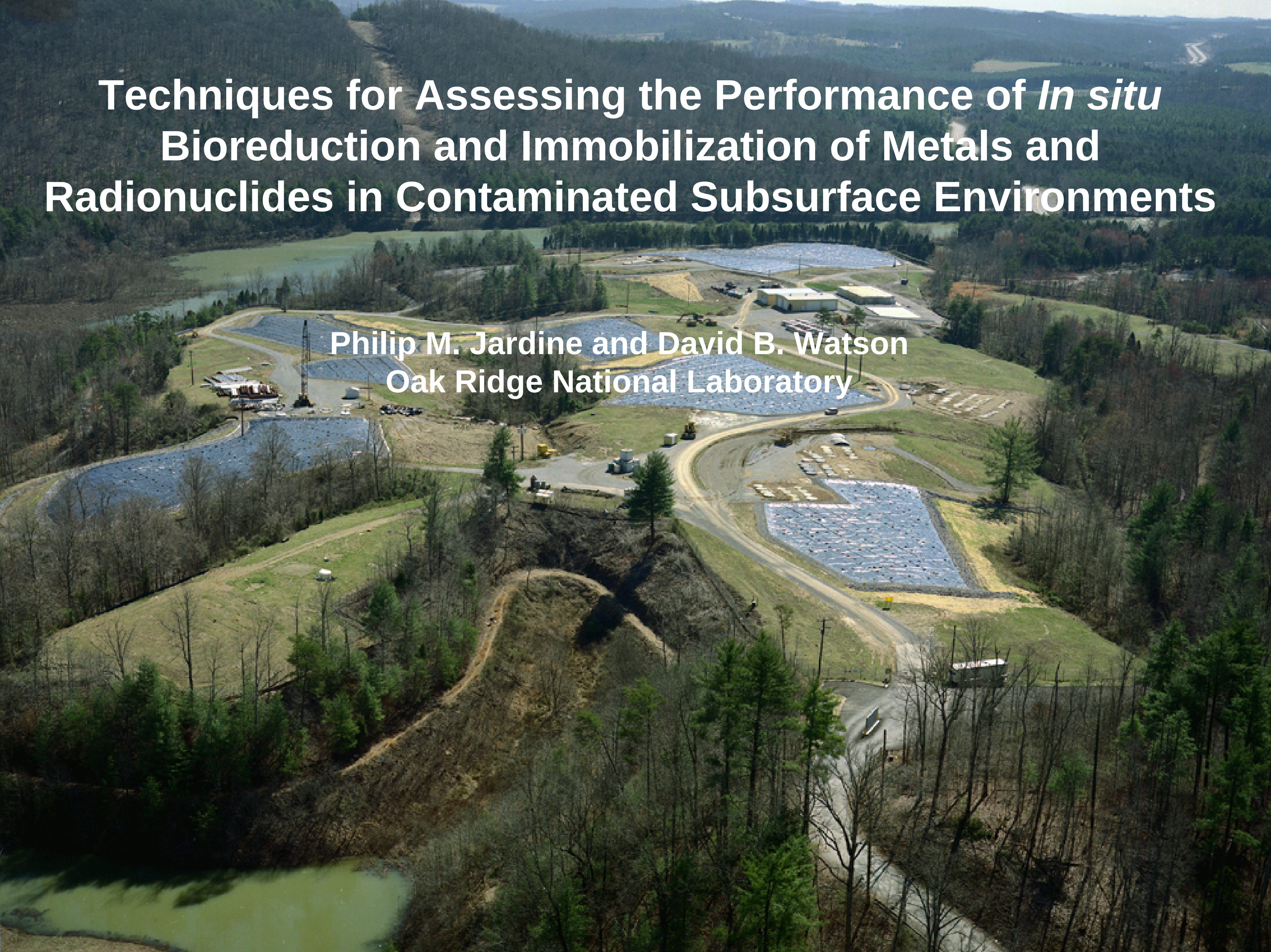
Techniques for Assessing the Performance of *In situ* Bioreduction and Immobilization of Metals and Radionuclides in Contaminated Subsurface Environments

Philip M. Jardine and David B. Watson
Oak Ridge National Laboratory



Presentation outline

Contaminant fate and transport problems in humid and semi-arid regimes

Efforts to immobilize metals and radionuclides *in situ* via bioremediation

Techniques for assessing the performance of i*n situ* bioreduction and immobilization of metals and radionuclides

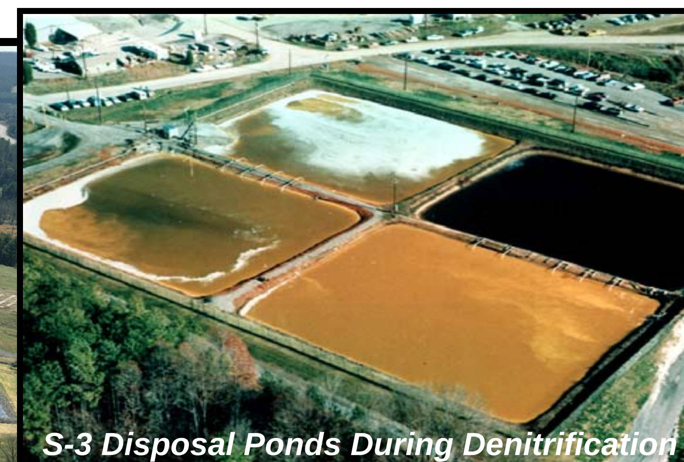
- **In situ solution and solid phase monitoring**
- **In situ and laboratory microbial community analysis**
- **Noninvasive geophysical methods**
- **Solid phase speciation via high resolution spectroscopy**

Subsurface contaminant problems in humid regimes

Research is driven by contaminant transport issues at the meter to kilometer scale. Many DOE facilities have literally thousands of unlined pits and trenches filled with low- and high-level radioactive waste. Unlined surface impoundments were used to dispose of acidic nitrate and U-bearing waste at rates of 10 million liters / year for several decades.

Large annual rainfall inputs in humid regimes have resulted in a huge secondary contaminant source where radionuclides have been disseminated across vast subsurface environments.

Historical remediation has targeted “hot-spots” with *in situ* and *ex situ* treatment of high-risk exit pathways (e.g. preferential flow zones, seeps).



S-3 Disposal Ponds During Denitrification

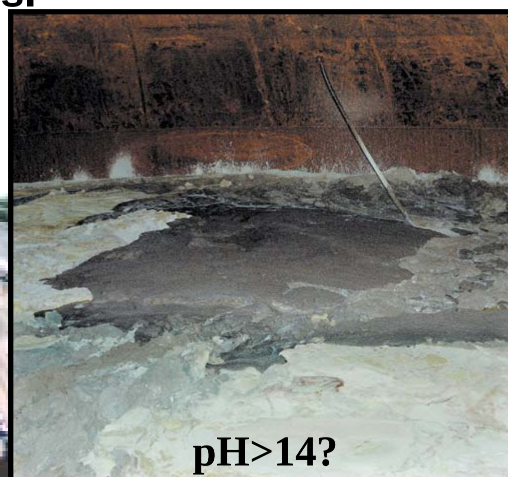
Subsurface contaminant problems in semi arid regimes

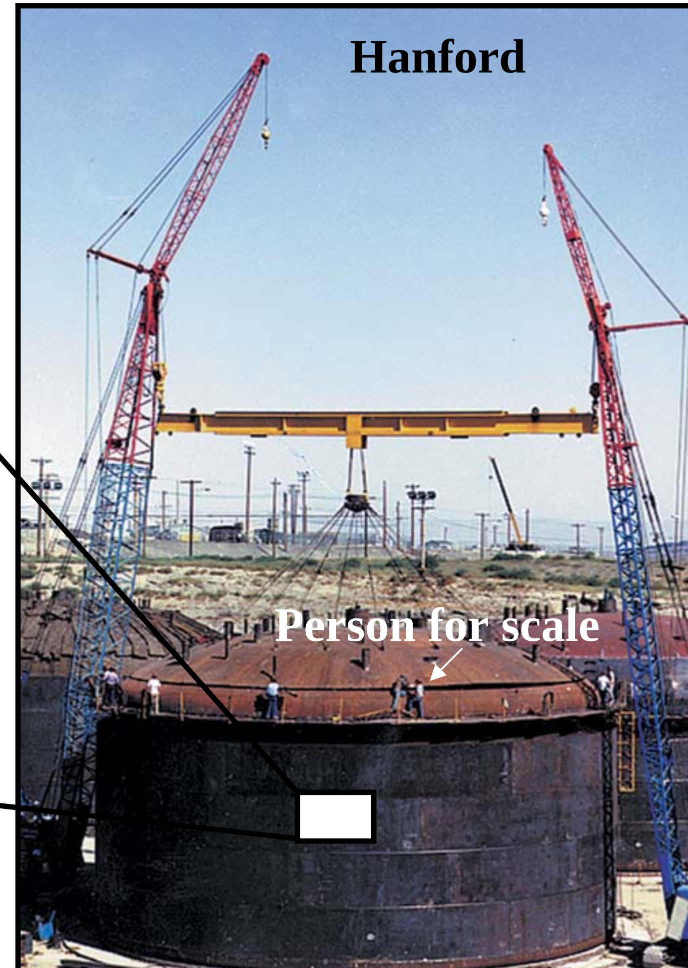
Research is again driven by contaminant transport issues at the meter to kilometer scale.

