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Evaluating the Efficacy of Uranium Bioremediation in the Subsurface: Technical Bases and Performance Indicators

Letter Report to the
Nuclear Regulatory Commission

P.E. Long
S.B. Yabusaki

January 2007

Hydrology Group
Natural Resources Division
Environmental Technology Directorate
Pacific Northwest National Laboratory



Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Acknowledgments

Preparation of this document was funded by the U.S. Nuclear Regulatory Commission, Research Division, Thomas Nicholson, Manager. Our research in uranium bioremediation at the Rifle site is funded by the U.S. Department of Energy, Office of Science, Biological and Environmental Research, Environmental and Remediation Sciences Program. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC05-76RLO 1830.

We thank Ken Krupka, Pacific Northwest National Laboratory; Susan Hubbard, Lawrence Berkeley National Laboratory; and Aaron Peacock, Haley & Aldrich, Inc. for their reviews of this document.

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Acronyms and Abbreviations

Organizational Acronyms

BER	Office of Biological and Environmental Research in DOE/SC
DOE	U.S. Department of Energy
DTW	Depth to water
EPA	U.S. Environmental Protection Agency
ERSD	Environmental Remediation Sciences Division of DOE/SC/BER
ERSP	Environmental Remediation Sciences Program administered by DOE/SC/BER/ERSD
NABIR	Natural and Accelerated Bioremediation Research; program superseded by Environmental Remediation Sciences Program
PNNL	Pacific Northwest National Laboratory
SC	Office of Science in the DOE
UMTRA	Uranium Mill Tailings Remedial Action program (DOE)

Terminology

16S rRNA clone library	technique to identify microorganism phylogeny by comparison to known gene sequences
Ca	calcium
DGGE	denaturing gradient gel electrophoresis; gene sequence comparison technique
DNA	deoxyribonucleic acid
DO	dissolved oxygen
Fe	iron
Fe(II)	iron in the +2 oxidation state
Fe(III)	iron in the +3 oxidation state
GW	groundwater
ISL	<i>in situ</i> leaching
MCL	maximum contaminant level; drinking water standard established by the U.S. Environmental Protection Agency
MLS	multi-level sampler
Mn	manganese
Mn(II)	manganese in the +2 oxidation state
Mn(IV)	manganese in the +4 oxidation state
mRNA	messenger ribonucleic acid
O ₂	oxygen gas
ORP	oxidation reduction potential

pH	negative log ₁₀ of the hydrogen ion activity
PLFA	phospholipid fatty acid; analysis for microbial community structure using fatty acid biomarkers
rDNA	ribosomal DNA
RNA	ribonucleic acid
rRNA	ribosomal RNA
S	sulfur
<i>Sp.</i>	biological species
TD	total depth
TEAP	terminal electron accepting process
U	uranium
U(IV)	uranium in the +4 oxidation state
U(VI)	uranium in the +6 oxidation state

1.0 Introduction

The purpose of this letter report is to identify performance indicators for *in situ* engineered bioremediation of subsurface uranium (U) contamination. In this report, a performance indicator is a measurable quantity that contributes to the confirmation and/or assessment of a site conceptual model for engineered processes.

This report focuses on *in situ* treatment of groundwater by biostimulation of extant microbial populations (see <http://www.lbl.gov/ERSP/generalinfo/primersguides.html> for background information on bioremediation of metals and radionuclides). The treatment process involves amendment of the subsurface with an electron donor such as acetate, lactate, ethanol or other organic compound such that *in situ* microorganisms mediate the reduction of U(VI) to less mobile, sparingly soluble U(IV). Dissolved U(VI) precipitates as uraninite (ideally U^{IV}O₂) or other insoluble U(IV) phases. Uranium is thus immobilized in place by reduction processes, but can be subject to reoxidation that may remobilize the reduced uranium. This concept was first proposed as a possible field-scale remediation process by Lovley et al. (1991). Additional background on uranium biogeochemistry can be found in Burns (1999a) with the chapters on geomicrobiology (Suzuki and Banfield, 1999) and *in situ* remediation (Abdelouas et al., 1999b) of particular relevance. Related processes include augmenting the extant subsurface microbial populations, adding electron acceptors, and introducing chemically reducing materials such as zero-valent Fe. While metrics for such processes may be similar to those for *in situ* biostimulation, these related processes are not directly in the scope of this letter report.

The field of subsurface bioremediation has many facets and is rapidly evolving. This report, however, is a limited effort targeting an overview of the underlying scientific basis for immobilization of U(VI) in groundwater via *in situ* biostimulation, and recommendations for the monitoring of performance indicators. It is based primarily on the authors' ongoing research in this field and is not intended to be a comprehensively detailed review of bioremediation technologies, uranium geomicrobiology and geochemistry, or field sampling and characterization methods.

The organization of this report is based on a staged approach to full-scale field deployment that begins with a pre-existing characterization of the processes controlling uranium mobility and transport that leads to a credible conceptual model for future uranium behavior. Bench-scale studies are used to establish the proof-of-principle viability of uranium bioremediation and support the design of a field deployment strategy (Komlos and Jaffe, 2004; Long et al., 2005; Lovley et al., 1993). A pilot-scale implementation of the uranium bioremediation strategy is designed to test understanding and address uncertainties in the field conditions and behaviors that cannot adequately be addressed by bench-scale studies (Anderson et al., 2003; Vrionis et al., 2005; Yabusaki et al., 2007). The elements of the approach are summarized in Figure 1.1.

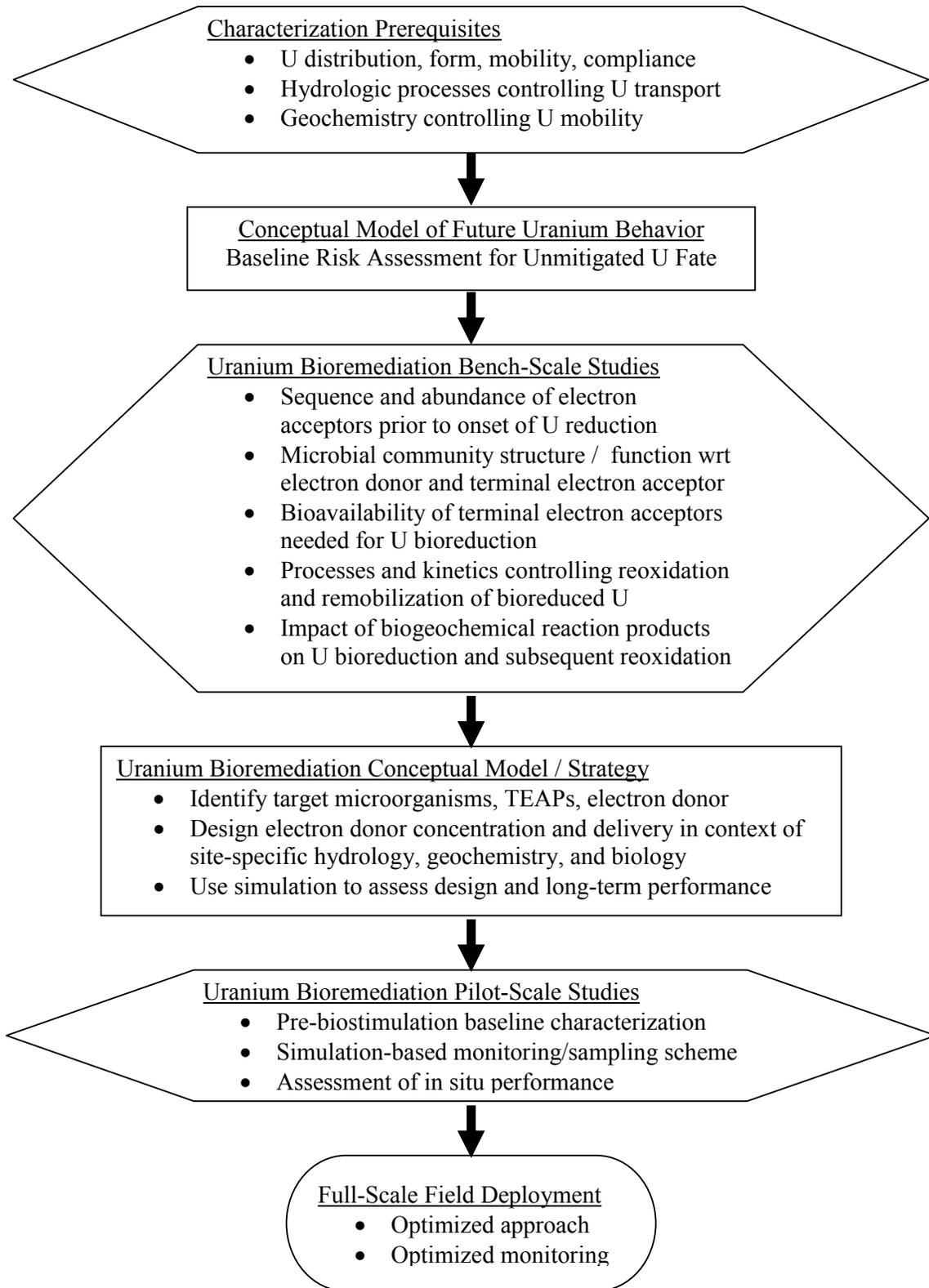


Figure 1.1. Summary of activities leading to full-scale bioremediation deployment in the field. Hexagons represent characterization steps. Rectangles represent analysis and design steps.

2.0 Prerequisites for In Situ Bioremediation of U(VI)

2.1 Characterization of Uranium Contamination

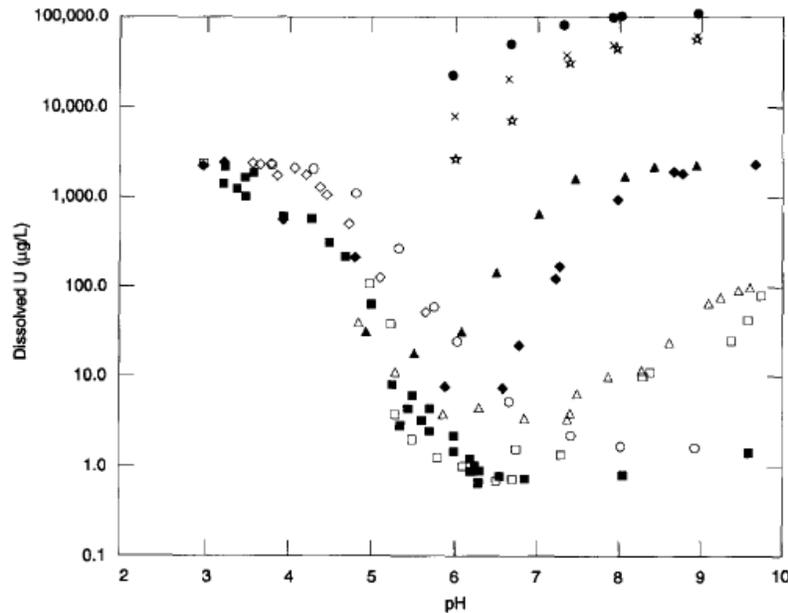
Uranium contamination must be sufficiently characterized in terms of source, mobility, and compliance to support selection of a remedial strategy. Furthermore, and more importantly, the individual elements of this characterization must be reasonably well understood in a systematically holistic context to lead to the identification of bioremediation as a cost-effective solution.

