Oak Ridge Field Research Center

Current Opportunities and Future Research Directions

April 21, 2005

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Presentation Outline

• Current FRC research opportunities
  – Current research results and findings
    • Field scale reduction
    • Inhibition/oxidation
    • Characterization and monitoring tools
    • Rates and mechanisms
    • Modeling
  – Near-term research opportunities
• Potential future research directions
Original FRC Research Focus

• Objectives
  – Understand fundamental biogeochemical processes influencing the use of bioremediation approaches for cleaning up, managing, or understanding fate and transport of metals and radionuclides at DOE’s contaminated legacy waste sites
  – Promote coordination and efficient use of resources, and facilitate comparison and integration of data

• Establish a field laboratory
  – Source of subsurface samples for NABIR, EMSP, GTL, JGI investigators
  – Resource for
    • Evaluation of new characterization and monitoring methods
    • *In situ* accelerated bioremediation research
Multi-disciplinary *In Situ* Accelerated Bioremediation Field Research Projects

- **In situ uranium reduction experiments using push-pull techniques** (Oregon State University, Oklahoma University, PNNL, ORNL located in Areas 1 and 2)
- **In situ immobilization of uranium in structured porous media via biomineralization at the fracture/matrix interface** (PNNL, ORNL, and University of Alabama, located in Area 2)
- **Field-scale bioreduction of uranium** (Stanford and ORNL, located in Area 3)
Multiple Hydrogeologic Environments Available for Study
FRC Sample Collection, Analysis and Distribution

- 2,880 samples distributed to researchers for laboratory studies
  - Samples distributed to NABIR, GTL, EMSP, and JGI researchers
  - Samples shipped overseas to Switzerland, Denmark, and UK
  - Hg samples collected and shipped
- >12,000 samples collected for field studies
- Drilling
  - 111 wells installed – 2,900 feet
  - 114 coreholes (no wells) drilled – 2,200 feet
- Analyses (excludes analyses for PIs)
  - 20,000 FRC new analyses results
  - 39,000 historical analyses results entered into the database
FRC Publications

- Over 25 publications published or in press
- Many more submitted or being prepared

1. Impacts on microbial communities and cultivable isolates from groundwater contaminated with high levels of nitric acid-bearing uranium waste (Proof available online as of 2/26/2005).
2. Plume and Lithologic Profiling with Surface Resistivity and Seismic Tomography.
3. Change in Bacterial Community Structure during In Situ Biotreatment of Subsurface Sediment Cocontaminated with Uranium and Nitrate.
4. Coupling of functional gene diversity and environmental data from environmental samples.
5. Isolation, characterization, and U(VI)-reducing potential of a facultatively anaerobic, acid-resistant bacterium from Low-pH, nitrate- and U(VI)-contaminated subsurface sediment and description of Salmonella subterranea sp nov.
7. In situ bioreduction of technetium and uranium in a nitrate-contaminated aquifer.
8. Sorption and binary exchange of nitrate, sulfate, and uranium on an anion-exchange resin.
10. A cultivation-independent investigation of microbial communities during in situ biostimulation of subsurface sediment co-contaminated with uranium and nitrate.
11. Composition and diversity of microbial communities recovered from surrogate minerals incubated in an acidic uranium-contaminated aquifer.
12. An application of Bayesian inverse methods to vertical deconvolution of hydraulic conductivity in a heterogeneous aquifer at Oak Ridge National Laboratory.
13. Utilization of microbial biofilms as monitors of bioremediation.
15. Geochemical reactions and dynamics during titration of a contaminated groundwater with high uranium, aluminum, and calcium.
16. Potential for in situ bioremediation of a low-pH, high-nitrate uranium-contaminated groundwater.
17. Conceptual and numerical model of uranium (VI) reductive immobilization in fractured subsurface sediments.
19. A prohibitin-like protein of Shewanella oneidensis MR-1 is involved in iron homeostasis and oxidative damage protection (in press).
20. The Three-Point Problem, Vector Analysis and the Extension to the N-Point Problem.
21. Enumeration and characterization of iron(III)-reducing microbial communities from acidic subsurface sediments contaminated with uranium(VI).
22. Inhibition of bacterial U(VI) reduction by calcium.
23. Mass-transfer limitation for nitrate removal in a uranium-contaminated aquifer at Oak Ridge, TN.
24. HYDROGEOCHEM 4.0: A coupled model of fluid flow, thermal transport, and HYDROGEOCHEMical transport through saturated-unsaturated media: version 4.0.
25. HYDROGEOCHEM 5.0: A three-dimensional model of coupled fluid flow, thermal transport, and HYDROGEOCHEMical transport through variably saturated conditions: version 5.0.
26. U L3-Edge EXAFS Measurements of Sediment Samples from Oak Ridge National Laboratory, Tennessee, U.S.A.