Hundreds of multi-million gallon below-ground storage tanks filled with high-level radioactive waste. Many have leaked and have created an artificial recharge scenario allowing contaminants to migrate through an otherwise semi-arid vadose zone.

Uncertain as to whether groundwater contaminants migrated through the vadose zone or are an artifact of unlined monitoring wells.

Leakage has created a large secondary source whose long-term stability is uncertain

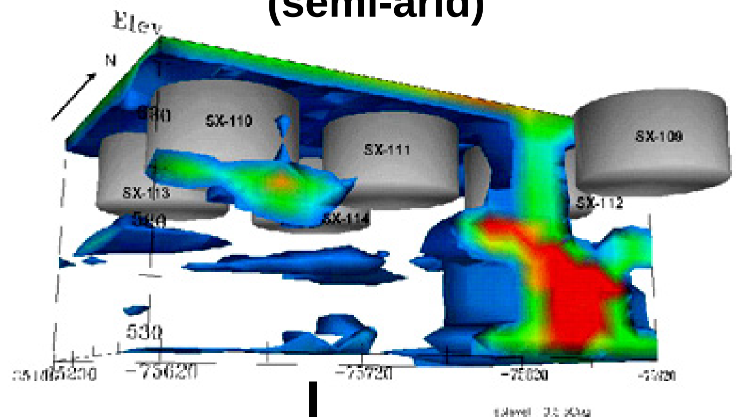




The scope of the problem is massive

ORNL Waste Area Groupings (humid)

Hanford Tank Farms (semi-arid)



Remediation Dilemma for Secondary Sources

- **Large scale *in situ* treatment of contamination in the soil and rock matrix difficult if not impossible.**
  - **No feasible removal or immobilization technologies are immediately available for large volumes of contaminated subsurface saprolites, bedrock, groundwater.**
  - **Sites have often resorted to capping which typically does <u>not</u> "immobilize" contaminants in humid regimes.**
  - **Natural processes for immobilizing contaminants.**
    - **Natural physical attenuation via diffusion into high porosity, low permeability matrix.**
    - **Natural chemical attenuation via sorption, redox transformation, degradation, dissociation, and precipitation reactions.**
    - → **Bioremediation and immobilization *in situ*.**

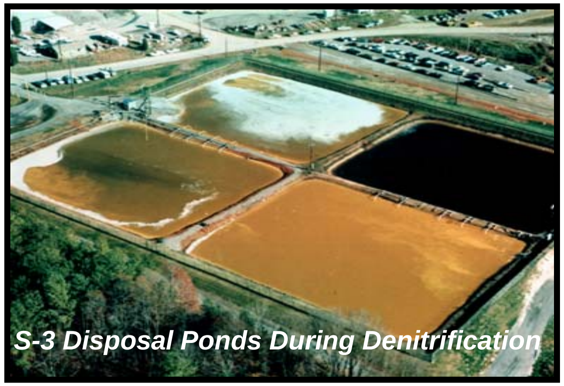
Constructing a cap over waste trenches at ORNL

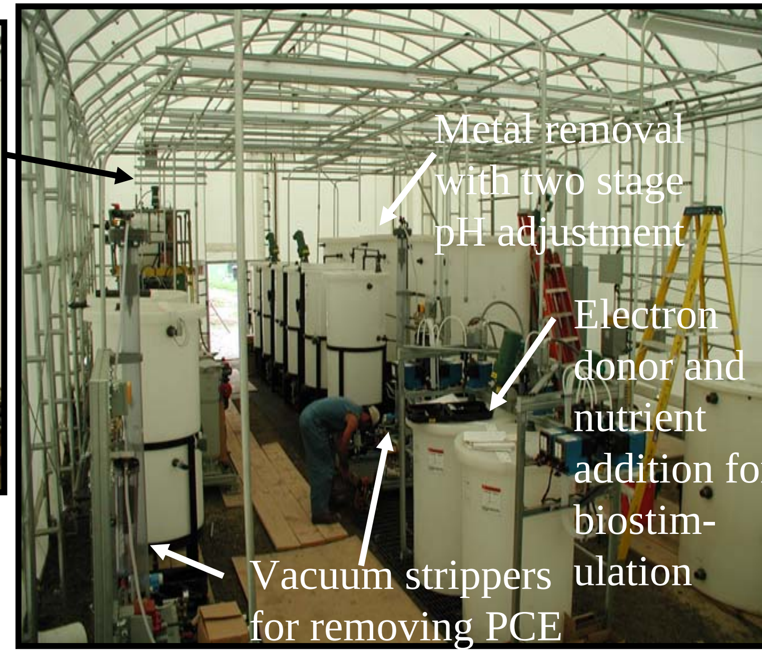
Efforts to immobilize metals and radionuclides *in situ* via bioremediation

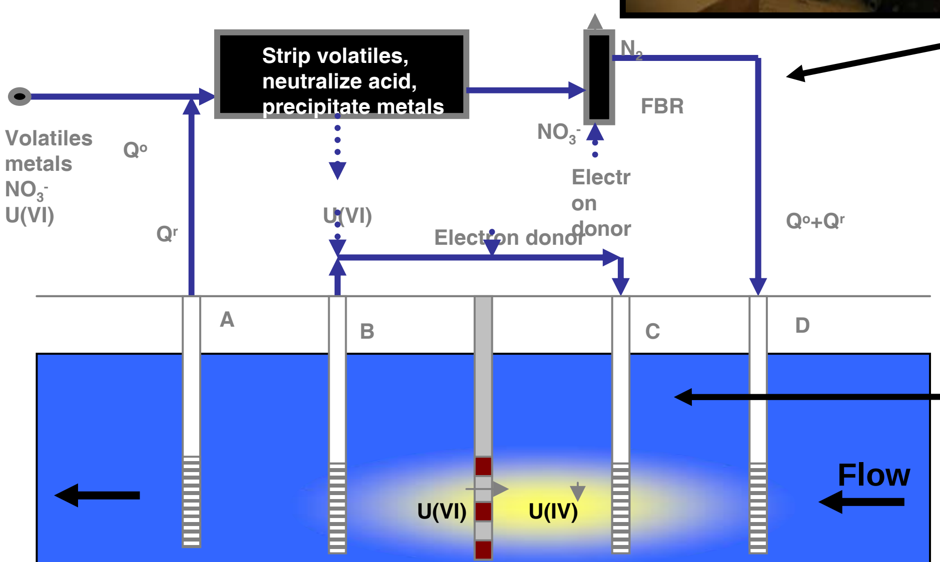
Biocage designed to intercept nitrate and uranium plumes with *in situ* immobilization via bioreduction at ORNL