2.1.1 Uranium Inventory

The expectation is that the total uranium inventory is well-characterized in the sense that the contamination history and characterization activities have identified both current and potential future sources. The extent and concentration of uranium sources are critical considerations for the bioremediation deployment strategy. Our experience has been that many groundwater uranium contamination problems are associated with primary sources and/or secondary accumulations in the vadose zone. In this case, the vadose zone sources may be most active during hydrologic transients: episodic infiltration events; and diurnal, seasonal, and episodic water table events. Typically low recharge rates in western arid environments in conjunction with uranium retardation may preclude significant contribution from recharge-driven vadose zone uranium transport. Moreover, cyclical water level fluctuations of relatively small magnitude tend to deplete a stable subsurface uranium source in the saturated zone over time frames of decades or more. However, episodic events of extended duration and/or extreme magnitude can liberate contaminants from relatively unleached contaminated sediments. For this reason, it might be necessary to consider augmenting bioremediation with technologies (e.g., surface barriers) that limit longer-term, recharge-driven vadose zone uranium transport.

2.1.2 Uranium Form, Concentration, and Mobility

Uranium has a broad range of mobility that is dependent on the ambient water chemistry and the surface reactivity of the sediments. We assume here that the hexavalent (+6) oxidation state of uranium [U(VI)] is the nominal valence for the bulk of the aqueous uranium species. While the hexavalent form of aqueous uranium is considered to have the most potential for transport, sorption processes for U(VI) are particularly sensitive to pH, carbonate complexation, and aqueous uranium concentration (Curtis et al., 2004; Davis et al., 2006; Davis and Kent, 1990; Davis et al., 2004). Figure 2.1 is taken from Morrison et al. (1995). It shows the changes in aqueous uranium concentrations due to adsorption on amorphous ferric oxyhydroxide are a function of pH and concentrations of dissolved inorganic carbon (i.e., bicarbonate/carbonate), sulfate, nitrate, and U(VI). Particularly noteworthy is the minimum in uranium concentrations at circum-neutral pH conditions.



Set	C(IV)	NO ₃	S(VI)	Initial U(VI)	Fe(OH) ₃
	(mol/L)			(µg/L)	(g/L)
1	0.0	0.1	0.0	2,380	1.0
2	0.001	0.1	0.0	2,380	1.0
3	0.001	0.1	0.0	2,380	1.0
4	0.01	0.1	0.0	2,380	1.0
5	0.0	0.1	0.0	2,380	0.15
6	0.0195	0.1	0.0	2,000	0.52
7	0.0195	0.0	0.07	100,000	1.0
8	0.0	0.0	0.07	2,380	1.0
9	0.0195	0.0	0.07	50,000	1.0
10	0.0195	0.0	0.0	50,000	1.0

Figure 2.1. Dissolved uranium as a function of pH, carbonate, nitrate and sulfate (Morrison et al. 1995)

Typically, the characterization of uranium geochemistry in field samples is done in laboratory studies with contaminated and uncontaminated site sediments. Extraction procedures attempt to classify the uranium pools on sediments in terms of leachability with different extractants (e.g., labile versus nonlabile using carbonate and acid extraction (Davis et al., 2006; Kaplan and Serkiz, 2001). A critical issue is to differentiate the labile uranium from the rest of the sediment-associated uranium. Non-labile uranium may be in the form of 1) sparingly soluble uranium minerals and/or uranium co-precipitated at trace concentrations in one or more of the secondary minerals (e.g., calcite), or 2) uranium that is not easily desorbed under ambient or engineered chemical conditions. Under circum-neutral pH and calcite-controlled carbonate chemistry in western arid sediments, we have seen the (labile) uranium partitioning coefficient, K_d (ml/g), for the less than 2 mm sediment size fraction range from less than 1 (DOE, 1999) to greater than 20 (Qafoku et al., 2005). The geochemistry and ranges of observed K_d values are reviewed in EPA (1999). More mechanistically detailed sorption models are necessary in cases where the temporal and/or spatial variability of the geochemical environment is significant with respect to uranium mobility. In the absence of electrostatic information on mineral surfaces, non-electrostatic surface complexation models have been used to address situations where uranium sorption is controlled by the sorption site density and/or solution chemistry cf. (Davis et al., 2004).

The significance of the uranium concentration is also important from a compliance perspective. The drinking water MCL of 30 µg/L may not be the regulatory compliance criteria for sites that are not drinking water sources. For example, the Old Rifle, Colorado UMTRA site cleanup criteria is 44 µg/L, which is based on the EPA standard for inactive uranium mill tailings sites (EPA, 1998). In any case, negotiated compliance standards relative to the existing contamination levels should play a role in the level of cleanup required and thus, the remediation technology selection.

2.2 Characterization of Relevant Transport Processes and Properties

In addition to the characterization of the uranium source term and geochemistry, an equally important prerequisite to the selection and design of a remediation technology is the characterization of the relevant transport processes and properties that are operative at the site for uranium. The objective here is to develop an understanding of the environmental properties and process dynamics on the site that will control/influence uranium fate.

2.2.1 Hydrologic System Dynamics

Focusing site characterization and assessments on the groundwater system alone may ignore a significant and persistent long-term source from the vadose zone. Even if the vadose zone does not need to be explicitly addressed, hydrologic impacts from natural processes and land-use activities should be considered with respect to recharge and water table fluctuations. A critical issue is the dynamics of the principal transport pathway to compliance points/surfaces, especially in the case of directional changes in the regional and local groundwater flow field.

2.2.1.1 Boundary Conditions

The driving forces for the hydrologic system must be identified and their magnitudes known to be able to identify the various transport pathways and timescales.

Recharge. Spatially and temporally variable (Gee et al., 2002) recharge may be an important hydrologic component for some aquifer systems but must definitely be addressed for the case of uranium mobilization from contaminated vadose zone sediments. This is especially important when a uranium front has already reached the groundwater. If the surface sites for uranium sorption are fully loaded in the system at this point, aqueous uranium will essentially travel through the vadose zone with the infiltrating water.

Recharge is the net result from a competing set of processes (e.g., precipitation, runoff, evaporation, transpiration) that vary with sediment properties, climate, and land use. An inexpensive technique for an integrated estimate of recharge is chloride mass balance (Joshi and Maule, 2000; O'geen et al., 2003; Scanlon, 2000; Scanlon et al., 2003; Scanlon et al., 2006), which is based on concentrations of chloride dissolved in meteoric and pore water and the volume of meteoric water. For point estimates, water fluxmeters work well for sands, while for silts and clays, the operational recharge range is above a few hundred mm/yr (Gee et al., 2002).

Water table fluctuation. Water table fluctuations are important for transferring uranium between the vadose zone and aquifer. In the case where uranium-contaminated sediments are present in the vadose zone just above the average or nominal water table, leaching of uranium by seasonally and/or episodically

rising water levels can result in a source to groundwater that can be significantly larger than recharge-driven uranium transport. Furthermore, water table fluctuation combined with groundwater uranium transport can displace uranium in the lower vadose zone and transport it to down-gradient locations. This can result in a distributed source of vadose zone uranium that is activated by seasonally and/or episodically high water tables. Figure 2.2 illustrates how peak U(VI) and dissolved oxygen (DO) concentrations are correlated with the spring water table peak in the Old Rifle alluvial aquifer.

Another potential consideration for any remedial action based on manipulating the subsurface oxidation-reduction potential (e.g., creating/maintaining chemically reducing conditions) is the presence of a vadose zone oxygen source. This can occur when the gas phase of the vadose zone is in direct communication with atmospheric oxygen at the ground surface. Reoxidation from oxygen diffusing through the water table can inhibit the effectiveness of engineered reducing conditions. This effect can be exacerbated by gas entrapment during water table rise that provides an enhanced pathway for oxygen to dissolve into the aqueous phase. This can be problematic if a significant part of the subsurface uranium inventory is near or above the water table. Figure 2.3A shows the situation in the Old Rifle alluvial aquifer, where a relatively thin layer of elevated DO just below the water table exists in otherwise low- oxygen groundwater. Figure 2.3B shows that the observation is consistent with a dynamic balance of oxygen depletion by microbial activity in the groundwater and diffusion of oxygen into the aquifer through the water table coupled with regional groundwater flow.

Recharge from seasonal and/or episodic flooding can result in changes to the water table, which may have major impacts on uranium fate and transport including impacts to bioreduction. One example is the Gunnison UMTRA site (DOE, 2001) where flood irrigation is practiced on pastures overlying part of the uranium plume at the site. Flood irrigation appears to have created a downward flux of dissolved organic carbon that provided a substrate for the resident microbial consortia to accelerate natural bioreduction of uranium. Depending on the interaction of floodwater with vadose zone and soil materials and the resulting geochemical or microbiological changes, flooding events could either decrease or increase uranium concentrations in a plume. If flooding is expected to occur at a site, it is particularly important to understand in advance its likely impact to the subsurface geochemistry, flow field, and microbial communities and devise a strategy for assessing and mitigating any anticipated increases in uranium concentration.

Piezometric heads. Understanding the driving forces for the groundwater flow field, especially when they are transient in time and spatially complex, is important for predictive purposes. Time series of piezometric heads from an adequate distribution of monitoring wells will usually be necessary to drive a flow model. If such a data collection network does not exist from earlier monitoring, it is relatively easy to equip existing wells with hourly-reading, self-contained water level monitors. In addition, new injection or monitoring wells installed for bioremediation provide opportunities to directly test prior flow models.

2.2.1.2 Vadose Zone Flow and Transport

If the vadose zone is important as a uranium source, characterization must address the material properties controlling flow rates and directions. Characterized parameters include porosity and constants for relationships between capillary pressure, saturation, and hydraulic conductivity (e.g., van Genuchten,

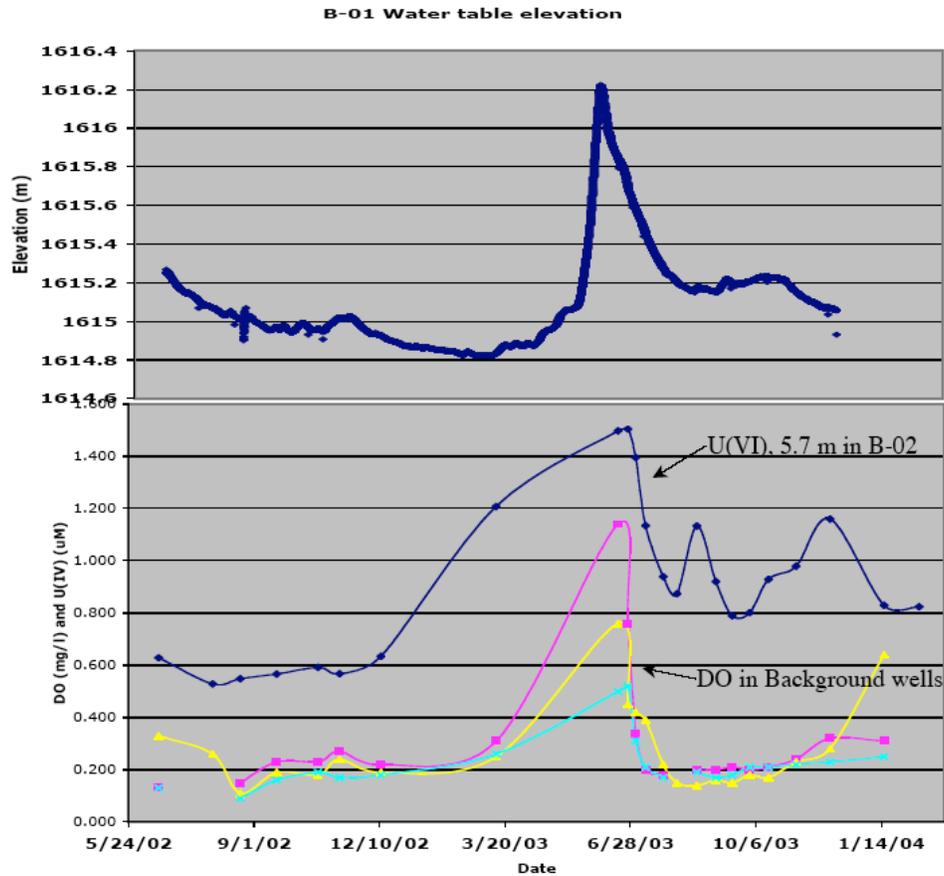


Figure 2.2. Changes in dissolved oxygen and U(VI) concentration with water table rise

