

# **PNNL SBR Scientific Focus Area Annual Report FY2010**

## **ROLE OF MICROENVIRONMENTS AND TRANSITION ZONES IN SUBSURFACE REACTIVE CONTAMINANT TRANSPORT**

### **1. Program Overview**

The PNNL Scientific Focus Area (SFA) is investigating fundamental Hanford subsurface science issues through integrated, multi-disciplinary, science-theme focused research on the role of microenvironments and transition zones in the reactive transport of technetium (Tc), uranium (U), and plutonium (Pu). Microenvironments are small domains within larger ones that exert a disproportionate influence on subsurface contaminant migration. They may be internal fractures or microbiologic niches within porous media lithic fragments; grain coatings, biofilms, or micro-colonies on larger mineral particles; or compact silt/clay stringers in gravel-dominated subsurface sediments. Transition zones are field scale features where chemical, physical, or microbiologic properties change dramatically over relatively short meter-scale distances. They exhibit steep, transport-controlled gradients of system-controlling chemical species such as O<sub>2</sub>, H<sup>+</sup>, or organic carbon. Microenvironments and transition zones can dominate subsurface contaminant reactivity, with strong effects resulting from the coupling of chemical reaction, physical transport (advection, diffusion), and microbiologic processes.

The overall goals of the SFA are to develop: i.) an integrated conceptual model for microbial ecology in the Hanford subsurface and its influence on contaminant migration, ii.) a fundamental understanding of chemical reaction, biotransformation, and physical transport processes in microenvironments and transition zones, and iii.) quantitative biogeochemical reactive transport models for Tc, U, and Pu that integrate multi-process coupling at different spatial scales for field-scale application. Targeted contaminant chemical reaction and biotransformation processes include heterogeneous/biologic electron transfer, precipitation and dissolution, and surface complexation. The SFA is emphasizing lab-based, coupled computational and experimental research using relevant physical/biologic models, and sediments and microbial consortia and isolates from multiple Hanford settings to explore molecular, microscopic, and macroscopic processes underlying field-scale contaminant migration. It will also pursue the refinement of geophysical and geo-statistical techniques to define, characterize, and map spatial structures, facies distributions, and reactive transport properties of microenvironments and transition zones in the field.

The SFA is partnering with the PNNL Environmental Molecular Sciences Laboratory (EMSL) to develop molecular understandings of key processes, and the Hanford Integrated Field Research Challenge (IFRC) for access to, and samples from subsurface environments where these zones exist and are important. The research program builds upon established areas of PNNL expertise in geochemistry, microbiology, and multi-scale modeling. Individual, but highly collaborative research projects are focused on different scales, coupled processes, and/or contaminants; each is managed by a PNNL-ERSP investigator of significant accomplishment and appropriate expertise. The projects fall in one of three scientific theme areas: 1.) molecular and microscopic electron transfer processes, 2.) pore scale reactive transport and up-scaling, and 3.) field scale microbial ecology and biogeochemistry. A new project was established in FY2010 to mentor a promising trio of new investigators. The PNNL research team is supplemented with 12 talented external investigators (lab, university) with complementary expertise. Cohesiveness and integration are achieved by close research coordination within theme areas, multi-scale modeling, and focus on a common field site where samples can be obtained and field experiments performed.

## 2. Scientific Objectives

Cross-cutting science themes were identified and developed in FY2010 to enhance meaningful collaboration between investigators and to strengthen scientific contributions along subject lines of critical importance to the SBR program. The theme topics were developed through a series of internal SFA workshops and each is now described by a short program plan assembled by coordinators. The theme areas will involve highly collaborative teams of PNNL and external researchers working toward common multidisciplinary scientific goals of high impact.

### **Theme Area 1: Molecular and microscopic electron transfer processes**

Scope: Molecular and microscopic studies of microbial and abiotic Fe(II/III) redox reactions in subsurface sediments, and their constitutive relationships to redox transformations of U(VI/IV), Tc(VII/IV), and Pu(IV/III). Interactive experiments and modeling using unique EMSL and DOE light-source capabilities are performed to elucidate the mechanisms and rates of bio-molecular and heterogeneous electron transfer processes and their implications to contaminant behavior in sediment systems.

Key Objectives:

- Identify and elucidate biomolecular electron transfer mechanisms of Hanford Fe(III)-reducing and Fe(II)-oxidizing microorganisms, and appropriate model systems, within context of Hanford mineralogy and with emphasis on interfacial biomolecule-mineral interactions.
- Determine the molecular basis for heterogeneous electron transfer reactions (reduction and oxidation) of U, Tc, and Pu on Fe-containing Hanford mineral materials assessing roles of surface structure, defects, and impurities; Fe(II/III) redox potential; surface oxidation or passivation; and contaminant molecular speciation.
- Iterate between experiments and modeling to propagate molecular scale understandings developed from model systems to microscopic systems containing mineralogically heterogeneous sediment particles.

### **Theme Area 2: Pore-scale reactive transport and upscaling**

Scope: Robust investigations of i.) pore-scale coupled physical, chemical, and biological processes that control the reactive transport of U, Tc, and Pu using novel modeling, experimental, and in-situ spectroscopic approaches, and ii.) the scale-dependence of geochemical and biogeochemical reactions in porous media (and models describing them) from the centimeter to meter-plus scale using flow-cell reactors, variable size columns with tomographic characterization of porous medium physical properties, and particle tracking and continuum models.