In situ U(VI) bioreduction and immobilization

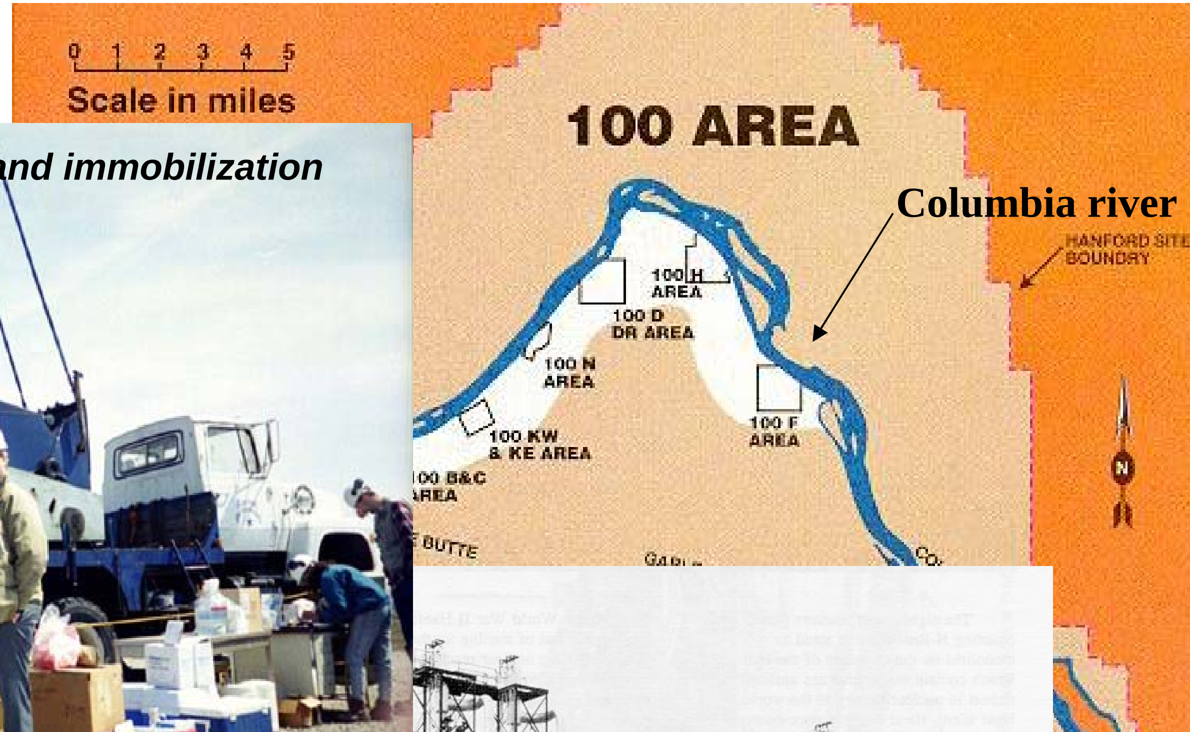
Near-source groundwater processing setup



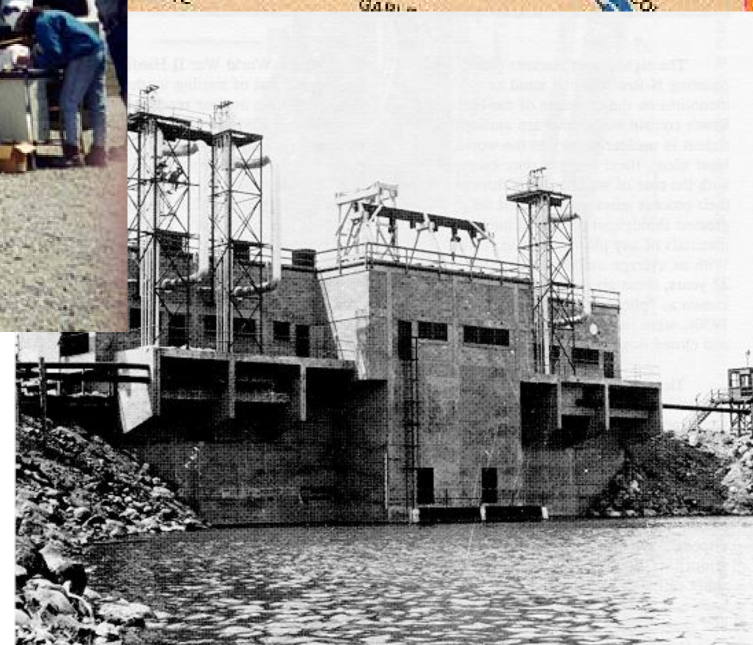




In situ immobilization of Cr(VI) via bioreduction at Hanford



In situ Cr(VI) bioreduction and immobilization



Reduction of mobile Cr(VI) to sparingly soluble Cr(III)

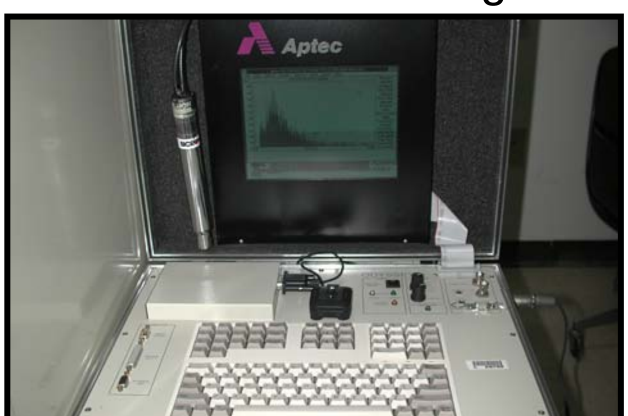
Techniques for assessing the performance of i*n situ* bioreduction and immobilization of metals and radionuclides

In situ solution / solid phase monitoring

In situ groundwater / solid phase contaminant analysis

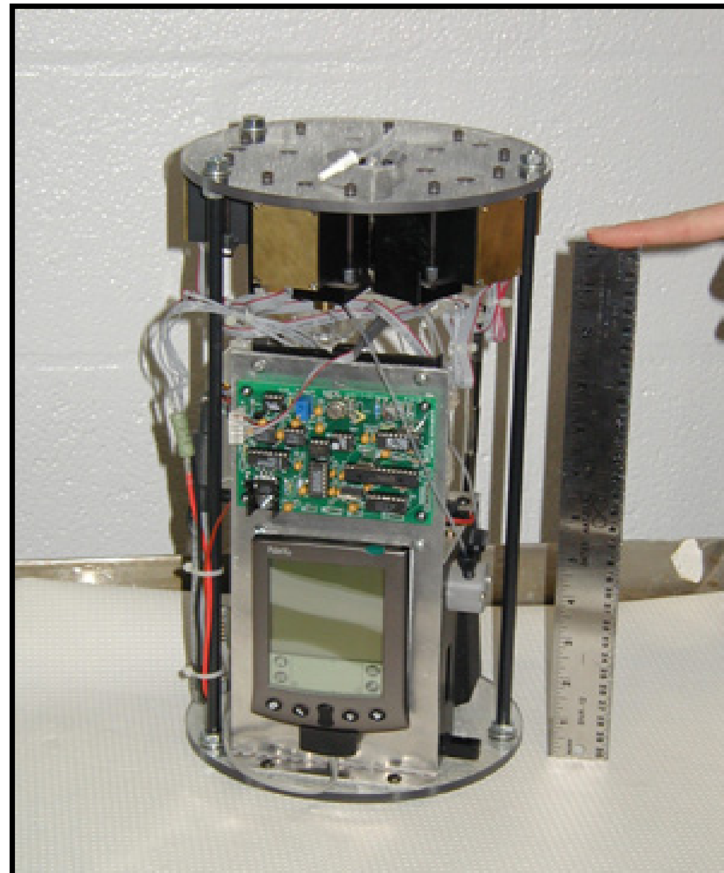
Flow-through chemiluminescence sensor for hexavalent chromium

NaI detector for in situ gamma



Field portable immunoassay biosensor developed for detection of U *in situ*

(Blake of Tulane University)



Groundwater geochemical monitoring

Continuous dissolved oxygen monitoring

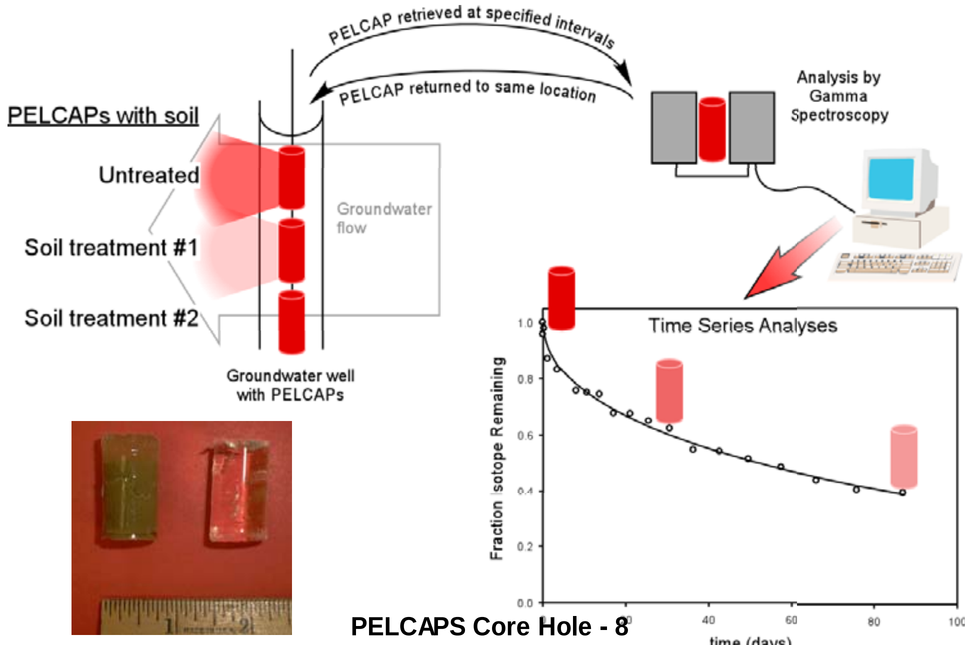
Analysis of redox couples (e.g. Fe(II)/Fe(III), S^{2-}/SO_4^{2-})