Brooks-Corey). Variably saturated flow modeling with these parameters, in the context of pressure head and recharge boundary conditions, will provide the flow and transport framework for analyzing and predicting the vadose zone component of uranium migration. Unsaturated permeability anisotropy created by bedded layers of fine and coarse-grained sediments are particularly important in creating lateral flow in the vadose zone, possibly causing uranium contamination to appear in the groundwater offset from its location of highest concentration in the vadose zone.

2.2.1.3 Saturated Flow Field

The saturated flow field will probably be the principal pathway for uranium transport to a compliance point or surface. Thus, the characterization of hydraulic conductivity and porosity in the context of accurate boundary conditions is critical to the prediction of long-term transport. Key saturated hydrogeologic parameters include hydraulic conductivity, porosity, and dispersivity. Because characterization of these point properties is challenging using conventional wellbore samples, several approaches have been used to extend this information to field-relevant scales. Crosshole geophysical methods have been used to characterize hydrological (e.g., Hubbard et al., 2001; Hyndman et al., 1994) and sediment geochemical properties (Chen et al., 2004) between boreholes, and hydrofacies concepts have been used to delineate the spatial distribution of geological units that have distinct hydrological property distributions.

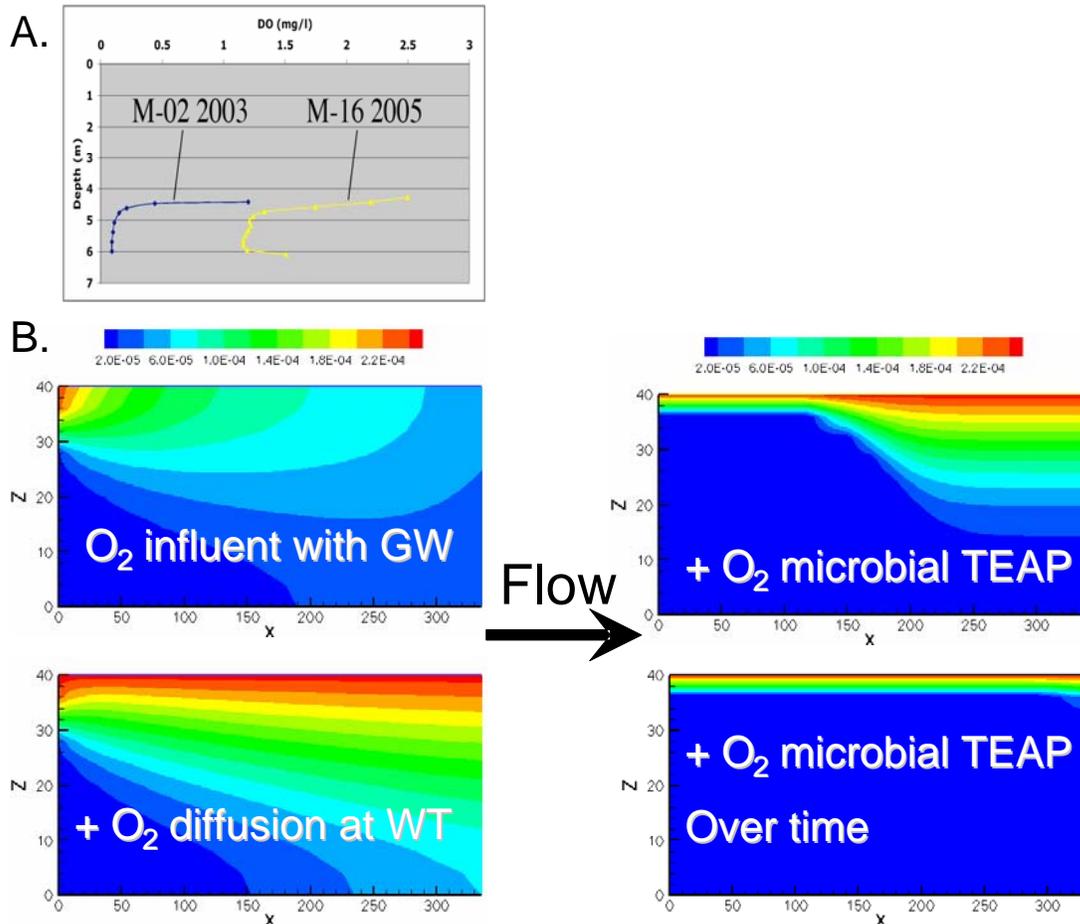


Figure 2.3. Oxygen stratification observations and modeling. A. Example of DO stratification showing overall differences of DO at different distances from the point of electron donor; M-02 is ~4 m downgradient and M-16 is ~12 m downgradient. M-16 also reflects seasonal increase in DO during water table rise. B. Four model cases showing that continuous microbial consumption of oxygen over time is needed to match observations.

2.2.2 Reactive Transport

2.2.2.1 Mineral Reactions

Transported uranium is typically attenuated through association with the solid phases of the porous media. This can occur through 1) precipitation of uranium mineral or 2) co-precipitation of uranium during formation of other secondary minerals. For the uranium concentrations and natural background geochemical conditions that we have encountered, dissolved uranium concentrations and/or ambient geochemical conditions are seldom conducive to the precipitation of uranium minerals. Increased uranium concentrations near exotic waste sources (e.g., chemical waste stream), modified geochemical conditions due to engineered systems (e.g., polyphosphate injection and resulting autunite formation) or naturally occurring but isolated zones of very low redox potential are generally required for the precipitation of uranium minerals. Uranium may also become associated with the solid phases as a co-precipitate during the formation of secondary minerals (e.g., calcite).

2.2.2.2 Sorption Reactions

For most natural systems, the dominant non-biotic uranium attenuation mechanism is sorption. Uranium partitions between the aqueous and solid phases as a function of the reactivity of surface minerals and water chemistry. Reactivity is typically measured in experimental studies over a range of aqueous chemical conditions with sediments from the field. Since laboratory analyses are typically limited to sediments of sand size (e.g., 2 mm and smaller), particle size distributions and mineralogical analyses [e.g., abundance of clays, Fe(III) minerals] can be useful, especially when there is significant variability in the sorption behavior. Sorption site density (e.g., surface complexation sites) is an input parameter to mechanistic sorption models that is often related to mineral surface area (Davis and Kent 1990). There is a large body of work focused on Fe(III) minerals as the principal surface complexation site for U(VI) cf. (Waite et al. 1994; Payne et al. 1996). Other researchers cf. (Arai et al. 2006) have identified poorly crystalline aluminosilicate mineral as potential primary sorption surfaces.

2.2.2.3 Water Chemistry

Spatial and temporal variability in field water chemistry should be known a priori to guide the chemical conditions for the experimental studies. For uranium sorption, important aqueous measurements include pH, alkalinity, calcium. For redox chemistry, the list includes oxidation-reduction potential (ORP), DO and redox couples for nitrogen, iron, manganese, and sulfur species. Dissolved organic carbon concentrations are also useful as an indicator of background electron donor support for natural bioreduction of U(VI). These measurements provide the basis for the characterization of the field water chemistry but must be augmented by analyses for reagents used and by-products formed during biostimulation. It should be noted that some of these measurements require special sampling and handling techniques to preserve the *in situ* geochemical conditions of the water samples taken at depth.

2.3 Conceptual Model of Future Uranium Behavior

The prerequisite characterization of uranium contamination along with relevant transport processes and properties will form the basis of a conceptual model for evaluating future uranium behavior. The extension of this conceptual model to a systematic and quantitative coupled process prediction of unmitigated uranium fate can then be used in a baseline risk assessment. The risk assessment usually drives the decision-making for engineering intervention, regulatory compliance, and rationale for selecting specific remedial technologies. A key issue is uncertainty in the characterized uranium inventory and transport processes. Sampling and measurement errors can propagate through the process model parameters contributing to uncertainty in predicted uranium behavior cf. (Ye et al., 2004, Helton et al. 2006). Well thought out monitoring schemes that match the time and space scales of the sampled field processes and properties can be used to reduce some of this uncertainty, especially when there is sufficient flexibility to address episodic or extreme events.

Understanding uranium fate and transport in terms of the uranium extent, magnitude, form, and mobility, and the environmental process dynamics is critically important to the reliability of the risk assessment. Attenuation mechanisms such as sorption, precipitation, and dilution, need to be understood in terms of known variability in hydrologic, geochemical, and biological conditions. Thus, it is important that the monitoring of performance indicators include confirmation of the processes and conditions that form the basis of the conceptual model of future uranium fate.

In summary, pre-remediation monitoring of groundwater parameters and characterization of site uranium contamination are critical prerequisites for a mechanistically systematic understanding of site-specific uranium behavior. Targeted data for hydrology and water chemistry should include recharge, hydraulic head (transient water level data), dissolved total uranium and U(VI), nitrogen species (nitrate, ammonium), total Fe and Fe(II), Mn species, sulfur species (sulfate and sulfide), alkalinity, DO, pH, and ORP. These measurements will be most useful if made using event-based sampling (e.g., low and high water table, after major storm events) as well as on a more regular frequency. Once key behaviors and the presence or absence of constituents (e.g., sulfate) are established, the analyte list can be shortened and sampling frequency reduced to capture known trends and event responses. The monitoring list above presumes the fundamental information for hydraulic properties, boundary conditions, uranium sorption, etc. are known.