Key Objectives:

- Extend current pore-scale reactive transport theories and simulators by incorporating charge and species coupling, species-based interfacial geochemical reactions, and intra-grain reactive diffusion.
- Develop experimental approaches for observing pore-scale reactive transport processes and quantifying the properties and parameters controlling them; and use these measurements for theory, concept, and model validation.
- Establish theories for upscaling the rates of geochemical and biogeochemical processes for reactive transport modeling at different scales including the field that explicitly include evolving system properties (physical, chemical, and biological) and their statistics.

- Document the validity of physically-based upscaling theories by comparisons to reactive transport experimental data at increasingly higher scales leading to the field.

### **Theme Area 3: Field scale microbial ecology and biogeochemistry**

Scope: Investigations of coupled microbiological, geochemical, and physical/hydrologic processes controlling field scale microbial community structure and function, and causal connections between the identity and diversity within specific microbial functional groups and the biogeochemical processes that they mediate. The Hanford IFRC and local environs extending to the Columbia River are used as the primary study site.

Key Objectives:

- Define microbial community structure and biogeochemical processes across subsurface transition zones of different type (e.g., redox, facies with physical contrast, groundwater-river mixing) to identify effects of local chemical and hydrologic environment.
- Identify primary energy sources (e.g. electron donor/acceptor couples) and locations driving microbial metabolism and biogeochemical reactions across transition zones.
- Monitor in-situ biogeochemical processes rates at different scales and establish their relationships to microbial community structure and spatially/temporally variable hydrogeochemical fluxes.
- Assay phylogenetic and functional heterogeneity of subsurface microbial communities as a basis for interpreting in-situ biogeochemical processes and process rates.

### **3. National Laboratory Program Structure**

The PNNL SFA includes a Laboratory Research Manager (Dr. Harvey Bolton, Jr.), two chief scientists [Drs. John Zachara (PI) and Jim Fredrickson (PI)], and a core research team of technical leads, investigators, and post-docs. The investigator team evolves each year in response to research directions, scientific needs, new hires, and collaboration/publication/productivity issues. Additional discussions on staffing are provided in **Section 5**. The PNNL SFA staff is carefully selected and managed to attain the highest level of research excellence, collaboration, and publication quality possible.

Listed below are the key staff members for the SFA in 2010, their role, and the task or tasks they are responsible for.

Harvey Bolton, Jr., Laboratory Research Manager. Dr. Harvey Bolton serves as the management point of contact between PNNL/SFA and BER/ERSP. Dr. Bolton also ensures that the significant accomplishments of the SFA are relayed to PNNL management, and that BER guidance and scientific direction is properly relayed to SFA principal investigators.

John Zachara, Principal Investigator. Drs. Zachara and Fredrickson jointly manage the science portfolio of the SFA and are responsible for its scientific outcome. Dr. Zachara coordinates SFA activities with the Hanford Site and is responsible for assuring and managing site impact. He also facilitates all coordination with PNNL's Hanford IFRC, working toward synergy on field experiments performed by both projects. Dr. Zachara is the technical lead for the SFA project titled "Reactive Transport of U and Tc in Sediment Systems Containing Microenvironments and Transition Zones" which contributes to Theme Area 2. He collaborates with external investigators Davis and Brooks.

Jim Fredrickson, Principal Investigator. Dr. Fredrickson is the technical lead for the SFA project titled “Pore-Scale Biogeochemical Processes Controlling Contaminant Fate and Transport” and it’s interfacing with SFA companion projects and key external collaborators. Dr. Fredrickson coordinates microbial biomolecular and ecology activities to ensure integration with contaminant biogeochemistry research, and is a co-coordinator of Theme Area 3. He collaborates with external investigators Kemner and Roden.

Andrew Felmy. Dr. Felmy is the technical lead for the SFA project titled “The Chemical Form and Transformation Reactions of Plutonium and Uranium in Hanford Soils and Sediments” that is located within Theme Area 1. He has long experience in actinide chemistry research and thermodynamic modeling. He collaborates with external investigator Conradson.

Allan Konopka. Dr. Konopka is the technical lead for the SFA project titled “Microbial Ecology” and co-coordinator of Theme Area 3. He is responsible for the experimental design and interpretation of multiple types of analyses needed to define the complex microbial ecology of the Hanford vadose zone and saturated zone. He collaborates with external investigator Knight.

Mary Lipton. Dr. Lipton is technical lead for the SFA project “Proteome Analyses of Subsurface Microbial Systems” that is part of Theme Area 1 research.

Chongxuan Liu. Dr. Liu is the technical lead for the SFA project titled “Microscopic Mass Transfer of U and Tc in Subsurface Sediments” and co-coordinator of Theme Area 2. Dr. Liu has a unique combination of skills involving biogeochemistry, applied mathematics, and coupled reaction transport modeling at different scales. He collaborates with external investigators Ewing, Fendorf, and Wood.

Matt Marshall. Dr. Marshall is the technical lead for the SFA project titled “Biomolecular Studies of Microbiological Processes Controlling Contaminant Fate and Transport” that is located within Theme Area 1. He is an environmental microbiologist with significant experience in biological redox transformations of U and Tc. He collaborates with external investigator Löffler.

