acceleration of field-scale bioreduction of U(VI) in a shallow alluvial aquifer: temporal and spatial evolution of biogeochemistry

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NABIR PI Meeting
April 18-20, 2005
Outline of Presentation

- Background and overall objectives of field-scale experiments
- Predictions for U(IV) re-oxidation
- Observed U(VI) behavior
- Possible mechanisms for prolonged U(VI) loss
- Planned future experiments
- Summary
### Old Rifle UMTRA Site Collaborators

<table>
<thead>
<tr>
<th>Collaborators</th>
<th>Principal Activities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Derek Lovley, Kelly Nevin, Helen Vrionis, Regina O’Neil, Irene Ortiz-Bernad,</td>
<td>Microbiology, genomics, 16s clone libraries, mRNA, geochemistry</td>
</tr>
<tr>
<td>Dawn Holmes (Umass)</td>
<td>--------------------------------------------------------------------------------------</td>
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<tr>
<td>David White, Aaron Peacock, Janet Chang (Univ. of Tennessee)</td>
<td>Phospholipid fatty acid profiles, Stable isotope probing (SIP), in-well coupons</td>
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<tr>
<td>Richard Dayvault and Stan Morrison (S.M. Stoller Corp.)</td>
<td>Drilling and sampling field activities, sorption measurements</td>
</tr>
<tr>
<td>Peter Jaffe (Princeton), John Zachara (PNNL)</td>
<td>Reoxidation column studies, solids characterization</td>
</tr>
<tr>
<td>Susan Hubbard, Ken Williams (LBNL)</td>
<td>Geophysics (complex resistivity)</td>
</tr>
<tr>
<td>C. Tom Resch, Phil Long, Jim McKinley (PNNL)</td>
<td>Field sampling, in-well incubator analysis, geochemistry, hydrology</td>
</tr>
<tr>
<td>Steve Yabusaki, Yilin Fang (PNNL)</td>
<td>Reactive transport modeling</td>
</tr>
<tr>
<td>Darrell Chandler (ANL), Ann Jarrell, (PNNL)</td>
<td>DNA Chip and Bead Arrays</td>
</tr>
</tbody>
</table>
Background and Overall Objectives

Uranium mill tailings sites provide access to uranium-contaminated groundwater at sites that are shallow and low hazard, making it possible to address the following scientific objectives:

- **Determine the dominant electron accepting processes at field sites with long-term metal/rad contamination**
- **Define the biogeochemical transformations that may be important to either natural or accelerated bioremediation under field conditions**
- **Examine the potential for using biostimulation (electron donor addition) to accelerate reduction of U(VI) to U(IV) at the field scale**
# Summary of Field Experiments

<table>
<thead>
<tr>
<th>Field Experiment</th>
<th>Objectives</th>
<th>Observations</th>
<th>Conclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>2002</td>
<td>Determine if biostimulation removes U(VI) from groundwater</td>
<td>U(VI) loss; loss rate decreases with sulfate reduction; Geobacter growth</td>
<td>Electron donor amendment works at the field scale, Geobacter responsible for U(VI) loss</td>
</tr>
<tr>
<td>2003</td>
<td>Extend Fe(III) reduction and U(VI) loss in time and space by increasing acetate concent.</td>
<td>Extensive sulfate reduction, Fe(III) reduction down gradient, U(VI) loss; prolonged U(VI) reduction post-acetate addition</td>
<td>Increasing electron donor works, but sulfate reduction may be problematic or may help limit reoxidation</td>
</tr>
<tr>
<td>2004</td>
<td>Replicate U(VI), obtain genomic and mRNA samples, stable isotope probing, test geophysics for detecting biostimul.</td>
<td>U(VI) similar to 2002 experiment. Geobacter dominance, $^{13}$C observed in PLFA, complex resistivity response</td>
<td>U(VI) loss replicable at field scale, mRNA promising for site assessment and monitoring of remediation, others TBD</td>
</tr>
</tbody>
</table>
The experimental plot is located in a part of a uranium plume with ~ 0.6 to 1.2 uM U(VI), residual from when the site was used as a uranium ore processing facility. The Colorado River flow has a major impact on groundwater flow at the site.
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Stratigraphy, Well B-02

Compacted fill 0.0 to 5.0 ft

Alluvium (cobbly sand) 5.0 to 11.5 ft
~ position of water table

Alluvium (sand) 11.5 to 12.5 ft

Alluvium (gravelly sand) 12.5 to 20.0 ft

Wasatch Formation 20.0 to 21.0 ft (TD 21 ft) (relatively impermeable)

Well construction

PVC sched. 40, 2” or 4” dia.

