L. R. Krumholz, D. Watson, M.-A. Bogle, A. Peacock, Y-J. Chang, and D.C. White. 2004. In Situ Bio-Reduction of Technetium and Uranium in a Nitrate-Contaminated Aquifer. Environmental Science & Technology Vol. 38, pp: 468-475.
- North, N.N., S.L. Dollhopf, L. Petrie, J.D. Istok, D.L. Balkwill, and J.E. Kostka. 2004. Change in Bacteria Community Structure during In Situ Biostimulation of Subsurface Sediment Cocontaminated with Uranium and Nitrate. Applied and Environmental Microbiology, Vol. 70, No. 8, pp: 4911-4920.
- Peacock, A.D., Y-J. Chang, J. D. Istok, L. Krumholz, R. Geyer, and D.C.White. 2003. Utilization of Microbial Biofilms as Monitors of Bioremediation. Journal of Microbial Ecology, Volume 47, 284-292.
- Senko, J.M., M. Yasser, T.A. Dewers and L.R. Krumholz. 2005. A Role for Fe(III) Minerals in Nitrate-Dependent Microbial U(IV) Oxidation. Env. Sci. Technol. (ASAP article, In press).
- Senko, J.M., T.A. Dewers and L.R. Krumholz. The effect of the form of Fe(II) and oxidation rate on microbial nitrate-dependent Fe(III) mineralogy. Appl. Env. Microbiol. (submitted).
- Gu, B., H. Yan, P. Zhou, D.B. Watson, M. Park, and J.D. Istok. 2005. Natural Humics Impact Uranium Bioreduction and Oxidation. Environmental Science & Technology, 39, p. 5268-5275.
- Senko, J.M., J.M. Suflita and L.R. Krumholz. Geochemical controls on microbial nitrate-dependent U(IV) oxidation. Geomicrobiol. J. (submitted).

Push-pull tests

Site groundwater is amended with nonreactive tracers and various combinations of bicarbonate, electron donor(s), humics, electron acceptors, inhibitors, and injected into existing monitoring wells. Composition of injected test solution is monitored over time. Multiple tests are conducted simultaneously to assess reproducibility and spatial variability in microbial activity.

Desired metabolic capability is widespread in the shallow subsurface (< ~ 7 m). Donor additions stimulated microbial activity in a wide range of subsurface environments in FRC Areas 1 and 2.

Initial Conditions

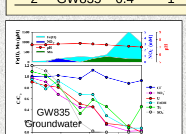
pH	NO_3^- (mM)	SO_4^{2-} (mM)	U(VI) (µM)	Tc(VII) (pM)
3.3-3.9	100-140	0-1	5-12	10000-15000
5.2-5.6	90-100	0-1	5-12	10000-15000
5.6-7.2	0-6	1-2	1-7	200-1000

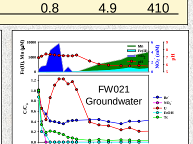
In situ rates of denitrification, sulfate reduction, and U(VI) and Tc(VII) reduction measured at the FRC.

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

U(IV) but not Tc(VII) is readily oxidized and remobilized by NO_3^-.

Area	Well	pH	NO_3^- mM	SO_4^{2-} mM	^{238}U µM	Tc, pM
1	FW21	3.3	142	0.4	5.8	18000
2	GW835	6.4	1	0.8	4.9	410





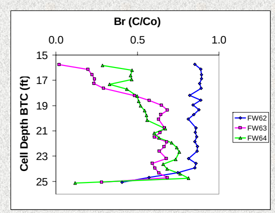
Current Field Activity

MLS

Multi Level Samplers are being used to obtain small-scale spatial variability in groundwater geochemistry,

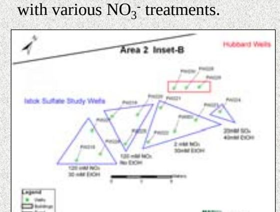
- to quantify the distribution of injected solutes during push-pull tests,
- to incubate mineral samples in the biostimulated aquifer.

Example use of MLS to investigate tracer transport during push-pull tests.

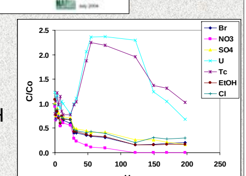


Investigation of the stability of U(IV) with added sulfate.

Area 2 wells were "fed" with GW835 groundwater amended with 40 mM ethanol and 20 mM SO_4^{2-} to deposit U(IV) under sulfate reducing conditions. Tests in progress are investigating the stability of biogenic U(IV) to varying NO_3^- levels. The map below shows wells in Area 2 that have been tested with various NO_3^- treatments.

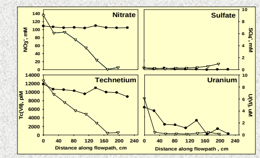


100mM NO_3^-
440mM EtOH



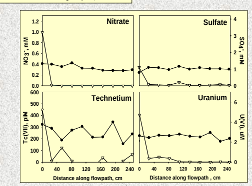
Intermediate-scale physical models

Can long-term immobilization of U and Tc be achieved in permeable reactive barriers ? Four intermediate-scale physical models have been operated continuously for 16-20 months. Example results show complete U(VI) and Tc(VII) removal from groundwater. Ethanol additions have ceased and reoxidation is being monitored.



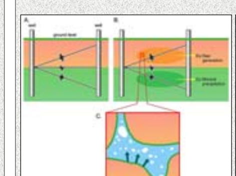
Area 1

Area 2



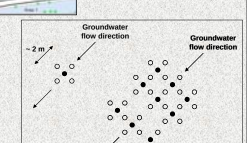
LBNL Collaboration

Geophysical methods are being used to monitor the formation of gases and precipitates formed during biostimulation in Areas 1 and 2.



Proposed Area 3 Experiment

We propose to investigate the effect of long-term donor additions on aquifer hydrology, mineralogy, and microbiology in a field experiment in Area 3.



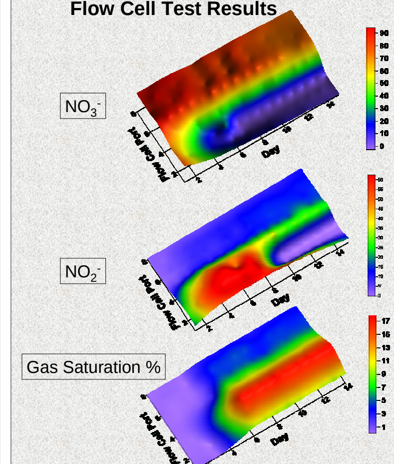
EMSL collaboration

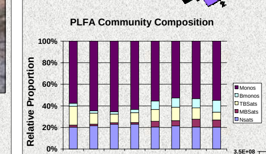
What is the fate of N_2 gas produced by denitrification (Oostrom and Wietsma at PNNL)?

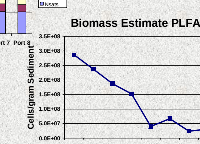
EMSL Flow Cell

- Packed with FRC background sediment and Maynardsville limestone.
- Denitrifying activity stimulated with ethanol.
- Gas saturations monitored using dual-energy gamma attenuation.
- Injected with 150mM NO_3^- and 300mM Ethanol.

Flow Cell Test Results







- 150 mM NO_3^- consumed by stimulated microbial community resulting in growth and N_2 gas production.
- Measured gas saturations are smaller than predicted and observations confirm gas is released to sediment pack surface.
- The effect on hydraulic conductivity is small.

Acknowledgments

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