Jim McKinley. Dr. McKinley is a biogeochemist with significant field experience and expertise in electron microscopy. He is a key contributor to Theme Area 3 and is responsible for the design, deployment, and analysis of down-hole microcosms and multi-level samples placed in IFRC wells for SFA field biogeochemical studies.

Carolyn Pearce. Dr. Pearce is a new hire with expertise in molecular biogeochemistry, bio-mineralogy, and x-ray spectroscopy. She is a key contributor to the Rosso project in Theme Area 1, and is a Co-PI on a new young investigator project with Mike Wilkins and Changyong Zhang.

Tanya Peretyazhko. Dr. Peretyazhko is a new hire with expertise in soil chemistry and biogeochemistry. She is a key contributor to the Zachara project in Theme Area 2.

Kevin Rosso. Dr. Rosso is molecular geochemist and the technical lead for the SFA project titled “Molecular Scale Mechanisms of Biogeochemical Electron Transfer Underlying Subsurface U/Tc Valence Transformation and Stability”. He is also co-coordinator of Theme Area 1. He is responsible for scientific direction and coordination of all abiotic molecular scale studies, and for close collaboration with molecular scale, biochemical research performed in Theme Area 1. He collaborates with external investigator Blumberger (FY2011).

Timothy Scheibe. Dr. Scheibe is the technical lead for the SFA project titled “Multi-Scale Reactive Transport Modeling” and co-coordinator of Theme Area 2. In this role, Dr. Scheibe is collaborating with

multiple SFA laboratory projects investigating pore scale and macroscopic reaction and transport processes to develop robust coupled process models of porous media systems containing microenvironments and/or transition zones.

Liang Shi. Dr. Shi is the technical lead for the SFA project titled “Functional Characterization of Microbial Macromolecules” and co-coordinator of Theme Area 1. As a microbial biochemist, Dr. Shi is developing model macromolecular experimental systems and approaches to investigate electron transfer and other bio-directed reaction processes responsible for the biogeochemical transformations of Hanford contaminants. He actively collaborates with external investigator Richardson.

Andy Ward. Dr. Ward is the technical lead for the SFA project titled “Facies-based Characterization of Hydrogeologic Structures and Reactive Transport Properties” that is located within Theme Area 2. Dr. Ward is a soil physicist performing properties measurements, and developing geostatistical relationships and scaling laws for field-scale hydrogeologic and transport models.

Mike Wilkins. Dr. Wilkins is a new hire with expertise environmental microbiology and subsurface biogeochemistry. He also applies proteomics to investigations of natural microbial communities. He is an important contributor to the Konopka and Lipton projects, and is a Co-PI on the young investigator project with Carolyn Pearce and Changyong Zhang in Theme Area 2.

Changyong Zhang. Dr Zhang is a new hire with expertise in the design and synthesis of micro-models for pore-scale experimental research. He is an important contributor to the Liu project in Theme Area 2, and is a Co-PI on the young investigator project in Theme Area 2 with Carolyn Pearce and Mike Wilkins.

#### **4. Performance Metrics and Milestones**

Here we present research progress for 2010 and identify key objectives for FY 2011. Progress is given for each project funded in FY2010. In next year’s annual report we will move beyond a reporting structure based on individual projects, and provide integrative performance highlights for each of the three theme areas. The individual progress reports will be presented in theme area groupings: Theme Area 1 (Shi; Marshall; Lipton, and Rosso), Theme Area 2 (Liu; Zachara; Scheibe; Pearce, Wilkins, and Zhang; and Ward), and Theme Area 3 (Konopka; Fredrickson), although it should be pointed out that individuals may contribute at various levels to one, two, or all three theme areas.

##### ***4.1 Performance Metrics***

Our primary performance metrics are publications that distribute our findings and accomplishments to the scientific community. In FY2010 we submitted or published 48 papers (Appendix A). SFA staff also gave 47 presentations or posters at programmatic and national scientific venues (Appendix A).

##### ***4.2 FY2010 Individual Project Summaries***

The individual project investigators have provided the following summaries of their research.

## Functional Characterization of Microbial Proteins Involved in Biogeochemical Electron Transfer Reactions

Principal Investigator: L. Shi

Internal Participants: S. Belchik (Post-doc), Z. Wang, D.W. Kennedy, M.J. Marshall, K.M. Rosso, J.M. Zachara and J.K. Fredrickson

External Collaborators: D.J. Richardson (UEA)

### Project Summary

A molecular-level understanding is being developed of key microbial protein-mediated Fe(II/III) redox reactions in the subsurface and their constitutive relationships to redox transformation of U(VI/IV), Tc(VII/IV), and Pu(IV/III) as part of Theme Area 1 research. The redox proteins of Hanford-derived and model microorganisms are being investigated using complementary laboratory experiments and modeling to elucidate the electron transfer (ET) reactions that affect the availability and supply of reactive Fe(II). The results of these studies will contribute to resolution of PNNL SBR SFA hypotheses pertaining to the role of subsurface microenvironments and transition zones as dominant regions of contaminant oxidation-reduction reactions at Hanford.