3.0 In Situ Bioremediation

Once the decision is made for engineering intervention to achieve compliance goals, the evaluation of remediation alternatives should be based on the site conceptual model and the attributes of the various remediation technologies. Immobilization is currently the most feasible *in situ* approach for uranium remediation in environmental systems. *In situ* approaches are typically preferred over pump and treat systems because of considerations of generated waste, worker safety, and accumulation of cost over very long time horizons. To implement immobilization approaches, biological and/or chemical conditions are manipulated to drive reactions that result in the conversion of mobile aqueous U(VI), typically complexed with hydroxyl, carbonate, or other anions, to immobile forms. Bioremediation typically accomplishes this through the microbially mediated reduction of aqueous U(VI) [+6 oxidation state] in porewater to insoluble U(IV) [+4 oxidation state] resulting in precipitation of U(IV)-containing minerals. The most common U(IV) target form is the mineral uraninite (UO₂), although a number of other minerals can occur (Burns, 1999b). In laboratory settings, bioprecipitated uraninite has been shown to precipitate as nanoparticles (Suzuki et al., 2002) and recent column studies (Komlos et al. in prep.) suggest that uraninite precipitates may be transported as originally suggested by Suzuki et al. (2002). Results from field studies discussed below suggest that, at field scales, bioprecipitation succeeds in immobilizing U(VI) likely by a combination of aggregation of nanoparticles and attachment to mineral surfaces.

3.1 Microbially Mediated Processes

The reduction process occurs as microorganisms consume an electron donor (e.g., organic substrates such as ethanol, acetate, lactate), which are oxidized during metabolism to gain energy and build cellular material, while transferring electrons out of their cells to terminal electron acceptors [e.g., oxygen, nitrate, Fe(III), sulfate, bicarbonate]. Figure 3.1 is a schematic diagram of this process with an acetate-oxidizing dissimilatory metal-reducing bacterium that is transferring electrons to Fe(III) mineral and U(VI) electron acceptors resulting in reduction to Fe(II) and U(IV) mineral. The sequence of the various terminal electron accepting processes (TEAPs) is related to the energy yield from particular microorganism – electron donor – electron acceptor combinations. For typical microbial consortia, this sequence is similar to the thermodynamic “ladder” of redox couples in aquatic chemistry (Table 3.1): O₂/H₂O, NO₃⁻/NO₂⁻, MnO₂/Mn⁺⁺, FeO(OH)/Fe⁺⁺, SO₄⁻⁻²/HS⁻, CO₂/CH₄ (Bohn, 1985; Di Bonito, 2005). Uranium, in this context, is typically present in trace quantities when compared to the dominant biogeochemical conditions maintained by the background microbial consortia, major ion chemistry, and primary reactive surfaces. At these trace concentrations, uranium bioreduction is not easily differentiated from the concomitant dominant TEAP. At the Rifle site, for example, acetate-oxidizing dissimilatory iron reducing bacteria (i.e., *Geobacter sp.*) are mediating uranium bioreduction (Anderson et al., 2003). Conversely, ethanol-oxidizing sulfate reducing bacteria appear to be responsible for the primary uranium bioreduction observed at the Oak Ridge FRC (Scheibe et al., 2006). Thus, the fate of uranium at these sites is controlled by the principal TEAP, which is specific to a particular electron donor – microorganism – electron acceptor combination.

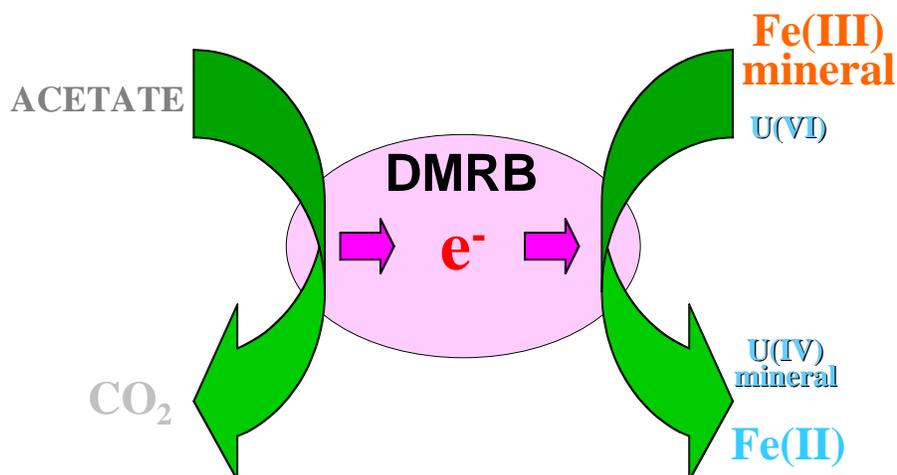


Figure 3.1. Microbial mediation of Fe(III) Reduction. U(VI) is the mobile valence state of uranium, whereas reduced uranium, U(IV), is insoluble as uraninite. Reduction of U(VI) to U(IV) within aquifers precipitates and immobilizes uranium per laboratory studies that suggest a simple strategy to promote U(VI) reduction in contaminated aquifers is to add acetate as an electron donor to stimulate dissimilatory metal-reducing microorganisms. U(VI) is reduced concurrently with Fe(III). Original concept from Lovley et al. (1991). Field implementation by Anderson et al. (2003).

Table 3.1. REDOX ladder for principal electron acceptors in soils, Eh at pH 7 (from Bohn et al., 1985 – as modified by DiBonito, 2005); pe calculated by DiBonito (2005).

Microbially Mediated Process	Observed Chemical Change/ Representative Reaction	Eh (V)	pe (15 deg. C)	
Aerobic Respiration	O ₂ disappearance $1/2 O_2 + 2e^- + 2H^+ = H_2O$	0.82	14.34	Decreasing Energy Yield ↓
Denitrification	NO ₃ ⁻ disappearance $NO_3^- + 2e^- + 2H^+ = NO_2^- + H_2O$	0.54	9.45	
Reduction of Mn	Mn ²⁺ formation $MnO_2 + 2e^- + 4H^+ = Mn^{2+} + 2H_2O$	0.40	7.0	
Reduction of Fe ⁺³	Fe ²⁺ formation $FeOOH + e^- + 3H^+ = Fe^{2+} + 2H_2O$	0.17	2.97	
Reduction of Sulfate	HS ⁻ formation $SO_4^{2-} + 6e^- + 9H^+ = HS^- + 4H_2O$	-0.16	-2.80	
Methanogenesis	CH ₄ formation $(CH_2O)_n = n/2 CO_2 + n/2 CH_4$	-0.24*	(not calculated)	
Hydrogen Production	H ₂ formation $H^+ + e^- = 1/2 H_2$	-0.41	-7.17	

*From Craig Tobias, http://people.uncw.edu/tobiasc/GLY%20472%20572/gly_472.htm

3.2 Methodology Selection

In addition to the general issues associated with the design of any subsurface remediation technology (e.g., inventory, characterization, placement), specific issues of redox-based technologies include 1) the sequence of chemical components that must be reduced before uranium bioreduction can take place, 2) bioavailability of terminal electron acceptors, 3) reoxidation and remobilization, and 4) evolving reactivity. The objective of the methodology selection is to identify a bioremediation approach that is best suited to the attributes of the uranium inventory and the environmental system.

In addition to oxygen, there are several potential oxidizing agents present in natural systems. Depending on pH, nitrate and minerals with Mn(IV) and/or Fe(III) may be the dominant oxidizer after oxygen. At circumneutral pH, the thermodynamically favored sequence would follow the redox ladder in Table 3.1. oxygen, nitrate, Mn(IV), Fe(III), sulfate, carbonate. Unless there are kinetic limitations, stronger oxidizers must be depleted prior to the availability of weaker oxidizers for reduction. Thus, it may be necessary to include the removal of oxygen and nitrate in the bioremediation methodology. While this may not be a significant issue at low nitrate, suboxic sites like the Rifle site, many sites have high nitrate concentrations (e.g., Hanford, Oak Ridge) that could drastically increase the cost and complexity of bioremediation, especially where there is a continuous influx of oxygen, nitrate, and U(VI) into the treatment zone. Vadose zone sources of these oxidized components could be important if enhanced through high recharge and/or water table fluctuation. Post-biostimulation reoxidation and remobilization of uranium, which have been observed in laboratory settings (Komlos et al. in press), may also be accelerated in the field by the presence of these oxidizers.

Remobilization of sorbed, precipitated, or co-precipitated uranium may be dependent on the dissolution kinetics of the secondary minerals that also precipitated during the stimulation of reducing conditions and incorporated or coated the sequestered uranium. Furthermore, secondary minerals can contribute to the long-term stability of biogenic uraninite by slowing the reoxidation process. Abdelouas et al. (1999a) found that when oxidizing background conditions returned after biostimulation ended, mackinawite (FeS) that precipitated during biotransformation of U(VI) to uraninite provided an oxygen sink that slowed the oxidation of uraninite. Changes in the structure and function of microbial community dynamics, mineral dissolution and precipitation, and biomass production at bioremediation sites are indicative of the evolving reactivity of the subsurface system and should be monitored in the context of long-term uranium mobility. It is also possible that precipitation of stable secondary phases may serve to isolate previously precipitated sorbed or reduced U, thus removing it from direct contact with pore waters. In this context it is important to note that the goal is to maintain a sufficiently low rate of remobilization such that groundwater standards are maintained.

A key consideration is thus the maintenance of the desired TEAP. At the Rifle site, the principal uranium bioreduction occurs during the Fe(III) TEAP, which has been attributed to the iron-reducing *Geobacter* species (Anderson et al., 2003). As bioavailable Fe(III) minerals were depleted near the point of acetate injection at the Rifle site, acetate-oxidizing sulfate reducers succeeded the iron-reducers. The transition to sulfate-reducing conditions was accompanied by less effective removal of U(VI) from the groundwater. The inefficiency of U(VI) removal when acetate-oxidizing sulfate reducers became dominant was identified by Anderson et al. (2003) as an important consideration in the optimization of a bioremediation strategy based on this approach. Clearly, the selection and implementation of a successful bioremediation strategy requires a reasonably good understanding of the site-specific geochemical conditions and the maintenance of specific microbial populations.

3.3 Bench-Scale Testing For Proof-Of-Principle

The sensitivity of bioremediation efficacy to field attributes (e.g., uranium inventory, properties of vadose zone and aquifer materials, biogeochemistry, hydrology) is sufficiently high that engineered solutions must be appropriately tailored. From this perspective, a set of bench scale tests using site materials (e.g., uncontaminated and uranium-contaminated sediments, groundwater) is necessary to address proof-of-principle as well as methodology optimization (e.g., electron donor selection and delivery). Bench-scale testing can address:

1. Characterizing unmitigated uranium behavior in terms of variable
 - a. geologic materials
 - b. water chemistry
 - c. geochemistry
2. Selecting electron donor; density and composition issues for delivery
3. Achieving onset of principal TEAP associated with uranium bioreduction
4. Maintaining bioreduction efficacy.

A significant range of bench scale tests has already been completed and published starting with Lovley's original bottle incubations showing microbial reduction of U(VI) (Lovley et al., 1991) and numerous others since (see Section 7, Bibliography). These earlier studies make it possible to perform a minimal set of new tests with site materials to achieve the objectives noted above. Knowledge from bench-scale testing in closed thermodynamic systems with fixed amounts of TEAPs in microcosms should be used to design open system (e.g., column experiments) studies that are more representative of the field-scale process dynamics.

Assessment of proof-of-principle needs to account for the impact of site complexity (geohydrologic, geochemical, and microbiological) on bioremediation performance. For example, low-permeability zones (silt or clay) may not only constrain flow in a system but may also slowly release U(VI) from dead-end pores, maintaining a flux of U(VI) not anticipated from consideration of coarser-grained materials (LaBolle and Fogg, 2001). Appropriate design of an electron donor system can address these situations (Roden and Scheibe, 2005).