Bentonite chips

PVC slotted 2” or 4” well screen, 0.020” slot size

Silica sand, 20-40

Natural cave-in material

Silica sand, 20-40
**Stratigraphy, Well B-02**

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- Bentonite chips
- PVC slotted 2” or 4” well screen, 0.020” slot size
- Silica sand, 20-40
- Natural cave-in material
Map of NABIR Biostimulation Well Field and Water Table Contours (04/07/05)
Old Rifle UMTRA Site, Rifle, CO

Water Level (m)
- 1615.01
- 1615.00
- 1614.99
- 1614.98
- 1614.97
- 1614.96
- 1614.95
- 1614.94
- 1614.93

Legend:
- Background Wells
- Injection Gallery
- Monitoring Row 1
- Monitoring Row 2
- Monitoring Row 3
- Mini gallery
- 2002 P-Wells
- 2003 P-Wells
- 2004 P-Wells
Sample Types

- **Geochemistry:**
  - Groundwater (pumped)
  - Groundwater (MLS)

- **Microbiology:**
  - Sediments (once per exp.)
  - Coupons (carbon beads)
  - Groundwater (pumped)
Simulated U Concentrations over 80 days

**Acetate injection stops at day 40**

\[ r_{\text{out}} = 1.0 \times 10^6 \text{ M}^{-1} \text{ yr}^{-1} \]
U(VI) Loss for the 2002 Field Experiment

Days

U(VI), μM

-5 0 5 10 15 20 25 30

B-02 2002
M-03 2002
2002 U(VI) loss

Days

U(VI) in M

-5 45 95 145 195 245

B-02 2002
M-03 2002

Pacific Northwest National Laboratory
U.S. Department of Energy
U(VI) at start of 2003

Uranium Concentration during 2003 Biostimulation
Old Rifle UMTRA Site, Colorado

06/18/2003
Uranium Concentration during 2003 Biostimulation
Old Rifle UMTRA Site, Colorado

10/12/2003 ACETATE INJECTION
U(VI) loss at 6 meters from B-02 to M-08.

Date:
- 11/5/01
- 5/24/02
- 12/10/02
- 6/28/03
- 1/14/04
- 8/1/04

U(VI) (uM):
- 0
- 0.5
- 1
- 1.5
- 2
- 2.5

Legend:
- B-02
- M-08
- Typical Tie Line (used to calc. U(VI) loss)
- 2002 Acetate Start
- 2002 Acetate End
- 2003 Acetate Start
- 2003 Acetate End
U(VI) loss for both 2002 and 2003 experiments

U(VI) Loss at 6 meters from B-02 to M-08

-1.5 -1 -0.5 0 0.5 1 1.5 2

-100 -80 -60 -40 -20 0 20 40 60 80 100

11/5/01 5/24/02 12/10/02 6/28/03 1/14/04 8/1/04

Date

% U(VI) loss

U(VI) (uM) loss

-1.5 -1 -0.5 0 0.5 1 1.5 2

-100 -80 -60 -40 -20 0 20 40 60 80 100

11/5/01 5/24/02 12/10/02 6/28/03 1/14/04 8/1/04

Date

% U(VI) lost

2002 Acetate Start
2002 Acetate End
2003 Acetate Start
2003 Acetate End
U(VI) (uM) lost
Current status as of April 7, 2005:
~50% loss 1.5 years post-acetate amendment
U(VI) loss in 1st, 2nd, & 3rd rows at 4.8, 5.2, & 6.0 m
Comparison of U(VI) loss in 2002 and 2004 Field Experiments
U(VI) vs time for 5.1m depth in M-18

Date

U(VI) (μM)

8/13/04 10/2/04 11/21/04 1/10/05 3/1/05 4/20/05
U(VI) vs time for 5.1m depth in M-18 with B-04 background data
What are possible mechanisms for prolonged U(VI) loss?