In FY2010, we characterized UndA-HRCR-6, a *c*-type cytochrome (*c*-Cyt) isolated from a *Shewanella* strain collected from the Hanford Reach of the Columbia River (HRCR). The purified UndA-HRCR-6 contained 11 hemes and exhibited reductase activity toward Fe(III)-citrate, -NTA and -EDTA. In vivo, UndA-HRCR-6 complemented the impaired phenotype of a *S. oneidensis* MR-1 mutant lacking MtrC and OmcA in both Fe(III) oxide- and U(VI)-reduction assays. In *S. oneidensis* MR-1, the recombinant UndA-HRCR-6 was translocated across the bacterial outer membrane (OM) by the type II secretion system. Collectively, these results indicate that UndA-HRCR-6 most likely has a functional role(s) in extracellular metal reduction.

To understand how electrons are translocated across bacterial OM, a trans-OM icosaheme complex, MtrABC of *S. oneidensis* MR-1, was characterized by Richardson's group. The MtrABC complex transferred electrons across a lipid bilayer after incorporation into proteoliposomes. A model is proposed for the modular organization of the MtrABC complex in which MtrC is an extracellular element that mediates ET to extracellular substrates, and MtrB is a trans-OM spanning  $\beta$ -barrel protein that serves as a sheath to embed the MtrA subunit in the membrane where it forms a trans-membrane electron delivery module that services MtrC. This is the first molecular model of electron translocation across the bacterial OM. Comparative genomics suggests this may be a general model applicable to other Gram-negative bacteria.

Structural determination of MtrF (an MtrC homologue) of *S. oneidensis* MR-1 revealed a quadri-directional ET junction that could equip the protein for three possible functions: direct ET to Fe(III) oxide; ET to flavins or soluble metal complexes; and/or multi-cytochrome complexes that could contribute to long distance ET. Electrons entering the junction could either flow onto the solvent exposed heme terminus on the surface of the protein, enabling direct ET to a mineral substrate or a cytochrome redox partner, or branch to the  $\beta$ -barrel domains where reduction of electron shuttles, such as flavins, could be envisaged. In collaboration with the Rosso SFA project, we measured the direct ET between purified OM *c*-Cyt OmcA and hematite with cyclic voltammetry. Investigation of microbial proteins involved in extracellular oxidation of Fe(II) is also being initiated.

Research in FY2011 will involve: i) crystallization trials of UndA-HRCR-6, ii) structural determination of MtrA and the MtrABC complexes, iii) imaging the orientation of MtrABC complexes in liposomes, iv) measurement of protein film voltammetry of MtrABC in liposomes, v) the determination of the electron transfer rate between MtrF and hematite, and vi) purification and characterization of microbial proteins involved in extracellular oxidation of Fe(II).

## Proteome Analyses of Subsurface Microbial Systems

Principal Investigator: M.S. Lipton

Internal Participants: H. Zhang, M. Wilkins, L. Shi, A. Konopka, M. Marshall

### Project Summary

Advanced proteomics techniques are being applied to understand the biochemical function of microorganisms that are important to subsurface radionuclide fate and transport at Hanford. Insights will be provided on the mechanisms of electron transfer for both model and Hanford-derived microorganisms, cell surface proteins and protein complexes will be identified that interact with the environment and other microbes, and heme moieties will be characterized that play important roles in extracellular electron transfer.

Proteomic characterization represents a powerful technology to elucidate the relevant biological processes when microbes and their communities interact with sediments and metal contaminants. We will use four different proteomic techniques: 1) global analysis of protein complements of lab strains and isolates from the Hanford subsurface, 2) specific labeling and identification of cell surface proteins, 3) selective enrichment of heme-containing proteins, and 4) protein cross-linking techniques to determine protein interaction areas. These measurements will support the characterization of the *S. oneidensis* MR-1 MtrDEF complex in the near term, and Hanford-derived iron reducing and iron oxidizing microorganisms after organism characterization and genomic sequencing.

The proteomic research is contributing to multiple scientific theme areas. Proteomic analysis will be used for the characterization of *Shewanella* strains isolated from the Hanford Reach of the Columbia River (HRCR) in collaboration with Marshall in Theme Area 1. These analyses will also include cell surface labeling and surface protein identification performed in collaboration with Shi in Theme Area 1 to further understanding of the workings of UndA-HRCR-6, an outer membrane 11-heme *c*-type cytochrome (*c*-Cyt) associated with a metal-reducing *Shewanella* strain isolated from Columbia River near-shore sediments. Proteomics measurements will also be an important component to Theme Area 2 (with Zhang, Pearce, and Wilkins) where studies of *Geobacter sulfurreducens* are planned in micro-models with different pore and aggregate structures.

A key accomplishment for FY2010 was the development of an analytical procedure to identify proteins that are present on the cell surface, including *c*-type cytochromes. Proposed research for FY2011 will begin with the specific labeling and identification of cell surface proteins on *S. oneidensis* MR-1, as a documentation example, with follow-on analyses performed on the HRCR isolates. Additionally, we will work with Shi on the characterization of the MtrDEF and UndA-HRCR-6 complexes, including the identification of interaction areas that may be involved.