In many cases, the understanding of these complexities is qualitative at best. However, considering their potential impact is still key to effective design of the bioremediation system and helps avoid surprises during implementation. Further, newly developed geophysical monitoring techniques, especially electrical methods (Williams et al., 2006), offer the promise of inexpensive, minimally invasive approaches that can be used to estimate initial geochemical heterogeneity and to monitor changes in the distribution of TEAP's during bioremediation.

3.4 Conceptual Model for Uranium Bioremediation

Based on the success of the bench-scale testing and the site baseline analysis, a conceptual model for the engineered bioremediation of a particular site can be formulated. Typically, this knowledge will be incorporated into numerical modeling of the dominant processes operative on the site before, during, and after biostimulation. The laboratory-based parameters used in the simulations will likely deviate from those in the field; thus, these analyses are preliminary in nature. The value of numerical modeling is being able to identify systematic responses to variations in design parameters. This will allow the assessment of implementation issues and comparison of bioremediation options in the context of the uranium inventory, environmental transport processes, and the characterized biogeochemical reactions.

3.5 Pre-Biostimulation Baseline Characterization

A key aspect of the performance monitoring program should be the pre-biostimulation baseline characterization that will be necessary for comparisons with monitoring performed during and after bioremediation or pilot-scale tests. It is possible that much of this baseline characterization may have already been a part of earlier characterization performed in support of the risk assessment. One particularly useful consideration is a transport experiment with multiple tracers that have different diffusion characteristics. This will provide important information regarding transport (e.g., effective porosity, preferential flow, transport time scales, multiregion behavior) that will have direct implications for the design of amendment delivery. Key baseline data required include groundwater geochemistry, sediment geochemistry, and hydrogeology.

Point samples from groundwater and sediment may be augmented by geophysical data collection to provide a geophysical baseline prior to conducting pilot-scale testing or full-scale bioremediation. Geophysical measurements (complex resistivity, self potential, cross-well radar, and cross-well seismic) can then be collected over time at the same locations, and the changes in geophysical attributes relative to the baseline datasets can be used to detect the transformations associated with the biostimulation treatment. With this approach, time-lapse geophysical data have been used during biostimulation experiments to indirectly monitor the spatiotemporal distribution of injected amendments, evolution of gas associated with denitrification, development of iron sulfides associated with sulfate reduction, and the changes in total dissolved solids associated with nitrate and sulfate reduction (e.g., Lane et al., 2006; Williams et al., 2005). Time-lapse complex resistivity and self-potential datasets collected at the Rifle site during different biostimulation experiments, indicate the utility of those data for distinguishing between iron-reducing and sulfate-reducing conditions and for identifying the spatial extent of electrochemical responses, respectively (Williams et al., 2006). Estimation frameworks, currently in development, will permit the use of the time-lapse geophysical attribute information for quantitative estimation of biostimulation transformations. Although the use of geophysical methods for monitoring biostimulation processes is a current topic of research, these studies highlight the potential that they hold for understanding complex transformations at the field scale and in the presence of natural heterogeneity.

3.6 Pilot-Scale Testing

There are many aspects of field-scale bioremediation that cannot be adequately addressed at the bench scale, including 1) > 2 mm sediment size fraction; 2) structured, multidimensional, multiscale physical and chemical heterogeneities; 3) microbial microenvironments; 4) density effects; and 5) seasonal and episodic hydrologic transients. The tradeoff with pilot-scale testing in the field is the diminished ability to control and observe the engineered reactions. For these reasons, and to reduce the risk of failure, pilot-scale field tests are likely to be cost-effective. Such tests provide a bridge to the full-scale deployment of the bioremediation technology that increase understanding of the *in situ* behavior and allow optimization of the final approach. Monitoring of performance indicators to confirm the field viability of the bioremediation approach is particularly important at the pilot scale, since the results can be used to select the necessary and sufficient performance indicators for full-scale deployment. Again, this is likely to reduce cost of full-scale deployment.

Figure 3.2 shows the layout of ERSP boreholes for the Old Rifle UMTRA Site at the end of the 2004 experiment, which provides examples of pilot-scale injection and monitoring well configurations. The larger borehole array shows one row of 3 background monitoring wells, one row of 20 injection wells, and three rows of 5 treatment-zone monitoring wells. The overall size of the plot is ~20 m on a side. The smaller borehole array consists of 1 background well, 5 injection wells, and 4 treatment zone monitoring wells. Our experience at this particular site suggests that pilot-scale borehole arrays will provide optimal results if they are intermediate in size between the two shown in Figure 3.2. For the Rifle site, this would mean ~10 m on a side with 3 background monitoring wells, ~10 injection wells, and ~8 down-gradient monitoring wells. This approach assumes that natural gradient pilot-scale experiments would be performed. Alternative well designs are possible for both natural and forced gradient experiments.

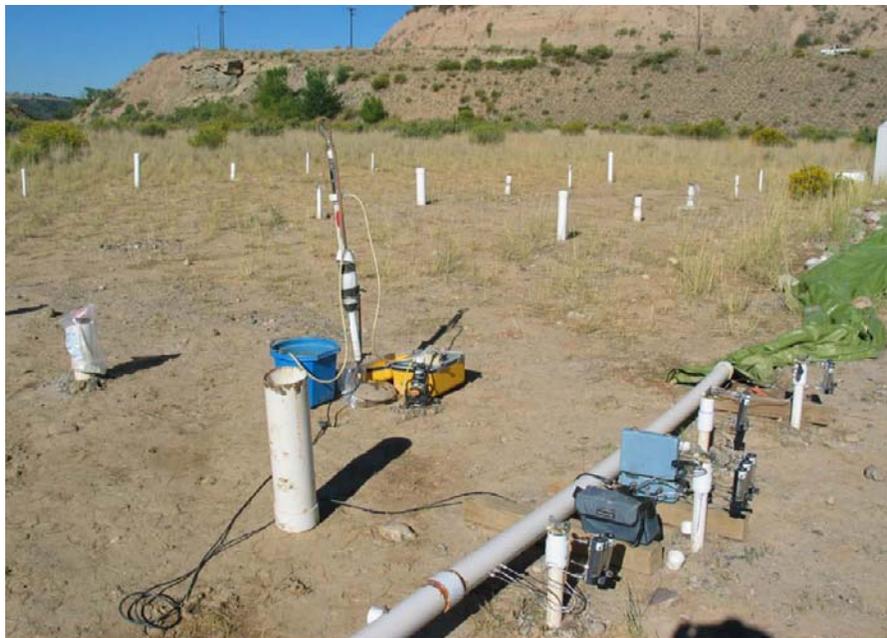
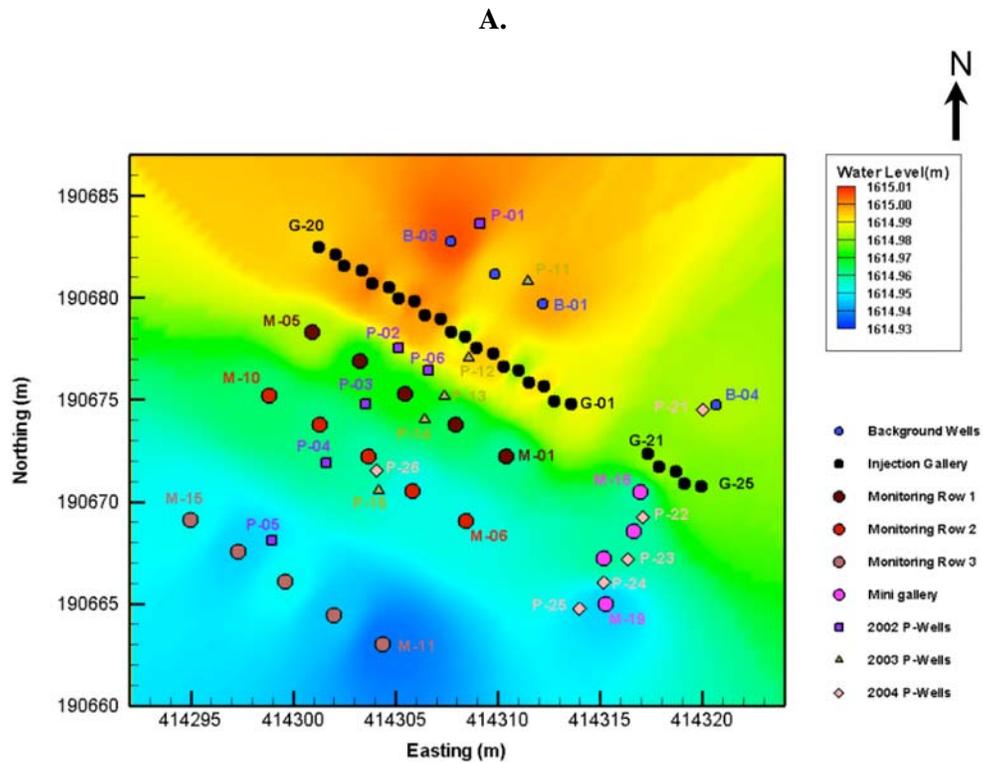


Figure 3.2. Borehole arrays for pilot-scale testing at the Rifle site. A. Layout of wells showing water table elevations. General groundwater flow direction is to the southwest. B. Photo of wells and sampling apparatus including flow cell for measurement of pH, Eh, DO, T, and conductivity during slow purge sampling. Foreground shows injection manifold and stainless steel injection lines to injection wells.

4.0 Performance Issues and Indicators

In this section, we describe monitoring of performance indicators that will address the potential issues related to uranium bioremediation. We divide the monitoring approach into three broad groups to assess and confirm: 1) uranium removal effectiveness, 2) environmental transport conceptual model, and 3) microbiological conceptual model. In Section 5, we provide our best estimate of the priority of the performance indicators.

A general consideration for all three groups is to provide performance indicators with regard to principal issues with engineering uranium behavior. The first is the identification of potentially uncharacterized sources (e.g., vadose zone uranium leached during water table fluctuation). At the Hanford Site 300 Area for example, the largest uranium plume is associated with the most recently used surface disposal facility that operated until 1994. Recent groundwater measurements, however, have identified a uranium hot spot near a small disposal trench that was decommissioned in 1963. The site conceptual model is also being revised to reflect a chronic source of uranium in the lower part of the vadose zone that is activated during periods of high water table.

A second performance issue revealed through groundwater monitoring during bioremediation is the presence of U(VI) in the treatment zone that is not immobilized. While this could be the result of an uncharacterized uranium source, the interest here is for zones that are not sufficiently exposed to electron donor (and associated tracer such as bromide). In early experiments at the Rifle site, a lack of mixing in injection gallery wells resulted in the delivery of electron donor that bypassed the uppermost part of the saturated zone. This resulted in high, unmitigated U(VI) concentrations near the water table (Figure 4.1). Injectate density effects apparently played a key role, but preferential flow paths were also evident as the highest acetate and tracer concentrations were found in the *second* row of monitoring wells down-gradient from the injection. This situation could be further complicated by the presence of enhanced DO and U(VI) near the water table. A key monitoring consideration that revealed the vertical variability and stratification during biostimulation at the Rifle site was depth-specific sampling for both groundwater (multilevel water sampling in and around the treatment zone, Figure 4.2) and sediments (core samples, Figure 4.3).