**Biotic**
- Residual Fe-reducer population
- “Maintenance” population

**Abiotic**
- FeS$_{0.9}$ oxygen buffering and/or U(VI) sorption
- Formation of new Fe(III) oxides sorbing U(VI)
- Redox impact on U(VI) sorption
Change in PLFA biomass 2003/2004 (matched depth data set)
Scatterplot: Cells vs. U(VI) (Casewise MD deletion)

\[ U(VI) = 0.82763 - 0.3 \times 10^{-5} \times \text{Cells} \]

Correlation: \( r = -0.7414 \)
What are possible mechanisms for prolonged U(VI) loss?

- **Biotic**
  - Residual Fe-reducer population
  - “Maintenance” population

- **Abiotic**
  - FeS\(_{0.9}\) oxygen buffering and/or U(VI) sorption
  - Formation of new Fe(III) oxides sorbing U(VI)
  - Redox impact on U(VI) sorption
Future Experiment at Old Rifle

Hypothesis: Prolonged U(VI) loss is controlled by TEAP reached during acetate amendment

- Construct a new minigallery
- Run two experiments in parallel
  - Drive the existing minigallery to sulfate reduction
  - Stop acetate amendment in new minigallery during Fe-reduction
- High-frequency monitoring of post-amendment response, including geophysics. Compare genomics, $^{13}$C PLFA/DNA, and mRNA of the two systems, during and post-amendment
- Additional laboratory studies are underway or proposed
- Reactive transport modeling (Yabusaki and Fang) will be used to explore match of mechanistic processes to field and lab data
Summary

- Amendment of acetate to the subsurface removes U(VI) from groundwater by direct enzymatic reduction to U(IV)
- Loss of U(VI) is sustained much longer than expected, >1.5 years locally in the system
- Sustained loss post-amendment does not appear to be controlled by microbial biomass alone
- Mechanisms for sustained loss will be addressed by a field experiment in 2005, and by on-going and proposed lab studies examining reoxidation of U(IV) and redox impact to U(VI) sorption using Rifle sediments
Additional future field experiments

- High DO site (effect on reduction and reoxidation rates)
- High Nitrate site (effect of nitrate reduction on subsequent processes)
- Other electron donors (lactate, ethanol)
- Hydrogeology differences (flow rate, porosity, permeability)
- Other metals (e.g. vanadium)
- In-well electrode biocapture of uranium
Acetate/Br in Well M-08 and from injection tank

Tank values 2003
Initial decrease ~ 62%

Tank values 2002

Well M-08
Initial decrease ~ 29%

Date
2/13/02 5/24/02 9/1/02 12/10/02 3/20/03 6/28/03 10/6/03 1/14/04

Molar Ratio of Acetate to Br
0 5 10 15 20 25 30 35 40

- Acetate/Br in situ
- Tank Acetate/Br
Scatterplot: Cells vs. U(VI) (Casewise MD deletion)

U(VI) = 0.46270 - 0.9E-6 \times \text{Cells}

Correlation: r = -0.1255
# Typical Groundwater Chemistry

<table>
<thead>
<tr>
<th>Parameter</th>
<th>M-02 Prior to Biostimulation (6-20-02)</th>
<th>M-02 After Biostimulation (8/13/02)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.06</td>
<td>7.23</td>
</tr>
<tr>
<td>Eh</td>
<td>144 mV</td>
<td>-41 mV</td>
</tr>
<tr>
<td>DO</td>
<td>0.26 mg/l</td>
<td>0.07 mg/l</td>
</tr>
<tr>
<td>Conductivity</td>
<td>2196 uS/cm</td>
<td>2116 uS/cm</td>
</tr>
<tr>
<td>NO₃</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>6.57 mM</td>
<td>5.25 mM</td>
</tr>
<tr>
<td>Sulfide</td>
<td>nd</td>
<td>0.78 uM</td>
</tr>
<tr>
<td>Acetate</td>
<td>nd</td>
<td>760 uM</td>
</tr>
<tr>
<td>Br</td>
<td>nd</td>
<td>253.1 uM</td>
</tr>
<tr>
<td>U(VI)</td>
<td>0.73 uM</td>
<td>0.23 uM (-68%)</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>53.1 uM</td>
<td>135.1 uM (7/30/02)</td>
</tr>
<tr>
<td>DIC</td>
<td>2.13 mM</td>
<td>2.40 mM (8/1/02) +13%</td>
</tr>
<tr>
<td>DOC</td>
<td>0.44 mM</td>
<td>2.60 mM (8/1/02) +493%</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>1.738 meq/l</td>
<td>2.063 meq/l (8/1/02) +19%</td>
</tr>
</tbody>
</table>
## Typical Groundwater Chemistry (cations)