## **Biomolecular Studies of Microbiological Processes Controlling Contaminant Fate and Transport from Hanford 300 Area**

Principal Investigator: M.J. Marshall

Internal Participants: O.V. Geydebrekht

External Collaborators: F.E. Löffler (UT), E. Roden (UWM)

### Project Summary

Microorganisms are being cultivated from and characterized from the Hanford 300A subsurface with potential for directly or indirectly influencing contaminant speciation and/or mobility as part of Theme Area 1 research. The project objectives are to identify the characteristics of functionally active organisms from Hanford capable of biogeochemical transformations of metals and radionuclides. Characteristics of interest include phylogeny, physiological properties including biotransformation of metal and Hanford-relevant mineral phases, and the production of putative terminal reductase proteins in order to better understand potential biological processes influencing contaminant mobility. A series of enrichment cultures were established using either sediment or groundwater from the Hanford 300A IFRC.

Subsurface sediment samples from the aerobic Hanford formation, the underlying Ringold oxic/anoxic transition zone, and the deep Ringold formation were added to a series of microcosms to isolate relevant microorganisms which are able to reduce Fe(III)-oxides. Isolation of indigenous Fe(III)-reducing microorganisms from groundwater has also been initiated using colonized BioSep beads deployed in two Hanford IFRC wells as the inoculums for enrichment cultures. Fe(III) enrichment cultures were transferred into a defined medium based on Hanford 300 Area groundwater geochemistry and amended with a synthetic Fe(III)-oxide as an electron acceptor and one of fourteen different electron donors.

The project collaborates with Lipton for proteomic characterization of microbes and microbial communities; Shi for biomolecule purification, characterization, and assessment of molecular pathways for reduction and oxidation of iron; Konopka for molecular analysis of community composition; and Fredrickson for understanding the nature and rates of biogeochemical processes. External collaborations are underway with Löffler involving isolation and characterization of Fe(III)-reducing microorganisms; and Roden for isolation and characterization of Fe(II)-oxidizing microorganisms.

From our enrichment studies, we have determined that three organic acids and four alcohols were electron donors supporting the reduction of Fe(III)-oxide and that responsiveness to the suite of electron donors varied between the enrichments initiated from the three different sediment strata. Fe(III)-oxide reduction also appeared to be influenced by the presence of sulfate, a component of Hanford groundwater. It appears that microbial sulfate reduction may have contributed to the abiotic reduction of Fe(III) by biogenic sulfide. Currently, we are analyzing the enrichments to determine the genetic diversity and to narrow the number of Fe(III)-reducing cultures on which to focus isolation and characterization efforts. Additional cultures of Fe(III)-reducing organisms will also be obtained through the Löffler and Roden SFA collaborations for genetic diversity screening.

Physiological and genetic analysis of selected metal-biotransforming isolates from Hanford will begin in FY2011 using relevant metal-containing mineral phases and/or radionuclides. We also anticipate that selected Hanford microorganisms will be submitted for genome sequencing to JGI's small scale microbial genome sequencing program to facilitate proteomic and functional gene analyses.

## **Molecular-Scale Mechanisms of Biogeochemical Electron Transfer Underlying Subsurface U/Tc Valence Transformation and Stability**

Principal Investigator: K.M. Rosso

Internal Participants: C.I. Pearce, J. Liu, O. Qafoku, L. Shi, T. Droubay, P. Zarzycki, A.R. Felmy, F.N. Skomurski, R. Kukkadapu, J. Fredrickson

External Collaborators: S. Heald (APS), E. Arenholz (ALS), D. Richardson (UEA), J. Blumberger (UCL), A. Navrotsky (UC Davis)

### Project Summary

Research is developing a molecular-scale understanding of key microbial and abiotic Fe(II/III) redox reactions in the subsurface, and their controls on the redox transformation of Tc and U as part of Theme Area 1 research. One objective is to understand rates and molecular mechanisms used by Hanford relevant microorganisms for mediating extracellular redox transformation of Fe. Another is to understand rates, mechanisms, and molecular-level characteristics controlling heterogeneous redox transformations of Tc and U catalyzed by Fe(II)-bearing solids.

Several important scientific questions motivate our research. How do microbial electron transfer biomolecules such as *c*-type cytochromes interface with and achieve molecular configurations that enable facile electron exchange with solid phase Fe-containing minerals? What molecular-scale characteristics of mineral-water and mineral-microbe interfaces control reaction potential and extent, such as mineral surface structure, defects, impurities, surface oxidation, or surface passivation? The research approach entails laboratory experiments, Hanford IFRC down-well field experiments, spectroscopic and microscopic characterization, and computational molecular modeling. This project makes use of well characterized and controllable microbial and mineralogic model systems to elucidate fundamental biogeochemical mechanisms.

Internal collaborations occur with Shi for biomolecule purification, characterization, and assessment of molecular pathways for reduction and oxidation of iron by model and Hanford-derived microorganisms, and Fredrickson for down-well experiments at the Hanford IFRC site involving exposure of model mineral structures to Hanford microenvironments and microorganisms. External collaborators include Richardson for biomolecule structure and characterization, Blumberger for biomolecule electron transfer modeling, E. Arenholz for XMCD spectroscopy, S. Heald for XANES/EXAFS spectroscopy, and A. Navrotsky for thermochemistry.