A third performance issue is the potential for changing bioremediation effectiveness. The transition from iron to sulfate reduction described earlier at the Rifle site was shown to significantly decrease the efficacy of U(VI) removal from groundwater. However, the post-biostimulation uranium behavior showed a subsequent evolution to another biogeochemical state where enhanced uranium removal took place only in the zones that experienced significant sulfate reduction. Thus, a key issue in monitoring these biogeochemical transitions is sampling frequency. The sampling scheme design should be based on the time scales of the process dynamics, which may be diurnal, seasonal, and/or episodic. Even the seasonal sampling during the spring runoff should be viewed as event-driven because the specific timing can vary from year to year.

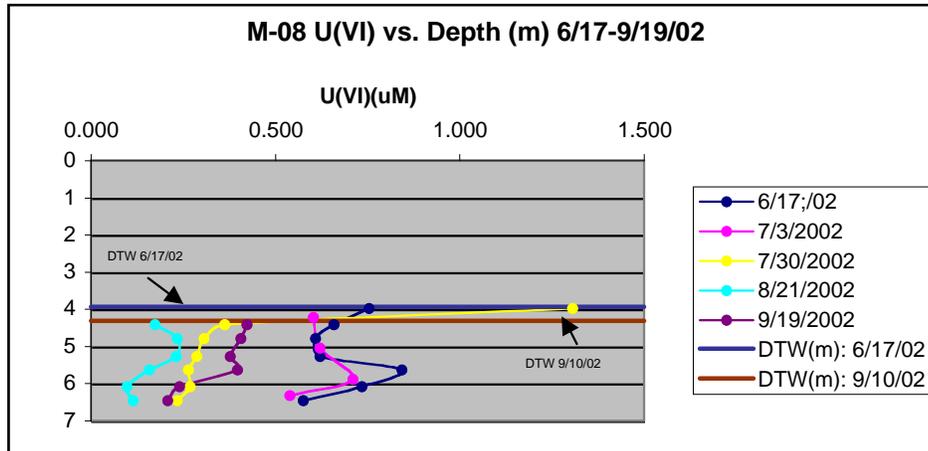


Figure 4.1. Distribution of U(VI) as a function of depth during a biostimulation experiment. Injection of acetate started on 22 June 2002 and ended on 23 Oct 2002. U concentration decreased through 21 Aug 2002 except in the upper part of the aquifer where acetate was not entrained in groundwater due to the delivery system. The increase in U(VI) concentration near water table on 30 July 2002 reflects absence of acetate and possibly a slight increase in water level. Data obtained using passive multilevel samplers (see Figure 4.2).

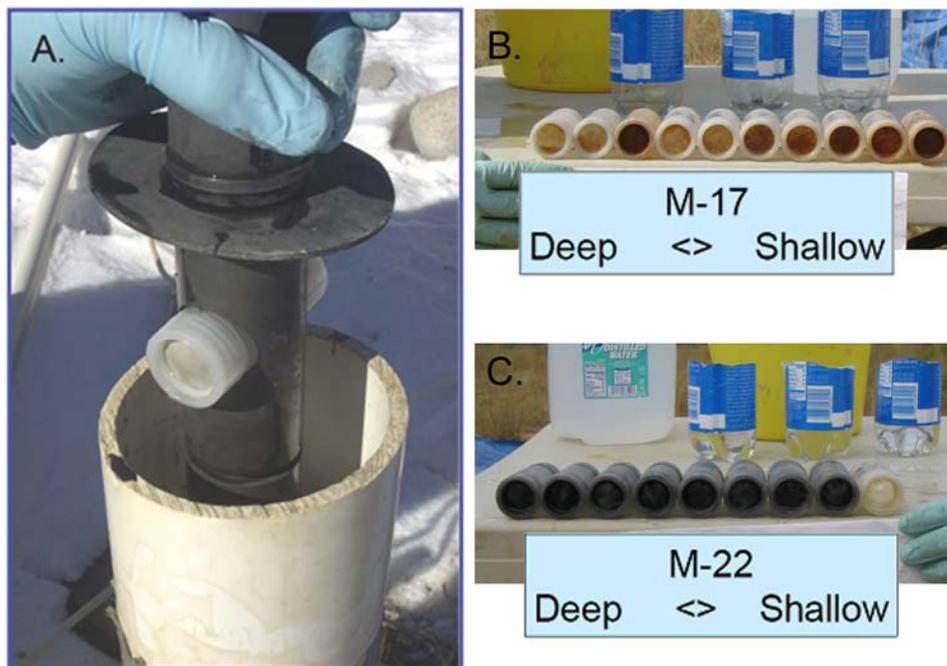


Figure 4.2. Passive multilevel samplers. A. Cell on support rod being lowered into monitoring well. Cells are initially installed with distilled and deionized water and equilibrate in a few days with in situ groundwater at a given depth. B. MLS cells from a background well (note rust colored coating indicative of Fe oxide stability). C. MLS cells from a treatment zone well undergoing sulfate reduction (note black coating from precipitation of FeS).

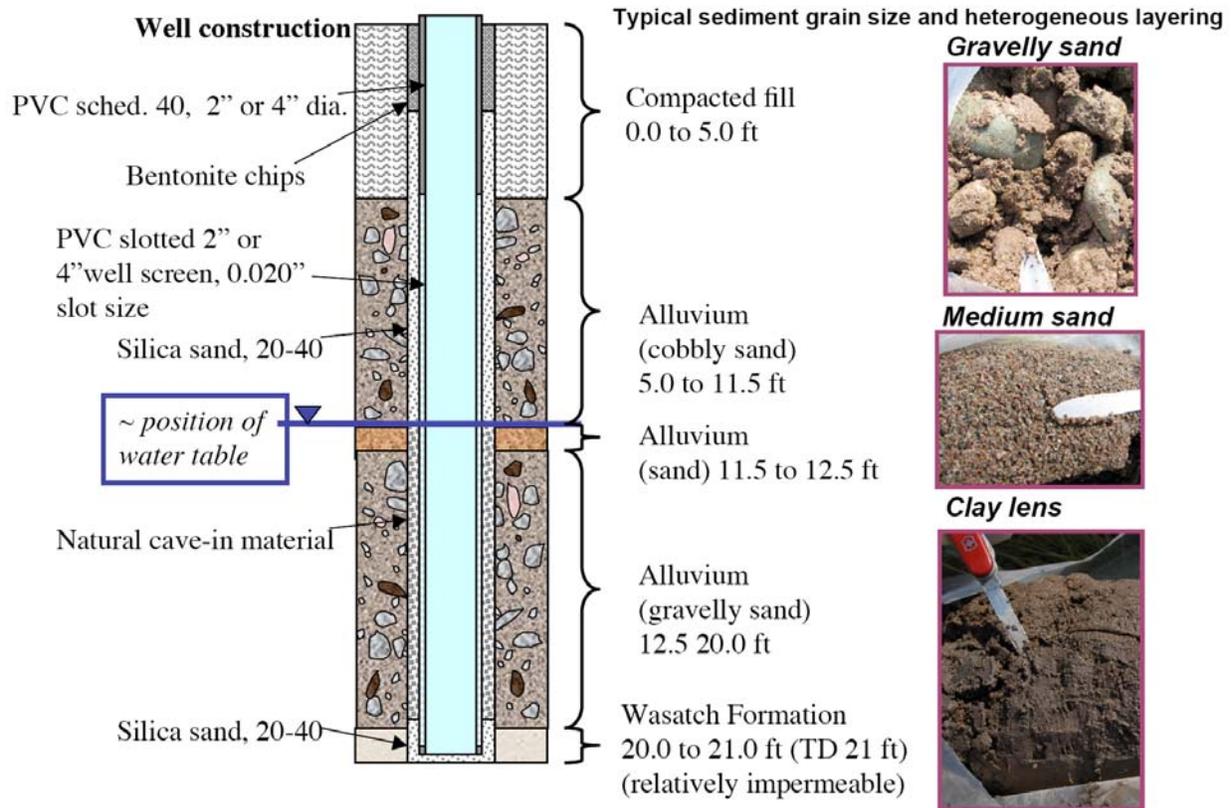


Figure 4.3. Example of heterogeneity in alluvial sediment. The wide range of grain size and mineralogy exerts significant control on permeability, porosity, U sorption, and overall reactivity of the sediments.

4.1 Group 1: Uranium Removal Effectiveness

The uranium removal effectiveness group (Group 1) provides a general perspective of the uranium distribution in the subsurface. It does not provide sufficient confirmatory information for the baseline conceptual model of uranium transport and fate addressed in Group 2, or the uranium bioremediation conceptual model addressed in Group 3.

Compliance standards are typically based on the aqueous uranium concentrations. Thus, the most direct indication of compliance status will be through monitoring of groundwater for uranium concentrations. Key components of the Group 1 groundwater monitoring indicators are to establish the initial uranium (i.e., pre-biostimulation) for both the background and contaminated aquifer zones while capturing the transient aqueous uranium entering the treatment zone. This will provide a basis for comparing uranium concentrations monitored during and after the biostimulation and linking observed changes with the biostimulation. In some cases (e.g., Old Rifle UMTRA site), the treatment zone may be small compared to the extent of uranium contamination such that an uncontaminated up-gradient zone is not sufficiently close to the treatment zone to reasonably compare changes. In these cases, the unmitigated contaminated zone up-gradient of the treatment zone should be monitored to identify the transient water chemistry and the background geochemical condition of the sediments. See Figure 4.4 for a depiction of the spatial distribution of U(VI) before and during biostimulation at the Rifle site.