Monitor for the intrusion of oxidants and competing electron acceptors (e.g. NO_3^-)

In situ solid phase contaminant analysis

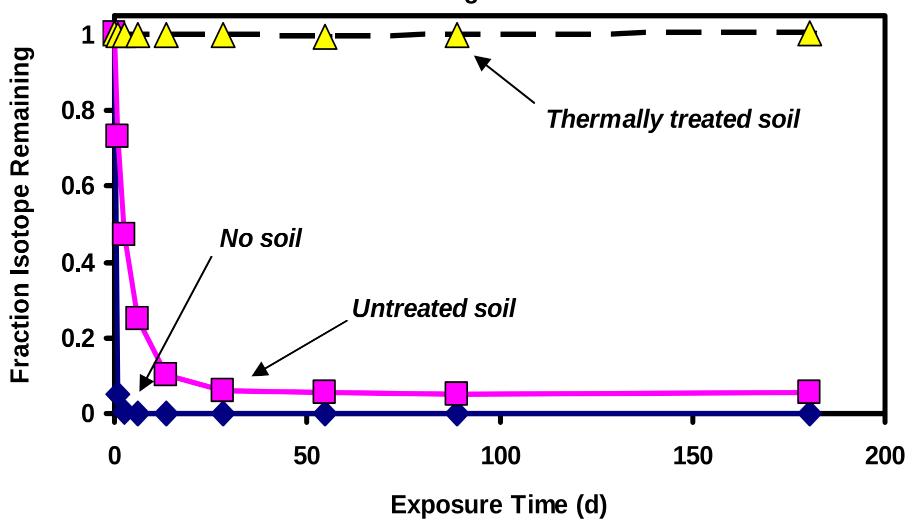
Nondestructive In Situ Quantification of Contaminant Immobilization

- **Permeable Environmental Leaching Capsules (PELCAPs)**
- **Nondestructive measurement of the amount of immobilized contaminant in a soil thereby avoiding the necessity for repeated, costly, and destructive soil sampling.**
- **Direct comparison of several immobilization treatments, including a no-treatment control, under identical field conditions within the same well.**
- **Internal PELCAP leaching calibration relative to specific reference tracers (^{233}U) that have predictable known environmental leaching behaviors. U(VI) would be mobile, U(IV) would be immobile.**
- **The immobilized contaminant is monitored directly in the soil via a gamma-emitting radioisotope tracer.**
- **Technique is applicable to many inorganic and radioactive elements (e.g., Cr, Cd, As, Pb, Hg, U, Tc, and Pu).**



PELCAPS Core Hole - 8

^{85}Sr Leaching Behavior

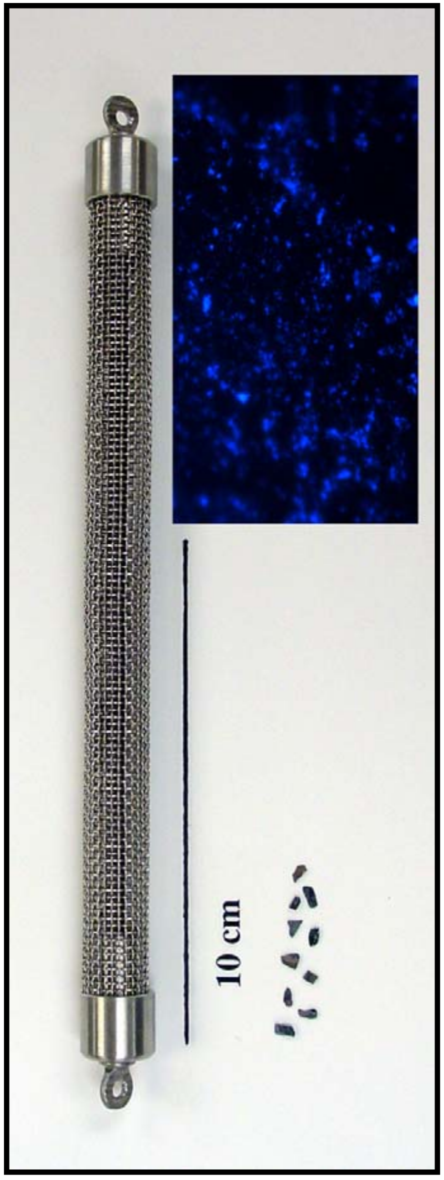


(Brooks of ORNL)

In situ and laboratory microbial community analysis

(Making sure that the groundwater conditions are conducive to bioreduction)

“Bug traps”



Coupons, or “bug traps,” for rapidly assessing *in situ* microbial activity.

Various material such as Fe-oxides and indigenous sediments used for colonization.

Rapid assessment of microbial community dynamics as a function of space and time.

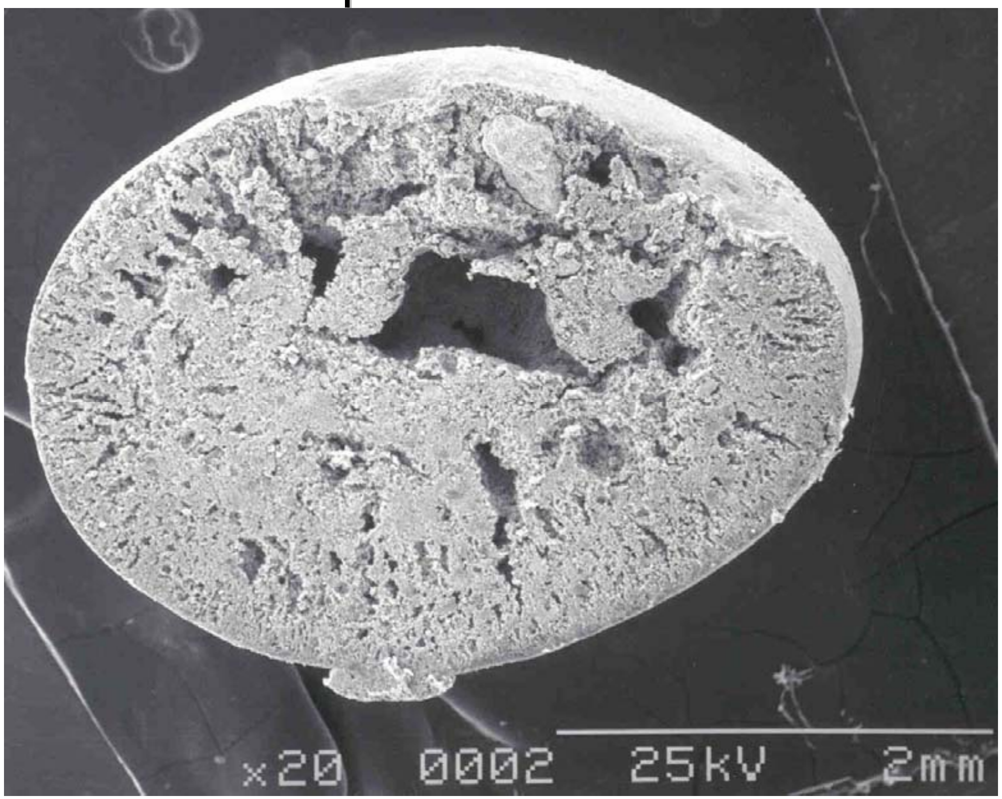
Provides evidence that the correct organisms remain active in the biostimulated zone.