Key FY2010 findings and scientific accomplishments include mechanistic understanding of heterogeneous Tc(VII) reduction kinetics by model Fe(II)-bearing metal oxides (titanomagnetites) of varying built-in structural Fe(II) content, and the dynamics of structural Fe(II) oxidation by aqueous oxidants such as dissolved oxygen and hydrogen peroxide. IFRC downwell experiments exposing these model oxides to reduced and oxidized horizons for several months show systematically varying attached microbial populations. Molecular modeling was used to examine possible incorporation mechanisms of Tc in iron oxide and to estimate rates and reduction extent of U(VI) by magnetite. Modeling has begun to simulate the structure, charging, and electron transfer kinetics within the outer-membrane cytochrome MtrF. This project also successfully acquired substantial beam-time at the ALS and APS through competitive user proposals. Proposed FY2011 research includes study of the competitive structural Fe(II) oxidation kinetics in our model oxides by dissolved oxygen and Tc(VII), and oxidation by model outer-membrane terminal oxidase cytochromes.

## **Plutonium and Uranium Speciation in Hanford Sediments and Redox Transformations Induced by Fe(II)**

Principal Investigator: A.R Felmy

Internal Participants: E.S. Ilton

External Collaborator: S.D. Conradson (LANL)

### Project Summary

The overall objective of this project is to provide knowledge on the different chemical forms of Pu and U in Hanford sediments and how these different chemical forms respond to changes in redox conditions driven by Fe(II). Research is investigating several key questions. What influence does the formed Fe(III) reaction product have on the solubility and further reactivity of Pu and U compounds? What is the mechanism of reaction of aqueous Fe(II) at the surface of insoluble Pu(IV) compounds found at Hanford? Specific activities include: 1) obtaining and archiving samples from field studies of Pu and U contamination at Hanford, 2) detailed molecular level characterization of the chemical form of Pu and U in the sediments, and 3) experimental laboratory studies of the transformations of these different chemical forms in response to changes in the chemical form of Fe(II).

Sediment samples from two different Pu-containing locations (Z-9 and Z-12 cribs) and as a function of depth have been obtained and archived from the Hanford 200 west area. XAFS characterization of these materials shows that the chemical form of Pu changes between different location and as a function of depth in the sediments. For example, at Z-9 the surface sediments are dominated by the presence of  $\text{PuO}_{2+x}$  which was either formed by contact of the acidic waste solutions with the sediments or directly released by Z-plant operations. However, the surface sediments at the Z-12, which did not receive the same acidic waste, do not show the presence as  $\text{PuO}_{2+x}$ . Instead, Pu at Z-12 appears to be present either as a monomeric form or as a disordered solid phase. The deep subsurface sediments at Z-9 also do not show the Pu-O or Pu-Pu distances characteristic of  $\text{PuO}_{2+x}$ , clearly showing a change in chemical form with depth. Thermodynamic modeling calculations of the solubility of  $\text{PuO}_{2+x}$  reveal potentially large changes in solubility depending upon both the nature of the initial Fe(II) present and the nature of the Fe(III) reaction product. New thermodynamic data have also been obtained for potentially important U and Pu containing compounds in Hanford soils and sediments.

Sediment samples from the deep subsurface are undergoing additional characterization by both XAS, NanoSIMS (via A. Kersting (LLNL), and other methods to gain further insight into the changes in the chemical speciation of Pu and U in Hanford sediments. Studies have also been initiated on the redox transformation of  $\text{PuO}_{2+x}$  with Fe(II) focusing on the influence of the iron reaction products. In FY 2011 we will examine changes in  $\text{PuO}_{2+x}$  solubility influenced by the formation of aqueous Fe(III), ferrihydrite, goethite, and hematite.

## **Microscopic Mass Transfer of U and Tc in Subsurface Sediments: Multispecies U(VI) Reactive Diffusion in Connectivity-Restricted Pore Domains**

Principal Investigator: C. Liu

Internal Participants: S. Kerisit, J. Shang (Post-doc), J.M. Zachara

External Collaborators: R. Ewing (ISU), S. Fendorf (SU)

### Project Summary

Research is investigating the coupling of chemical/microbiological processes with diffusion driven transport at the grain scale as part of Theme Area 2 research. Key objectives are to: i.) characterize and model reactive diffusion of Tc and U at the pore and grain scale, ii.) understand the molecular interactions controlling microscale behavior, and iii.) derive porous media scaling relationships of mass transfer and reaction parameters from the molecular to the continuum scales. An important goal is to understand how the coupling of microscopic mass transfer and geochemical/ biogeochemical reactions affect mass transfer and reaction rates at the macroscopic scale and above. The research uses experimental and numerical approaches at the molecular, pore, batch, and column scales. Internal collaborations occur with Zachara and Fredrickson through investigations of U and Tc biogeochemical reaction and transport in subsurface sediments of different textural fractionation, experimental scale, and degree of natural structuring. External collaborations occur with Ewing to investigate apparent grain-scale diffusion coefficients as a function of temporal scale; and with Fendorf to investigate pore-scale coupling of diffusion and redox reactions in Hanford sediments.

Significant new findings from FY2010 research are as follows.