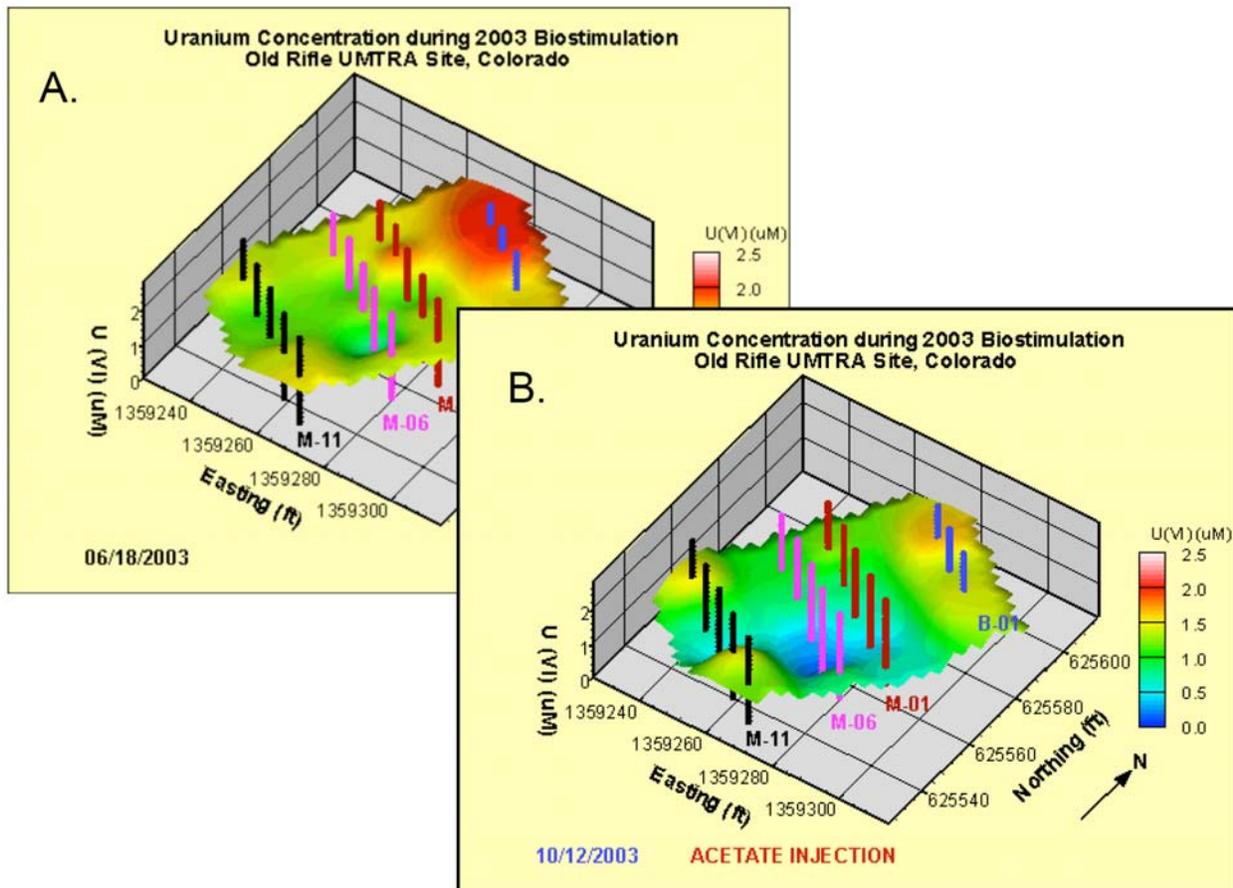


Figure 4.4. Plot of U(VI) concentration spatially before (A) and during (B) biostimulation. Note spatial and temporal variability of U(VI) concentration.

Two key facets of U(VI) concentrations are 1) the vertical distribution in the aquifer and 2) the temporal changes associated with water table fluctuations per discussions earlier in this document. In most cases, the amount of data that can be collected in both space and time is constrained by available funds. However, it is important to note that information on the spatial and temporal distribution of U(VI) may actually save remediation costs, if it is discovered that U(VI) concentrations are restricted to the upper part of an aquifer, for example. Furthermore, we have used passive multi-level samplers that only require a single well bore (see Vrionis et al. 2005 and Figure 4.2) to obtain data on the depth distribution of U(VI) as well as other dissolved constituents in groundwater.

Sampling frequency is a crucial parameter that needs to be adaptively established based on events suspected of impacting U(VI) (e.g., water table rise) or on time frames previously observed for response of U(VI) concentrations to biostimulation (7 to 10 days). We typically conduct sampling at frequencies ranging from two times per week at the outset of electron donor amendment to monthly during post-amendment monitoring. After event impacts are well established, monitoring could occur less frequently. It should also be possible to link sampling to near-continuous geophysical monitoring, where real-time changes in calibrated geophysical responses (e.g., a decrease in self-potential voltage) indicate the onset of a system transformation that requires sampling.

Concentrations of U(VI) in groundwater should be complemented by uranium extractions performed on sediments sampled before and after primary biostimulation. These are typically carbonate extractions designed to identify the labile uranium component (Yabusaki et al., 2007). In our experience at Rifle, spatial variability in the extractions performed on cored sediments at the Rifle site can be considerable. In this case, the spatial resolution of the sampling scheme should be guided by knowledge gained from the pilot study and cost considerations. We are currently researching in-well sediment incubators as possible surrogates for *in situ* sediment samples. Initial results suggest that it may be possible to use such incubators to inexpensively characterize both sorbed uranium and *in situ* microbial response under background and locally biostimulated conditions.

A key piece of information is the amount of U(VI) in groundwater that has been reduced to U(IV) and become associated with the sediments. In this case, preparation and maintenance of reduced uranium in cored sediments for subsequent analysis is a critically important task. A specialized laboratory experiment (Komlos, in prep.) was recently performed in which an entire column of sediment was brought intact to a nearby x-ray synchrotron for analysis of the uranium oxidation states in a biostimulated column. When compared to standard handling approaches in which sediment was removed from columns and shipped offsite, this approach resulted in considerably higher measurements of reduced uranium in sediments.

4.2 Group 2: Conceptual Model of Uranium Transport and Fate

We take the view that monitoring uranium levels in groundwater is a necessary but not sufficient performance indicator. The expectation of the Group 2 performance indicators is the assessment and confirmation of the conceptual model for uranium transport and fate. System complexity may affect the delivery of amendments to the subsurface as well as long-term effectiveness. This would include bypass from preferential flow paths, spatially variable depletion of bioavailable terminal electron acceptors that are critical to the maintenance of effective uranium bioremediation, changes in the geochemical environment (e.g., mineral precipitation) that affect uranium availability and reactivity, and the impact of hydrologic events (e.g., elevated water table, intense rainfall/recharge) on the reoxidation of reduced sediments. Evolving reactivity may also occur over longer time scales needed for permeability reduction due to formation of secondary minerals and post-biostimulation re-equilibration to ambient conditions.

It should be mentioned that the microbially mediated creation of low ORP conditions [e.g., through Fe(II) and sulfide formation] that thermodynamically favor abiotic uranium reduction have been shown to be quite limited kinetically in natural sediments (Jeon et al., 2005). Thus, the general concern with the maintenance of reducing conditions is with regard to preventing reoxidation of bioreduced uranium, not necessarily the continued production of U(IV). However, we also note that post-amendment removal of U(VI) at the Rifle site may result from biosorption of U(VI). The longevity of such immobilization is not yet known but appears to last at least 2 years, depending on abundance of sulfide precipitation during sulfate reduction.

Key monitoring quantities are summarized in Table 3.2. Aqueous conditions that can be automatically and continuously logged with an *in situ* sonde include water depth, pH, ORP, alkalinity, specific conductivity, temperature. At the Rifle site, we have four sondes that are continuously operated with bimonthly downloading of these data. An attractive alternative is to set up these systems with telemetry that will allow the data to be downloaded remotely. Water levels can be particularly important to the regional flow field as well as chemical conditions near the water table. Standard multilevel samplers are

very useful but it may not be feasible to deploy them in every well. We have supplemented our multilevel samplers with various passive samplers that can be used to economically collect depth-dependent distributions of aqueous and particulate components (Figure 4.2). In many cases, we can visually identify depth-dependent behavior by examining the sequence of the sampling cells.

Standard aqueous sampling should be directed at the transport of the injectate (e.g., tracer, electron donor, possibly electron acceptors), consumption of electron donors (e.g., ethanol, acetate, lactate) and electron acceptors (e.g., oxygen, nitrate, sulfate), and biostimulation reaction products [carbonate, ammonium, sulfide, reduced metals such as Fe(II), Mn(II)]. Most recently, a technique using tubing and syringes suspended in wells (Spalding and Watson 2006) has been used to provide the most accurate measurements of dissolved gases such as hydrogen, oxygen, carbon dioxide, and nitrogen. The adaptation of this technique to a passive depth-dependent sampling of the water column promises to provide key feedback on bioremediation progress (e.g., hydrogen and carbon dioxide byproduct) and reoxidation (e.g., DO and nitrogen).

Where possible, sediment extractions should be used to identify uranium form [e.g., U(IV), U(VI) as mineral, surface complex], iron form [Fe(II), Fe(III) as mineral and surface complex], and other secondary minerals (e.g., carbonate, sulfide). At the Naturita site, sediments were suspended directly in wells to provide cheaper and easier access to reacted sediments (Curtis et al., 2004), see also discussion under Group 1).

4.3 Group 3: Microbiological Conceptual Model

The Group 3 performance indicators are designed to assess and confirm the microbiological conceptual model underlying the engineered bioremediation. Key issues are the ability to differentiate, where necessary, the dominant microbial populations associated with major TEAPs in the bioremediation scheme. Although there is a sequential nature to these TEAPs, there is growing evidence from the field that multiple TEAPs (e.g., iron and sulfate reduction) can be operating simultaneously in the same aquifer sediments, although likely in different microniches. Succession to a new dominant TEAP ostensibly occurs when the preceding dominant terminal electron acceptor is exhausted, no longer bioavailable or reduced in concentration to a point where it no longer impacts the system. This is significant only if the succeeding microorganisms are less effective at uranium bioreduction than their predecessors, which appears to be the case with the acetate-oxidizing microbial consortia at Rifle.

Specialized sampling procedures (e.g., Colwell et al., 1992; Holmes et al., 2005; Long, 2002; Peacock et al., 2004; Vrionis et al., 2005) are necessary to identify the microbial community structure and measure the abundance and activity of the dominant microorganisms. Sampling techniques typically are focused on 1) groundwater, 2) sediments, or 3) in-well coupons or sediment incubators. For sampling groundwater, concentration of the planktonic microbial community by filtration is typical. The volume of sample that is filtered depends on the specific microbial analysis. 16S DNA sampling, for example, can be done by filtering relatively small volumes (1 to 3 liters) but more sophisticated techniques such as rRNA require larger volumes (~20 liters and more care in sample handling). Sediment sampling is the most challenging since drilling is usually required. Sample volumes again depend on the proposed analysis, ranging from 25 grams to 0.5 kg or more. In-well coupons such as Bio-Sep beads (see below) are attractive since no drilling is involved, but may be problematic if the well-bore environment is not representative of the surrounding formation and groundwater conditions. Recently, efforts have been made to develop an in-well sediment incubator that eliminates this issue by fully occupying part of the

well bore with sediment from the site (Peacock, personal communication). This approach makes it possible to track *in situ* sediment microbial population changes without drilling.

Microbial Analysis Techniques. Phospholipid fatty acid profiles (PLFA) provide a broad but reliable picture of microbial community structure with relatively small groundwater or sediment samples required. Furthermore, PLFA analyses are commercially available. Standard molecular biology techniques, such as 16-S Clone libraries, can also be routinely performed. For some microbial techniques, large volumes (~20 L) of groundwater must be filtered to concentrate sufficient biomass to perform analyses (e.g., gene expression or mRNA). However, molecular biology techniques are evolving rapidly, and it is now possible to track both gene expression and mRNA during the course of biostimulation (Holmes et al., 2004; Holmes et al., 2005). DNA chip arrays and bead arrays make it possible to screen samples for both microbial metabolic function and genetic identity. Many of these tools are used primarily for research but are quickly becoming available to meet the needs of applied bioremediation. Sediment analyses include the use of similar tools but require extraction of DNA prior to analysis.

A novel bio-trap technique that captures microbial community structure in the subsurface is Bio-Sep® Beads (Peacock et al., 2004). The beads are 2-3 mm in diameter, with high porosity and surface area. Biofilms form rapidly in the Bio-Sep® Beads and the biofilm community structure on the beads is more indicative of *in situ* microbial ecology than samples of planktonic organisms. Standard PLFA and DGGE analysis of DNA are performed on extracts from the samplers. The beads serve as an excellent technique for assessing the effects of biostimulation on microbial biomass, community composition, and metabolic state. Microbial analyses of these beads are commercially available.