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Research Findings – Field-Scale Reduction

- Microbially mediated reduction of U, Tc-99, and nitrate observed (Criddle and Istok experiments)
  - Aqueous phase reduction of dissolved U, Tc, nitrate, and ethanol; Increase in Fe(II)
  - Observation of reduced U(IV) near injection wells
  - Changes in solid phase Fe mineralogy observed (Stucki et al.)
  - Microbial populations increase and shift (SRB, FeRB, NRB)
  - Methanogenesis and sorption controlled via pH adjustments (Criddle et al.)

Uranium (VI) reduction during Area 3 field scale tests with addition of electron donor (ethanol)

Simultaneous uranium and technetium immobilization during field push-pull tests with addition of electron donor (ethanol)
Observing $U$ and $T_c$ reduction in flow cells for over 20 months

OSU Flow-Through Cells
- Simulating subsurface biocurtain
- Two Cells at Areas 1 and 2
- Test and control cells

Source water: FW021

Mandy Sapp
OSU
graduate student

Ellie Selko
OSU
undergraduate student
FRC intern

Limestone/sediment mixture
Manometer
Sampling ports

Ethanol Injection lines
Inlet
Research Opportunities
Field-Scale Reduction

- Area 2 manipulations to begin this spring (Scheibe – microbarriers)
- New Area 3 field plot proposed (Istok)
- New Areas 4 and 5 available (U, Tc, nitrate, and organics)
Research Findings – Inhibition/Reoxidation

- Nitrate, NO\textsubscript{x}, and Fe significant role in reduction and reoxidation (Senko, Krumholz, Istok, et al., Coates et al. Zachara et al.)
- Ca inhibition (Brooks et al.)
- Al and Fe oxide pH buffering and precipitates (Criddle et al.)
- Humics (Gu, Istok, et al.)
  - Increased U reduction rates even in presence of Ca or Ni inhibitors
  - U-HA complexes increased rate of reoxidation (minutes)

**Graphs:**
- Oxidation and mobilization of U during push-pull test due to the presence of NO\textsubscript{2}
- U reduction rates increase during push-pull tests with FRC HA
- U(IV) oxidation rates increase with FRC HA complexes
Research Opportunities
Inhibition/Reoxidation

- Future Area 3 field plot (Criddle) experiments will focus on reoxidation (O$_2$)
- Sequestration of U through reduction of sulfate and co-precipitation with sulfides (Istok)

Uranium (VI) reduction/reoxidation experiments in Area 3 field plot

Push-Pull experiments in Areas 1 and 2
Research Opportunities
Inhibition/Reoxidation

• Impact of aging of U, Tc, and other precipitates on sequestration and reoxidation

Changes in Area 2 PRB from 15 months to 30 months
- cementation was greater
- amorphous FeS transformed into mackinawite
- aragonite transformed into calcite
- akaganeite transformed to goethite and lepidocrocite
- iron (oxy)hydroxides and calcium and iron carbonate minerals increased

Phillips, Watson et al.
Research Opportunities
Inhibition/Reoxidation

- Aquifer clogging due to mineral precipitation and gas production
- Well screen clogging and refurbishment

Well screen clogging in Area 3 Field Plot
Reference well (FW106)  Inner injection well  Inner extraction well

Pre-Cleaning

Post-Cleaning

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FRC Research Findings – Microbial Communities (Kostka)

- Lower microbial biomass and diversity in the contaminated FRC compared to Background Area (Reardon et al., Fields)
- Observed shifts in the dominant members of FRC subsurface material clone libraries as a result of stimulations (North et al.)
- Bacterial strains of metal-reducers (Salmonella, Geobacter) and nitrate-reducers (Alcaligenes, Acidovorax, Pseudomonas, Klebsiella, Agrobacterium) isolated from the contaminated area make it possible to understand physiology of organisms relevant to bioremediation (Lovely, Kostka, Krumholz, and Fields)
- Pure cultures indicate that a pH of < 5 is lethal to nitrate-reducers obtained from the site
- Isolates shown to contain metal resistance genes; a functional gene array is being developed to screen for metal resistance
Research Opportunities

Microbial Characterization

• Physiology of organisms relevant to bioremediation
• Improved molecular approaches
  – Higher sample throughput
  – More quantitative
  – Better represent the *in situ* activity of subsurface microorganisms
• Competition and/or overlap of microbial communities catalyzing metal reduction, nitrate reduction, destruction of organics
• Sampling artifacts
  – Large diameter vs. small diameter wells, well purging etc.
  – Attached vs. detached organisms
  – Heterogeneity
• Spatial distribution of microorganisms
  – Relationship to geochemical and physical data
  – Scale of sampling between media

Microorganism observed in Area 2 large diameter trench well with colloidal borescope
FRC Research Findings – Rates and Mechanisms (Burgos), and Modeling (Parker)

- Rate data are being compiled in tables and report (Burgos)
  - To be enlarged and refined for submission as a peer-reviewed paper
  - Will propose and include different rate formulations and corresponding rate parameters

- Significant differences observed between rates measured in the lab with pure cultures, compared to rates estimated from push-pull tests
  - Some measured rates at the FRC 1,000 to 100,000 times slower than in laboratory experiments