- U(VI) diffusion coefficients for different uranyl species differ by a factor of 2 as revealed by molecular simulations. A diffusion model with a single diffusion coefficient was sufficient to describe the diffusion of multiple interactive uranyl species under constant chemical conditions, but not under transient chemical conditions. Pore and continuum scale simulations indicated that a multi-species diffusion model can be approximated by a multi-component diffusion model. The latter model only considers the difference in diffusion coefficients between chemical components, but not between the species within each chemical component. The multi-component treatment significantly enhances computational efficiency at the expense of minor charge conservation.
- A grain-scale reactive diffusion model can describe U(VI) adsorption/desorption kinetics in intragrain regions of natural sediment. However, intragrain pore connectivity can effect on the apparent grain-scale diffusion coefficient, and thus the rate of grain-scale U(VI) adsorption. The estimated apparent grain-scale diffusion coefficient decreased with increasing diffusion time as U(VI) adsorbs to or desorbs from increasingly connectivity-restricted intragrain pore domains.
- Stirred-flow and column experiments indicated that the apparent rate of U(VI) adsorption increased with increasing observation scale, an opposite trend as compared to U(VI) desorption.

Research in FY2011 will follow three primary lines. A challenging campaign will be initiated to determine how pore constrictively affects uranyl speciation, reactivity, and diffusivity in intragrain regions. Second, multi-scale experiments will be performed to investigate the scale-dependence of intragrain U(VI) diffusion coefficients in microporous sediment systems exhibiting kinetic surface complexation reactions. Lastly, pore-scale studies of coupled diffusion and redox reactions will be performed using low-permeability Ringold formation sediments from the Hanford IFRC (in collaboration with Zachara and Fredrickson).

## Reactive Transport Modeling

Principal Investigator: T.D. Scheibe

Internal Participants: A. Tartakovsky, G. Tartakovsky, M. Richmond, W. Perkins, B. Palmer, E. Ryan

External Collaborators: B. Wood (OSU)

### Project Summary

Pore-scale reactive transport models are being developed and applied in Theme Area 2 to understand coupled processes controlling subsurface chemical migration and for upscaling. Our objective is to provide a quantitative basis for prediction of macroscopic (e.g., column to field) scale behaviors based on microscopic (cell to pore) scale information. Our integrated contribution to the SFA is to define processes/parameters for reactive transport of uranium in Hanford Site sediments based on pore-scale modeling. The individual science contribution is to study surface complexation and dissolution, and intragranular diffusion at the pore-to-continuum scale. Research addresses several important upscaling questions. Can column transport observations be explained by diffusion-limited mass transfer into secondary porosity with small volume (thus insignificant impact on bromide transport) but large adsorptive capacity (thus kinetically controlling uranium transport)? Does the microscale topology of the secondary porosity matter, or can the upscaled behavior be quantified by simpler metrics.

Research involves five primary elements. i.) Define representative pore-scale geometry (by direct measurement and/or synthetic generation). ii.) Define quantitative microscale process descriptions (e.g., Navier-Stokes for flow, convective-diffusive transport, etc.). iii.) Implement pore-scale numerical models using SPH and CFD methods and perform pore-scale simulations. iv.) Develop upscaling theory that defines important integral measures of effective properties (e.g., sorption rates, mass transfer coefficients) and macroscale equations. v.) Test alternative upscaled representations against complete pore-scale simulations to determine which scaling approximations are valid and to identify those critical characteristics that prescribe upscaled behavior. This project is part of the SFA Theme 2. We rely on pore-scale geometric descriptions and column experimental data (Zachara), and process definitions from microscopic, batch, and column experiments (Liu/Zachara). Upscaling theory development and evaluation is in collaboration with Wood.

In FY2010 we implemented intragranular diffusion in our 3D parallel SPH code. SPH methods for modeling adsorption and microbial iron reduction processes were developed and tested in 2D. These methods are now being implemented in the 3D code. We completed studies of dispersion under inertial flows using the wavy tube model (CFD) and are writing up the results. We successfully tested the numerical volume averaging method using CFD, and are now initiating efforts to perform large pore-scale simulations using pore geometry measured by XMT on column sediments.

We will complete implementation of adsorption process in the 3D SPH code during FY2011, and will perform comparative tests of SPH and CFD simulations. We will develop upscaling theory for coupled adsorption and intragranular diffusion that addresses the key questions above, and perform pore-scale simulations on large 3D domains to test scaling approximations.

## Reactive Transport of U and Tc in Sediment Systems Containing Microenvironments and Transition Zones

Principal Investigator: J.M. Zachara

PNNL Participants: T. Peretyazhko, M. Oostrom, C. Liu, C. Pearce, and J. McKinley

External Collaborators: J.A. Davis (USGS), S. Brooks (ORNL)

### Project Summary

Macroscopic-scale studies of U(VI) and Tc(IV/VII) reaction and advective transport are being performed with Hanford Site sediments from different vadose and saturated zone locations in the Columbia River corridor (e.g., 300 A IFRC) and the 200 A plateau as part of Theme Area 2 research. Major goals are to understand and model kinetic processes controlling Tc and U solid-liquid distribution and associated transport in sediments with complex or variable geochemical or mineralogic conditions, and in-situ structures and heterogeneities. A key research objective is to understand the implications of scale transitions on geochemical reactivity, with emphasis on the role of intra-grain or intra-aggregate diffusion and reaction on higher scale transport behavior. Results and models are to be up-scaled to field systems, such as the Hanford IFRC, where field-scale measurements of migration are on-going and models can be tested. Research emphasis is placed on experimental studies of coupled, non-linear processes including geochemistry, hydrology, and microbiology; application of x-ray tomographies with different scale resolutions to define in-situ structures and reaction domains; and multi-component kinetic modeling for interpretation and system scale conceptual model development. Strong interactions occur with SFA projects investigating molecular (Rosso), thermodynamic (Felmy) and pore scale processes (Liu and Fredrickson), and reactive transport models (Scheibe), as well as with the Hanford IFRC.