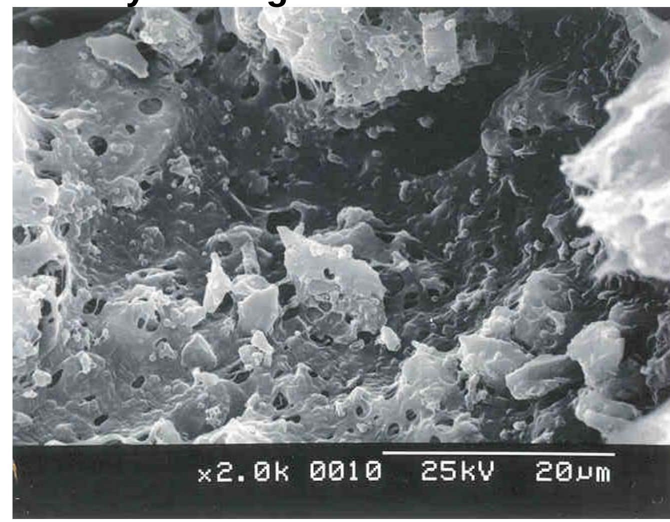
(Cummings / Geesey of INEEL)

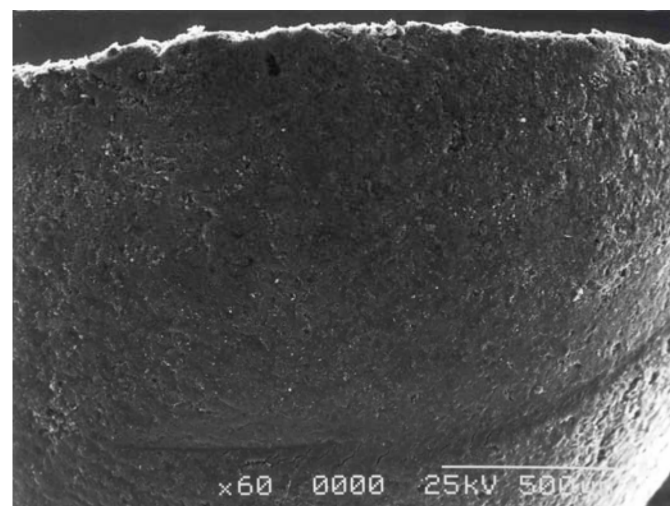
“Bio-Traps”

2-3 mm in diameter
25 % Nomex, 75% PAC
74% porosity
600 m^2 of surface area/g
Surrounded by ultrafiltration-like membrane with 1-10 micron holes
Autoclavable
Cleaned of fossil biomarkers by heating to 300°C

SEM of Bio-Sep® Beads







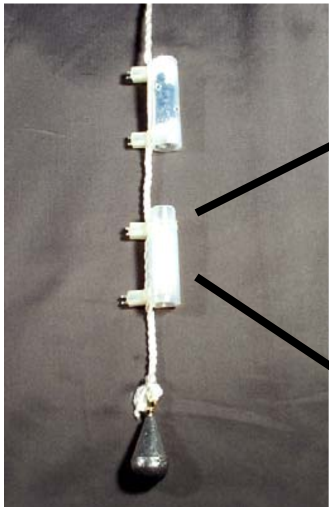
Biofilms Form Rapidly in Bio-Sep® Beads

(Peacock and White, Univ. Tenn)

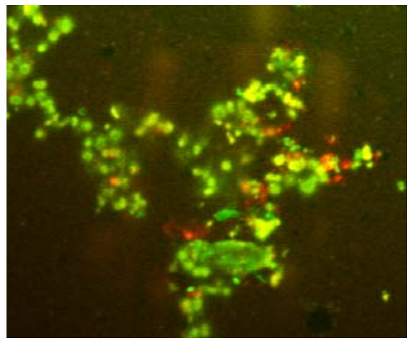
Down-well “bio-trap” coupons for enhanced microbial monitoring

(Peacock and White, Univ. Tenn)

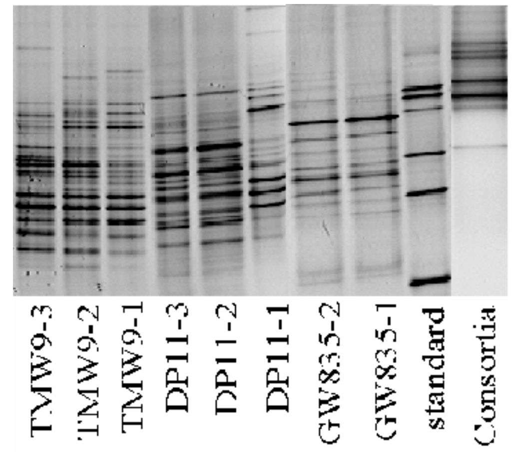
Traps



Colonized Surface



DGGE Profiles of 16S rDNA



Rapid and efficient sampling of biofilms

Biofilm community structure is more indicative of *in situ* microbial ecology than samples of planktonic organisms

Rapid and efficient prediction of the effects of amendments on *in situ* microbial ecology

Integrated response over time is better than “grab samples”

DNA Microarrays

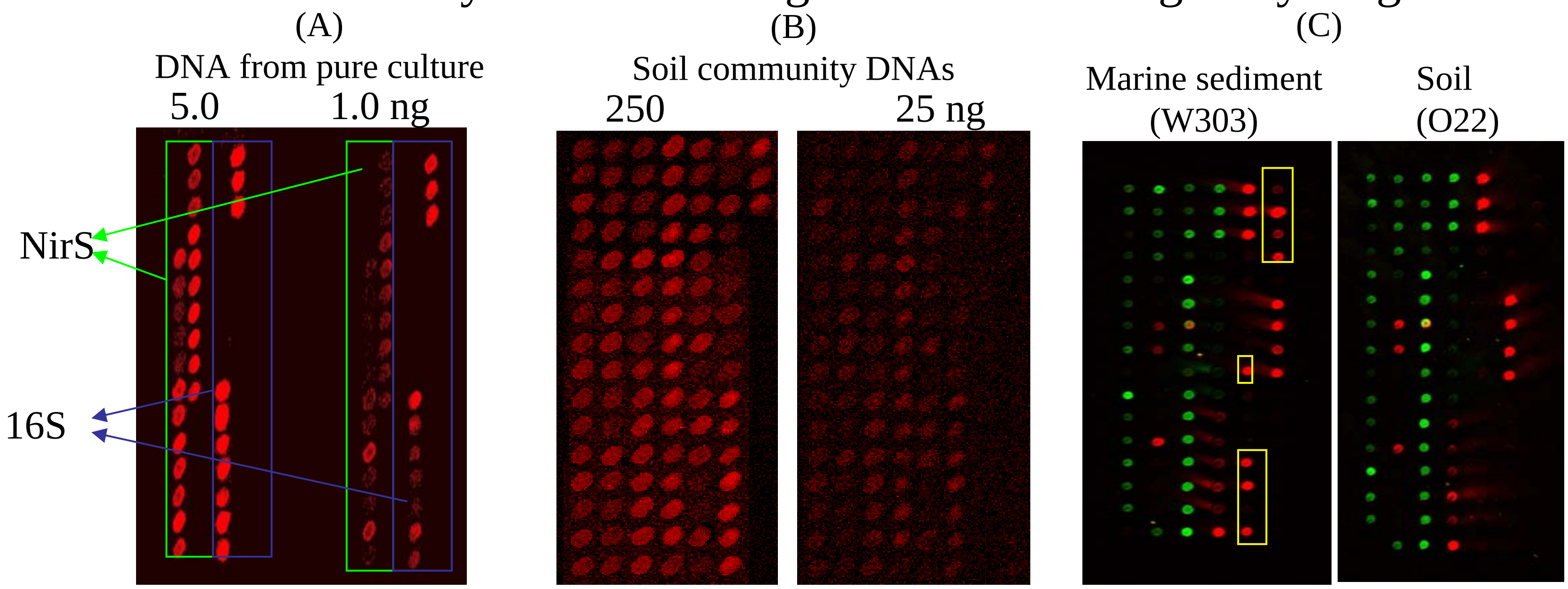
Rapid method to assess shifts in microbial community structure via gene detection and expression.