<table>
<thead>
<tr>
<th>Cation</th>
<th>B-01 (background) Prior to Biostimulation (6-25-03)</th>
<th>M-02 Prior to 2003 Biostimulation (6-25-03)</th>
<th>M-02 After 2003 Biostimulation (8/04/03)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Ba</td>
<td>0.41 uM</td>
<td>0.45 uM</td>
<td>0.41 uM</td>
</tr>
<tr>
<td>Ca</td>
<td>5.3 mM</td>
<td>5.2 mM</td>
<td>4.1 mM (-21%)</td>
</tr>
<tr>
<td>K</td>
<td>0.20 mM</td>
<td>0.22 mM</td>
<td>0.20 mM</td>
</tr>
<tr>
<td>Mg</td>
<td>5.1 mM</td>
<td>5.0 mM</td>
<td>4.2 mM (-16%)</td>
</tr>
<tr>
<td>Mn</td>
<td>0.014 mM</td>
<td>0.019 mM</td>
<td>0.014 mM (-26%)</td>
</tr>
<tr>
<td>Ni</td>
<td>0.84 uM</td>
<td>0.84 uM</td>
<td>0.70 uM</td>
</tr>
<tr>
<td>Sr</td>
<td>0.038 mM</td>
<td>0.035 mM</td>
<td>0.031 mM (-11%)</td>
</tr>
<tr>
<td>V</td>
<td>0.021 mM</td>
<td>0.068 mM</td>
<td>nd (-94%)</td>
</tr>
<tr>
<td>Na</td>
<td>8.21 mM</td>
<td>8.28 mM</td>
<td>12.4 mM (+50%)</td>
</tr>
<tr>
<td>Si</td>
<td>0.40 mM</td>
<td>0.45 mM</td>
<td>0.44 mM</td>
</tr>
</tbody>
</table>
Profile of Normalized Hydraulic Conductivity of Well M01

Profile:
- Top of Screen at 5305.89 FT NGVD (5.0 FT BGS)
- Water surface at 5298.77 FT NGVD (12.12 FT BGS) when pumping at .50 GPM

- Bottom of Screen at 5290.89 FT NGVD (20.0 FT BGS).
- Probe could only reach 5293.05 FT NGVD (17.84 FT BGS), remainder of data extrapolated.
Knowledge Gaps

- Mechanisms for sustained U(VI) loss post-amendment
  - Effect of sulfide precipitate
  - Biomass/ongoing microbially mediated U(VI) reduction

- Competing U(VI) sorption effects
  - U(VI) released by Fe-oxide reduction
  - Sorption increased by decrease in Ca-CO₃-U(VI) complexes

- U(VI) bioreduction rates (considering sorption parameters)

- Biomass impact on reactivity

- Fe(II) sorption, bioproduction rates, surface behavior

- Overall effect of redox on U(VI) sorption (abiotic)
  - Sulfide precipitate chemistry and micro-texture
  - Scaling
  - Fe(III) reduction
Simulated Uranium Concentrations over 80 days

Acetate injection stops at Day 40

- **B-02**
- **M-08**
- Typical Tie Line (used to calc. U(VI) loss)
- 2002 Acetate Start
- 2002 Acetate End
- 2003 Acetate Start
- 2003 Acetate End

U(VI) concentration, M

U(IV) concentration, M

U(VI) - Day 32
U(VI) - Day 16
U(VI) - Day 80
U(VI) - Day 64
U(IV) - Day 64
U(IV) - Day 80
U(IV) - Day 32
U(IV) - Day 16

µOU4 = 1.0 x 10^6 M^-1 yr^-1

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2002 U(VI) and SO$_4^-$

![Graph showing the comparison of U(VI) and SO$_4^-$ levels over days. The graph includes lines for U(VI) B-02 2002, U(VI) M-03 2002, and SO$_4^-$ M-03 2002. The x-axis represents days, and the y-axis represents concentration in uM.](image-url)