- Input rates and mechanisms to numerical Model (Parker)
  - Identify important processes, knowledge gaps and prioritize research
  - Tool for researchers to plan and evaluate experiments

![Simulated plume without density-dependent flow](image1)

Observed Plume

![Model shows density-driven flow moves nitrate plume deeper near source but reduces hydraulic flux to Bear Creek](image2)

![Simulated plume with density-dependent flow](image3)

Bear Creek
FRC Research Findings – Development of Characterization and Monitoring Tools (Jardine)

- Coupons or bug traps (Peacock et al. and Cummings, Reardon et al.)
- Novel hydraulic testing – point dilution, tracer and flowmeter testing
- Solid Phase Characterization - XRD, SEM- BSE-EDX, TEM, EXAFS, XANES, Mossbauer, extraction methods
- Microbial analysis – DNA microarrays (Zhou), Joint Genome Institute, Community Sequencing Program project (Zhou and Hazen), and Genomes to Life (GTL) Virtual Institute of Microbial Stress and Survival (VIMSS) project (Hazen)
- Field portable immunoassay biosensor for U (Blake)

Comparison of U obtained by gamma counting, (total), and nitric acid, AO, and CD extraction

Bromide tracer test in Area 2 (Brooks and Scheibe)

Coupons or bug traps Bio-Sep Beads® (Peacock)
FRC Research Findings – Development of Characterization and Monitoring Tools

- Geophysical characterization and monitoring of geochemical and hydraulic alterations
  - Conductivity probing, electromagnetic, *in situ* gamma
  - Resistivity and seismic tomography (Watson et al.)
  - Seismic, radar, and resistivity cross-borehole (Hubbard and Williams)

Seismic tomography in new Area 5 (2070m/sec contour)
ORR Environmental Cleanup Situation

- Easy problems have been addressed
- ORR environment challenging
  - High recharge, shallow water table, conditions transient seasonally and long-term
  - Huge reservoirs of contamination in the matrix and fractures
  - Plumes have migrated long distances offsite and to surface water discharge points through ill-defined preferred flowpaths (fracture sets and karst)
- Excavation and capping are primary means of dealing with source areas
  - Limited source term actions are being taken
  - Extensive groundwater plumes will be allowed to attenuate
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Stewardship issues that can be investigated at the FRC

- Attenuation and enhanced attenuation of mixed waste plumes and sources
  - Interactions of U, Tc, nitrate, inorganics and organics
  - Multiple hydrobiogeochemical environments
- Heterogeneity and scaling
  - What parameters need to be measured to understand and predict long-term attenuation and remediation?
  - Impact of coupled processes on reactive transport
- Characterization and imaging of preferred pathways
  - Understanding long-term impacts on transport
  - Relationship with matrix and source
- Improved characterization, sensors, and monitoring tools, and model predictions
- Mercury fate and transport studies, and remediation
  - Contaminated and Background Areas identified
  - Vapor versus dissolved phase transport
  - Microbial studies by Sorensen:
    - Bacterial mercury resistance tolerance/capacity
    - Attempting to culture mercury resistant bacteria, and characterize plasmids, Hg resistance genes, etc.

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Future Research Directions
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Conceptual Model Vs. Reality

Preferred Pathways Dominate in Reality

Conceptual model presented in Remedial Investigation Report

Observed conductivity plume model from surface resistivity (nitrate >3000mg/l)
Preferred Pathways

S-3 Ponds Examples

1) Man made
   - Carbonate gravel fill (porous media)
   - Higher pH

2) Naturally occurring
   - Saprolite and bedrock (structured media)
   - Fractures and solution cavities
Example 1 – Carbonate Gravel Fill Preferred Pathway

Gravel fill beneath tanks encountered in FWB408
High U detected in Area 4
Dolomite Gravel Fill (FWB408)

Gross Gamma Activity (cps)

Depth Below Ground Surface (ft)

Gravel Fill

Saprolite

Solid Phase  Groundwater

U
12,000 ppm  0.8 ppm
pH
5.9 - 6.8  6.2
NO₃
---  162 ppm

U
1,000 ppm  33 ppm
pH
3.4  3.2
NO₃
---  14,000 ppm

pH grades from 5.9 to 3.2

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High U detected in Area 4 Dolomite Gravel Fill

SEM-BSE element mapping

U material
Al oxide
dolomite

Saprolite/Gravel interface

Al oxide
Ca Mg Si
Extent of Shallow Gravel Preferred Pathway
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Advancing Scientific Understanding

DOE Plumes and Sources

Multi-process
Multi-scale

Fate and Transport
Monitoring and Characterization
Remediation, Stabilization, and Stewardship
Example 2 – Saprolite/Bedrock Preferred Pathway

Legend
- Existing Wells
- New geophysics lines
- Old geophysics lines

Primary zone of subsurface transport
Area 4 and 5 Seismic Tomography

Results

General depth of push-probe refusal

Low Velocity Zones
Discharge at Bear Creek Tributary is impacted by preferred pathways.

Correlating surface resistivity tomography profile at NT-1 and surface water quality helps locate preferred pathways and discharge.

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