Indirect detection of activity - presence of genes (DNA)

Direct measurement of activity - expression of genes (mRNA)

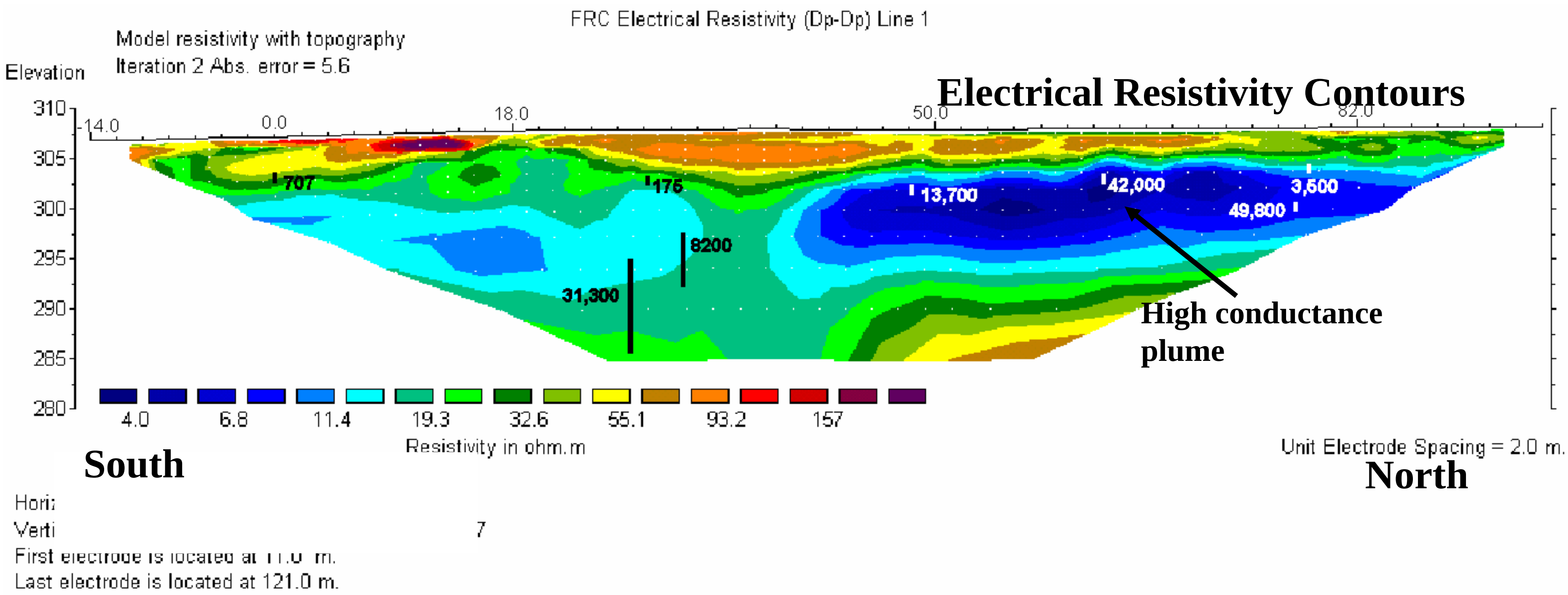
An increase in the quantity of a given gene (DNA) may indicate an increase in the numbers of the source organism. RNA would be a more direct measurement of activity but is more difficult to extract from environmental samples

DNA Microarrays for monitoring Bacteria in Nitrogen Cycling



Non- and semi-invasive geophysical methods

Electrical Resistivity



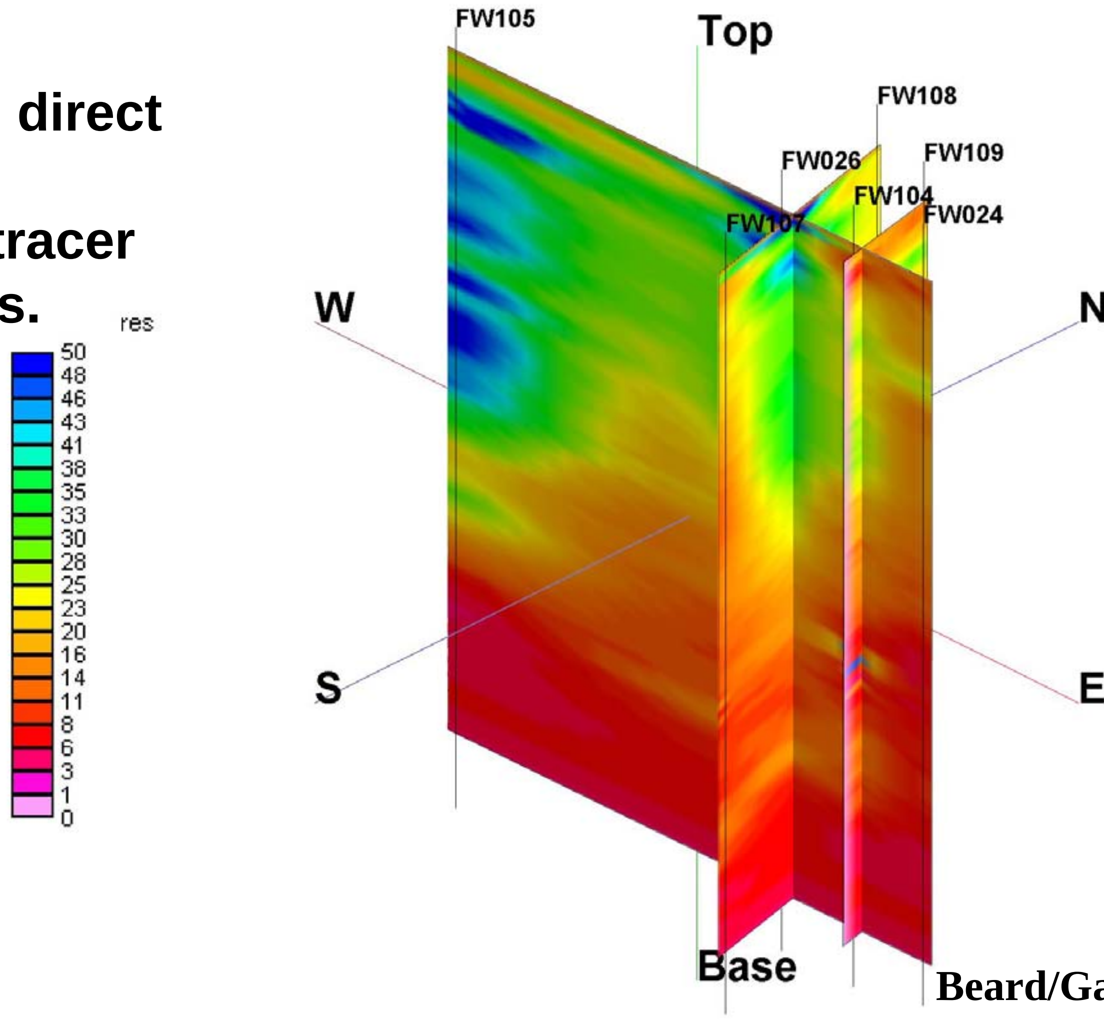
- Surface based geophysics used to identify probable areas of contaminant transport
- Electrical resistivity: light to dark blue = high ionic strength
- Monitor success or failure of biomanipulation by tracking conductivity of plume (e.g. nitrate reduction).

Doll, ORNL

Electromagnetic Induction Logging

Spatial and temporal plume mapping during manipulation.

Complements direct groundwater geochemical tracer measurements.