A recent workshop on molecular biological tools (SERDP and ESTCP, 2005) produced a summary of the current state of techniques for field applications. This document identifies currently available tools and tabulates their relative frequency of use, advantages, disadvantages, and current applications.

Iron-reduction and sulfate reduction TEAPs are also amenable to indirect assessment using geophysical monitoring via electrical methods (Williams et al., 2006). Recent unpublished results from the Rifle site using electrical resistivity tomography indicate that iron- and sulfate-reducing conditions are readily distinguished in adjacent electron donor amendment plots, one of which was driven to sulfate reduction and the other maintained in Fe reduction. Although these results are preliminary, they indicate the potential value of geophysical methods for monitoring microbial processes in the subsurface in a minimally invasive manner and over field-relevant scales.

5.0 Summary and Prioritization of Performance Indicators

Table 5.1 summarizes the performance indicators. Priorities are designated in three categories: mandatory, desirable, and optional. In addition, the temporal dimension of the monitoring regime is provided as a guideline for monitoring frequency. Mandatory performance indicators are those indicators judged to be the minimum set of data needed to validate a uranium bioremediation project. Desirable performance indicators are those, which, if included, could be used to make a stronger case for the success and effectiveness of uranium bioremediation. Optional performance indicators are the lowest priority but may provide valuable information in selected cases or enhance the understanding of system processes. This prioritization scheme was developed to minimize the cost of system assessment by focusing on low-cost measurements in the mandatory category while still ensuring that critical data are obtained. Site-specific conceptual or numerical models may indicate different priorities or the need for emphasis on specific measurements.

Table 5.1. Prioritized Information and Monitoring Parameters for Assessment of Bioremediation of U(VI) in Groundwater

Mandatory Site Information: Uranium Distribution, Magnitude, Form, and Mobility		
<i>Information area/parameter</i>	<i>Desired Range</i>	<i>Comments</i>
Site conceptual model for uranium source term	NA	Consideration of alternative conceptual models critical
Spatial extent of contamination zone (plume geometry)	±20% of estimate	Differentiate between vadose zone and aquifer concentrations; aqueous and sediment associated uranium; geometry drive layout of bioremediation system
Form and mobility/labability	± 30% of estimate	Experiments and sediment extractions to identify uranium form and potential for future mobility based on labile fraction
Mandatory Site Information: Hydrologic and Geologic Data		
<i>Information area/parameter</i>	<i>Desired Range</i>	<i>Comments</i>
Site conceptual model for subsurface (vadose zone and groundwater) flow and contaminant transport	NA	Consideration of alternative conceptual models critical
Temporal recharge	±20%	Seasonal and episodic impact to unsaturated flow, extreme recharge event and impact must be considered if flooding probable at the site
Vadose zone hydrogeology: porosity, water retention function parameters	±20% of estimate	Seasonal and episodic impact to flow direction critical
Groundwater flow velocity (Darcy flux) and direction	±30% of estimate	Seasonal and episodic impact critical
Water table dynamics (use hourly data as event-based geochemical sampling driver)	NA	Relationship between water table and U concentration critical
Site hydrogeology: hydraulic conductivity, porosity, dispersivity, hydrofacies	NA	Fundamental to both site and process conceptual model

Table 5.1. (contd)

Remediation process conceptual model	NA	Fundamental to prioritization of monitoring parameters
Particle size characteristics	NA	Reactive surface area, clays, upscaling lab to field
Mandatory Geochemical and Microbiological Performance Monitoring Parameters		
<i>Parameter</i>	<i>Desired Range</i>	<i>Comments</i>
Background U(VI) concentration, monthly or bi-monthly and event-base (e.g., high water table)	NA	Number of sampling points based on plume and treatment zone complexity and size (including depth)
Treatment zone and down-gradient U(VI) concentration	Below MCL	Number of sampling points based on plume and treatment zone complexity and size
DO, ORP, specific conductivity, and pH measured hourly to 4 times daily in background and treatment zone (autonomous multiparameter probes)	DO<0.5, ORP<0, conductivity initial increase, pH ~ steady	Values used as overall dynamic indicator of impact of bioremediation on subsurface geochemistry
DO, ORP, specific conductivity, and pH measured at time of groundwater sampling in background and treatment zone using flow-cell with multiparameter probe	See above	Linkage of U(VI) concentrations with parameter change evidence for bioremediation process conceptual model
Aqueous electron acceptors and reduction byproducts in background and treatment zone: nitrate, nitrite, ammonium, Mn(IV/II), sulfate, sulfide	NA	Significant concentrations of oxygen and/or other electron acceptors above the U TEAP on the redox ladder must be addressed by the bioremediation strategy and their reduction products monitored. Sulfur isotopic analyses may provide supplemental information.
Fe(III) mineral abundance	NA	Fe(III) minerals provide sorption sites for Fe(II) & U(VI), terminal electron acceptor for Fe-reducing bacteria, dissolved Fe(II) source
Fe(II), sulfide measured in field at time of sampling for U(VI) (up gradient, treatment zone, and down gradient)	Increasing Fe(II); sulfide indicator of sulfate reduction	Maintaining metal reduction may optimize U(VI) removal from groundwater; sulfate reduction may enhance long-term immobilization in sulfate-rich systems
Electron donor concentration in treatment zone	>0	Evidence of delivery and treatment zone distribution; consumption calculation based on tracer data
Tracer for electron donor	>0 in treatment zone	Typically Br is used for conservative tracer, accurate indication of donor distribution
Alkalinity (measured in the field)	NA	Indicator of carbonate geochemistry, dissolved carbonate/bicarbonate forms strong anionic complexes with U(VI) to decrease its adsorption and increase its solubility and mobility
Desirable Performance Monitoring Parameters		
<i>Parameter/Method</i>	<i>Desired Range or Response</i>	<i>Comments</i>
Depth discrete U(VI) data (upper/mid/lower part of contaminated zone)	Regulatory Compliance Criteria	Decreased effectiveness of treatment in the uppermost part of the saturated zone may be problematic

Table 5.1. (contd)

Major cations and anions	NA	Provides additional evidence for dominant geochemical aqueous complexation and mineral solubility reactions
Impact of treatment process on groundwater flow directions (hourly water level at minimum 4 points)	Dependent on background flow	Helps to provide assurance that groundwater is not rerouted around treatment zone
<i>In situ</i> redox status of U using <i>in situ</i> sediment incubators (ISIs)	Significant U(IV) present	Evidence that precipitation of U(IV) is occurring <i>in situ</i> obtained via differential U extraction.
Microbiological assessment using coupons or <i>in situ</i> incubators	Shift to metal and/or sulfate reduction	Evidence for desired <i>in situ</i> microbial respiration obtained from deploying coupons or <i>in situ</i> incubators in well bores and periodically measuring microbial parameters (see text for additional discussion)
Depth-discrete sediment sampling/extraction for U, Fe, AVS	NA	Evidence for conversion of terminal electron acceptors
Major dissolved gas components in groundwater	NA	Evidence for key TEAPs and microbial metabolism
Time-lapse GPR Cross-well or Electrical Measurements	Shift in geophysical attributes in zone of electron donor	Indicates 2-D distribution of electron donor, although impact of other transformations on geophysical signatures must be assessed and errors associated with tomographic inversion procedures can 'smear' amendment boundary.
Optional Performance Monitoring Parameters		
<i>Parameter/Method</i>	<i>Desired Range or Response</i>	<i>Comments</i>
Depth-discrete data for mandatory geochemical parameters	NA	Characterizes spatial distribution of fundamental biogeochemistry in aquifer
Depth-discrete data for desirable monitoring parameters	NA	Characterizes spatial distribution of desired biogeochemical reactions in aquifer
Impact of treatment process on hydraulic properties	<15% change	Documents possible system clogging of pores
Organic and inorganic carbon analyses	NA	More accurate documentation of carbonate geochemistry
Microbiological assessment performed directly on sampling of treatment zone materials	Shift to metal and/or sulfate reduction	Measurements directly on groundwater filtrates or sediment cores provide "gold standard" assessment of microbial community structure (e.g., PLFA, 16S, DNA/RNA chip arrays, or functional chip arrays)
<i>In situ</i> redox status of U by direct sampling of <i>in situ</i> materials		U(IV)/U(VI) measurements on <i>in situ</i> sediments provide "ground truth" for U bioreduction
Time-Lapse Electrical Resistivity and Self Potential Tomography	NA	Can indicate the 3-D distribution of dominant TEAP's
Time-Lapse Seismic Tomography	NA	Sensitive to gas evolution and secondary mineral precipitation

Table 5.1. (contd)

Temporal Dimension of Monitoring Regime (see also flow chart in text)		
<i>Information area/parameter</i>	<i>Desired Range</i>	<i>Comments</i>
1st Year: monthly or bi-monthly sampling	NA	Sampling during early stage of treatment increases chance of capturing metal reduction phase
2nd and 3rd Year: bi-monthly sampling	NA	Adjustments to sampling frequency needed based on expected life of electron donor or other facets of treatment system
3rd through 10th year: quarterly sampling conditioned on water table behavior	NA	Seasonal and water table fluctuations should drive sampling schedule
Beyond 10 years, adaptive sampling based on prior year results	NA	If a high level of confidence can be demonstrated based on sampling over fewer than 10 years, adaptive sampling strategies could start earlier

NA = not applicable

It is recognized that uranium contamination in groundwater occurs in a variety of hydrogeologic settings and that some settings may be amenable to different priorities. For example, reclamation and clean up of sites where uranium has been mined by *in situ* leaching (ISL) may have a different set of issues and drivers than alluvial aquifers contaminated during uranium milling operations. ISL sites are commonly deeper than milling tailings sites, but have the advantage that existing wells and infrastructure can be used for cleanup and monitoring using geophysical techniques. ISL cleanup is commonly done abiotically by sweeping clean water through the system to dilute uranium concentrations followed by reduction by H₂S and additional pumping to remove residuals. Bioremediation could decrease cost and increase the effectiveness of treatment. Geophysical and biogeochemical monitoring is likely critical in such cases to demonstrate effective spatial distribution of treatment and achievement of desired results over appropriate time periods.

The most complete set of performance indicators will not be useful unless effectively analyzed and communicated to problem holders, regulators, and stakeholders. Visualization of the spatial and temporal changes in performance indicators is a particularly useful analysis and communication tool. Such visualization can be as simple as performance indicator versus time plots posted on a borehole map. Figure 4.4 shows the concentration of U(VI) in space for the Rifle site. A series of such plots are used to animate the visual evidence for U(VI) removal over a 3-month period for the 2002 Rifle field experiment. The animation illustrates key points about the change in U(VI) reduction at the onset of sulfate reduction.

Performance indicators are typically also used to update numerical modeling of the system. For example, if groundwater elevations indicate that permeability of the treatment zone is changing, different values of permeability can be input to the numerical model to assess the extent of change that is consistent with water table elevations. The updated model can then be used to assess the effectiveness of treatment and degree of rerouting of groundwater flow that may be occurring. Such assessments can also be used to estimate the value of additional monitoring points or to indicate that some monitoring point may no longer be cost effective to sample.

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