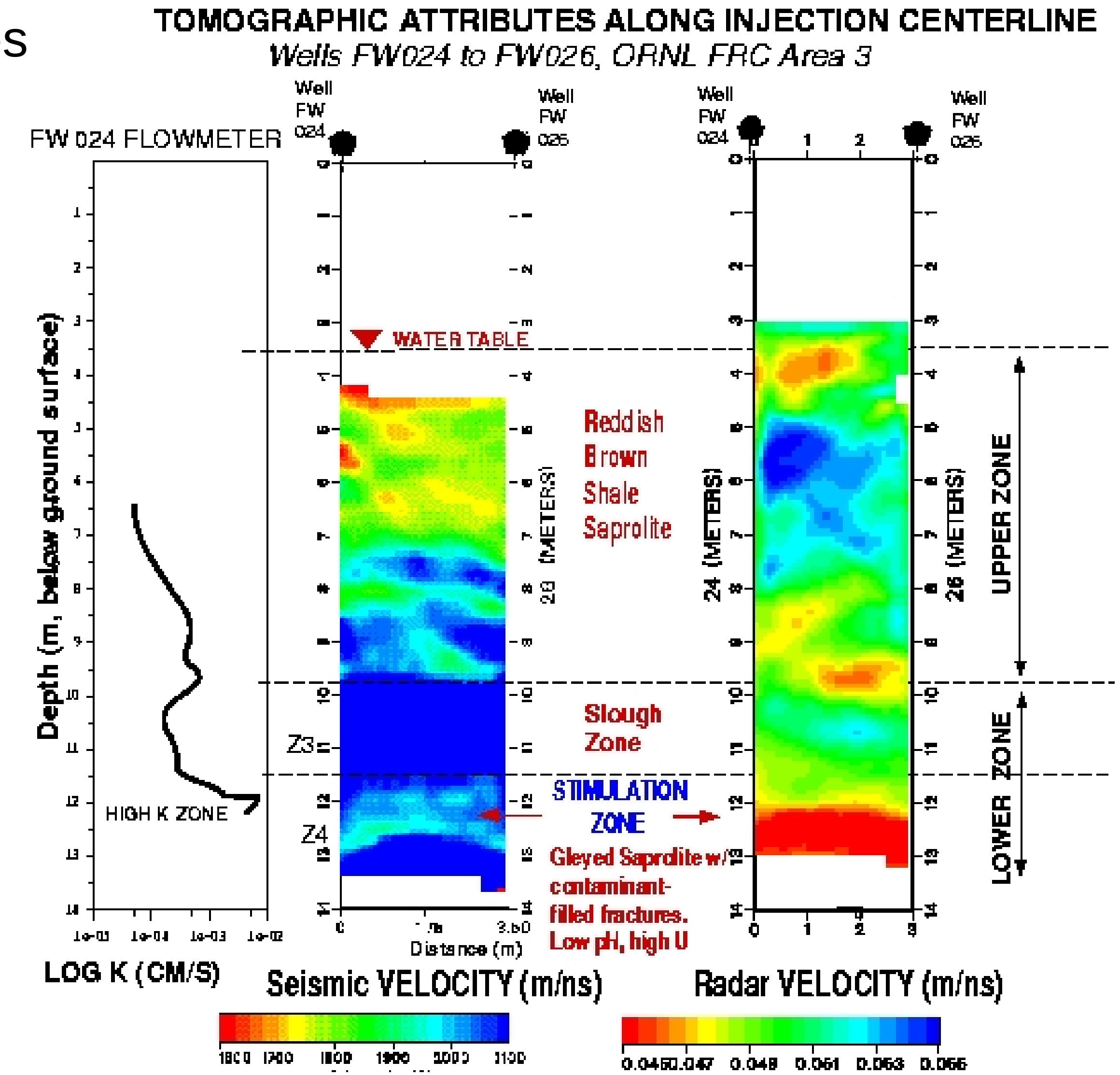


Beard/Gamey/Doll, 2003

Seismic and Radar Tomography

Mapping subsurface material heterogeneities using cross-borehole techniques

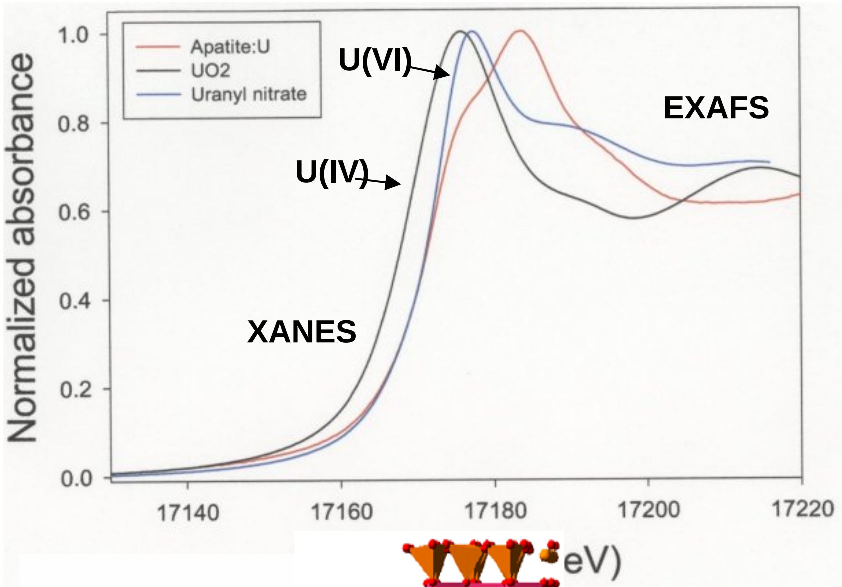
Potential use for assessing sustained bioreduction of metals and radionuclides

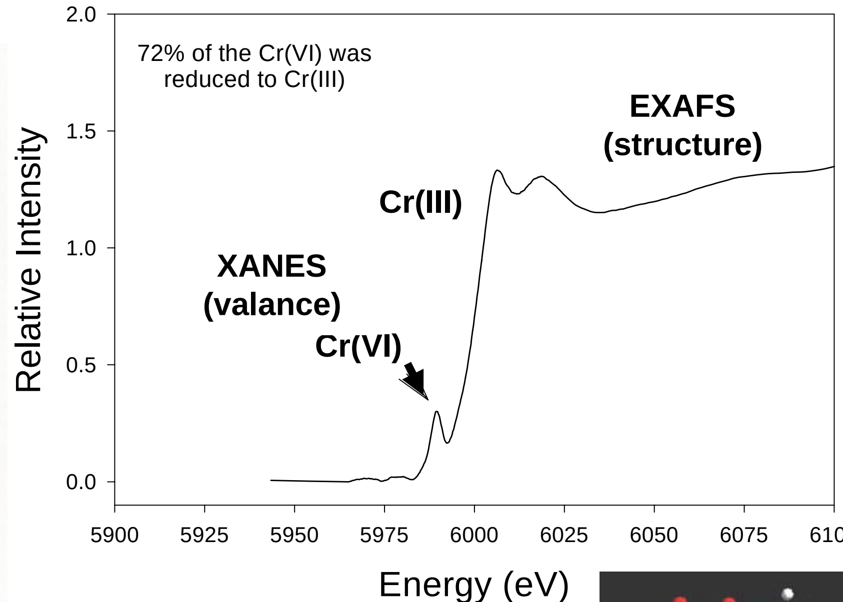


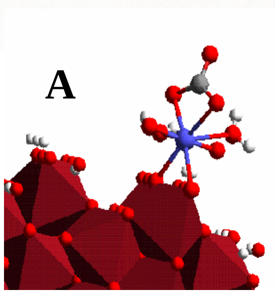
Hubbard et al., LBNL

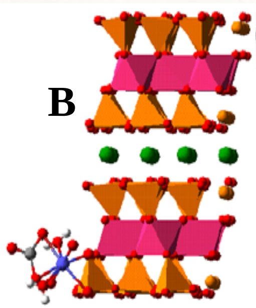
Solid phase speciation using high resolution spectroscopy

X-ray absorption spectroscopy



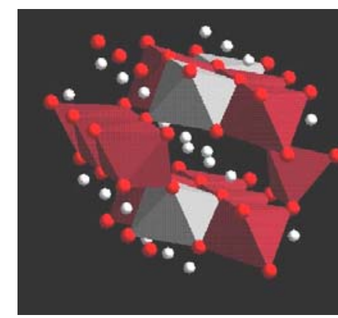






U-CO_3 complexes on (A) Fe-oxides and (B) 2:1 layered silicates.

Cr(VI) reduction to Cr(III) with subsequent formation of sparingly soluble Cr-hydroxide



Quantify valance state and chemical environment of contaminant species and various soil solid phases (e.g. Fe-oxides).

Indigenous solid phase is used (no alteration of subsurface media)

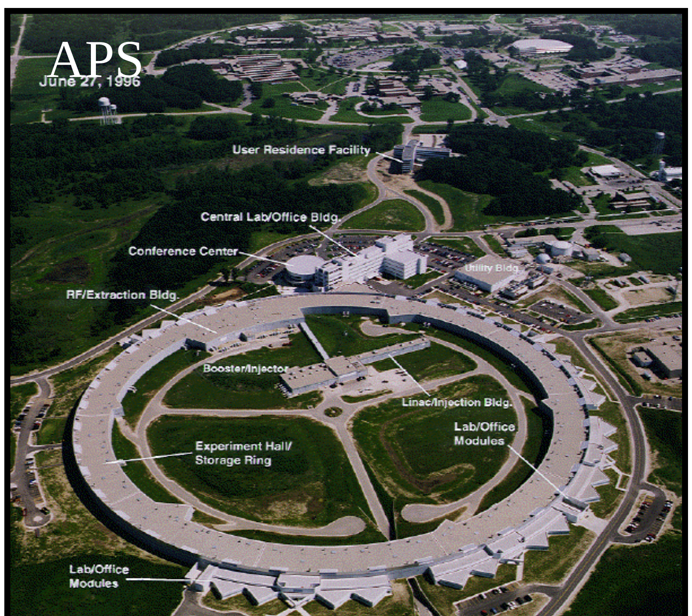
Can be coupled with x-ray tomography to assess mechanism of metal reduction

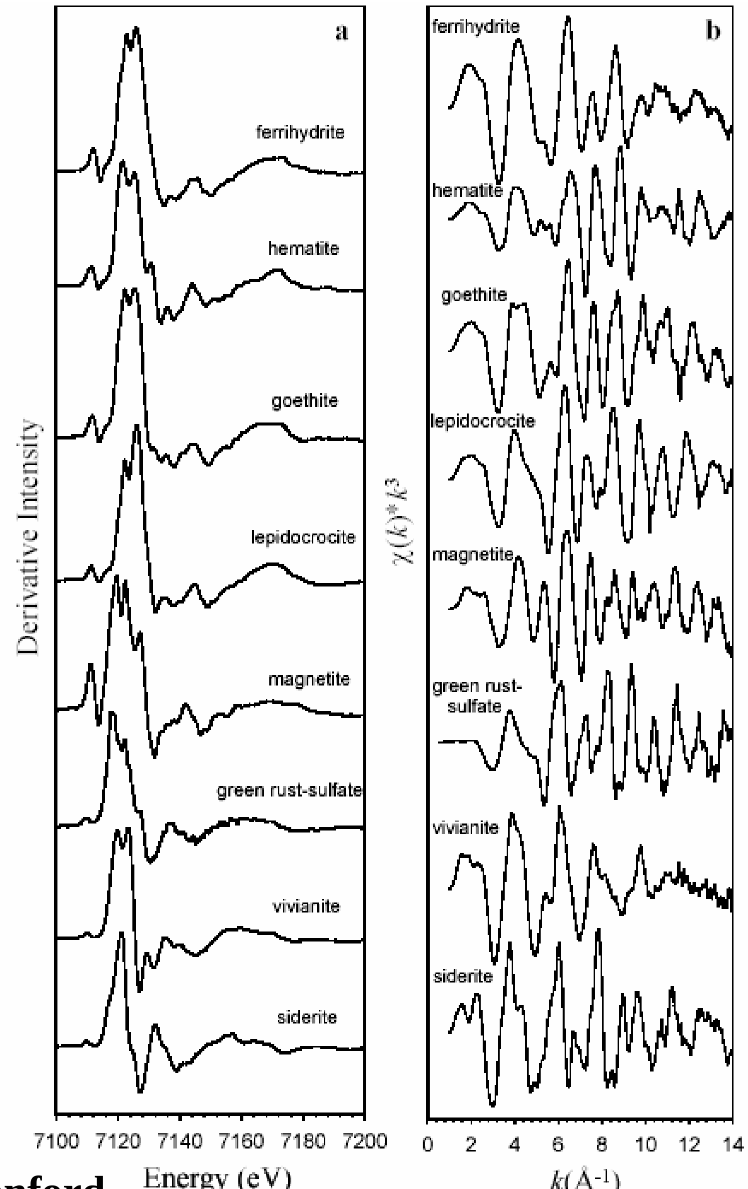
High-resolution spectroscopy for quantify reactive minerals in soils

Extended X-ray Absorption Fine Structure (XAFS) used to quantify the Fe-oxide mineralogy in heterogeneous samples from the FRC.

Quantifying biogenic Fe products and changes in mineralogy during biostimulation.

Information on chemical state of competing electron acceptors important towards knowing likelihood of sustained contaminant reduction.





Fendorf, Stanford

Mossbauer spectroscopy

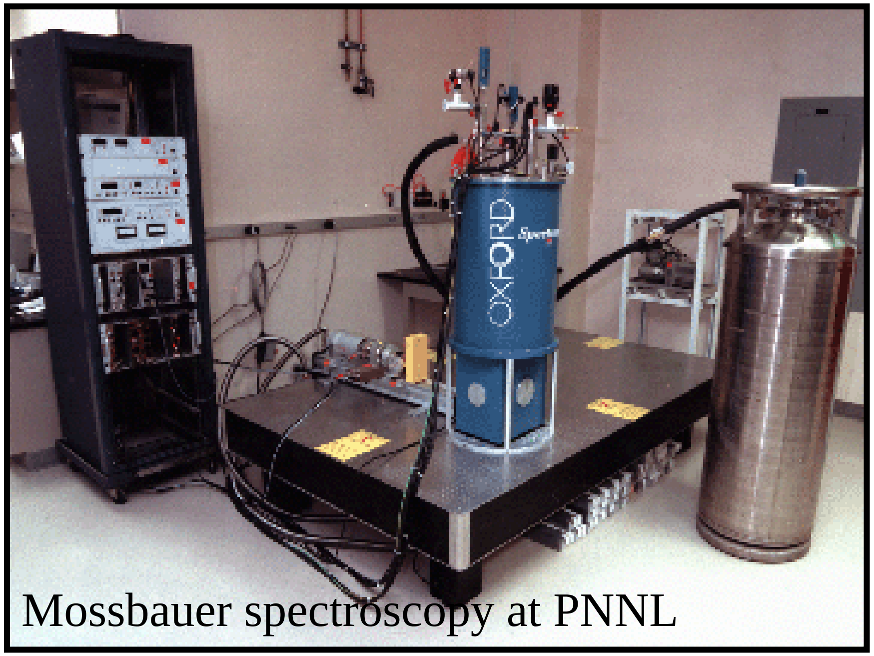
Characterizing the role of biogenic Fe(II) on contaminant bioreduction

Mossbauer used to quantity the types, amounts, and distributions of various Fe-bearing minerals and oxides in heterogeneous FRC background and contaminated samples.

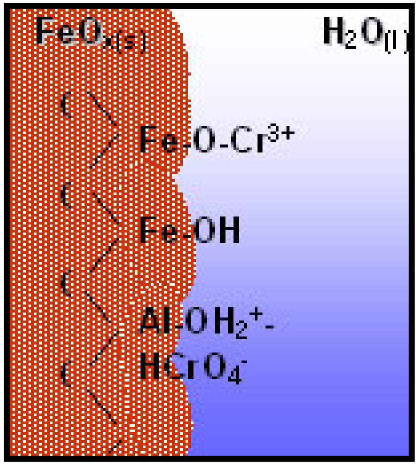
Quantify changes in Fe mineralogy following in situ biostimulation using various electron donors.

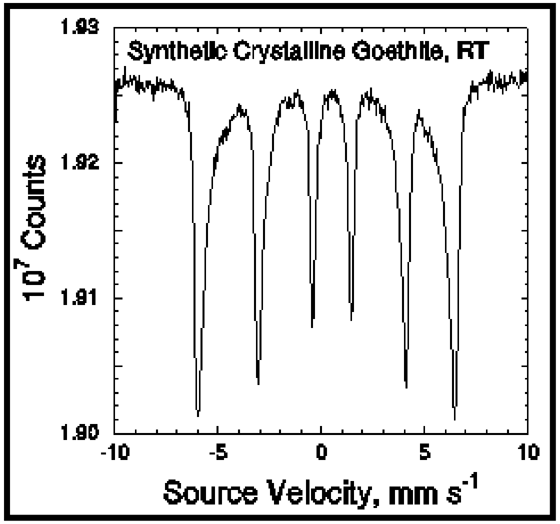
Quantify mechanisms of biogenic Fe(II) reactivity with the solid phase and its influence on the rate of contaminant bioreduction.

Zachara, PNNL



Mossbauer spectroscopy at PNNL





Conclusions

Performance assessment of in situ biostimulation strategies will require detailed monitoring of coupled hydrological, geochemical, and microbial processes.

Knowledge of the processes controlling bioreduction and metal immobilization is critical since competing terminal electrons acceptors and the intrusion of oxidants can impede or reverse the immobilization process.

Knowledge of the contaminant speciation and chemical environment will enhance the opportunity towards maintaining sustained bioreduction and metal immobilization.