Two primary research directions have been followed in FY 2010: i.) understanding the magnitude and causes for kinetic parameter change (U adsorption-desorption rate and site distribution) with movement from the grain to Darcy scale (an upscaling issue) using stirred reactors and intact sediment columns, and ii.) developing a mechanistic kinetic model for Tc(VII) reduction and Tc(IV) oxidation in presence of complex biogeochemical Fe(II) forms of different physical structure, composition, and mineralogy sampled from a subsurface redox transition zone. Important findings are as follows.

- Rate constants measured for U(VI) adsorption-desorption on < 2 mm sediment in flow-through reactors were one-two orders of magnitude slower than for an intact sediment column containing these same materials as the reactant diluted amongst coarse gravel. A scaling relationship that involves rate constant dependence on fine particle concentration is the only apparent explanation.
- Redox reaction rates of Tc in transition zone sediments of common mineralogic provenance show extreme variation associated with changes in minor phase Fe(II) speciation as determined by Mössbauer spectroscopy. Kinetic redox reactivity was much higher in sediments with historic evidence for biologic Fe(III) reduction (e.g., presence of biogenic siderite), than in sediments with current sulfate reduction and pyrite formation.

FY 2011 research will pursue more detailed hypotheses along these two research lines. In (i) we will perform batch and column kinetic experiments with the isolated <2 mm materials over a range of conditions (solid concentration and flow rate) and apply reactive transport modeling to evaluate the causes of scale dependence. In (ii) we will measure reaction rates between molecular oxygen and the transition zone sediments to correlate abiotic reaction rates observed for Tc(VII) and Tc(IV) with O<sub>2</sub>, and develop a generalized kinetic model that relates redox reactivity to specific Fe(II) biogeochemical speciation forms and their concentrations. We also anticipate the receipt of a highly valuable set of core materials from Hanford's 200 A where an acidic waste stream containing U has migrated to great depth in the vadose zone. The core materials will be subject to many measurements to establish U speciation and mineral association, and to flow-reactor and column experiments to assess release rates, extent, and geochemical controls.

## **In-situ Structures and Reactive Transport Properties**

Principal Investigator: A.L. Ward

Internal Participants: N. Hasan (Post-MS), K.E. Draper, W.J. Greenwood, C.E. Murray, A. Tartakovsky, Y. Xie

External Collaborators: T. Johnson (INL), R.J. Versteeg (Sky Research, Inc.)

### Project Summary

Robust petrophysical relationships are being developed as part of Theme Area 2 research for predicting flow and reactive transport properties in heterogeneous, unconsolidated, variably saturated porous media such as those at the 300 Area IFRC. The key research question is whether local-scale petrophysical properties can be predicted and subsequently upscaled using grain size moments. A combination of laboratory, field, and pore-scale measurements and modeling activities were used to achieve our objective. Our initial hypothesis was that petrophysical relationships could be developed entirely on grain size diameter and sorting index and this was evaluated using spectral gamma data collected in the laboratory and field.

Over 200 IFRC sediment samples and model mineral mixtures were analyzed to characterize particle size distributions, gamma energy response, mineralogy, surface electrical conductivity, and hydrophysical properties for correlation with field measurements. A comparison of several multivariate methods, including multiple linear regression, classification and regression trees (CART), partial least squares (PLS), multivariate adaptive regression splines (MARS), and neural networks (NN) showed MARS and NN to be the most robust methods for interpreting this data set. Detailed analysis of size separates using scanning electron microscopy and Rietveld refinement of x-ray diffraction patterns showed clay to be present in almost all size fractions. This observation, plus the very strong  $^{232}\text{Th}$ -clay ( $r^2=0.95$ ) relationship indicated that a robust petrophysical relationship, applicable to both Hanford and Ringold formations, could be based on clay content. Petrophysical relationships based on clay content were also derived for specific surface area ( $r^2=0.89$ ), cation exchange capacity ( $r^2=0.92$ ), porosity ( $r^2=0.90$ ), and surface electrical conductivity ( $r^2=0.98$ ) affirming the generality of the approach. Three-dimensional distributions of hydraulic, physical, and geochemical properties can now be derived from borehole spectral gamma logs.

Broadband (.001-1000 Hz) electrical experiments to characterize IFRC sediments are in progress at INL that will be completed by year-end. Results thus far show distinct electrical signatures associated with different facies, which will assist in the translation of electrofacies mapped through the Hanford IFRC site into lithofacies to be used in modeling. Additionally, measureable laboratory responses were observed for the migration of tracers (ionic, heat) at typically used field concentrations which will support quantitative interpretation of field experiments monitored by geophysical methods. Fitting of existing empirical models to the data give rise to parameters (effective particle diameter, surface area to pore volume ratio) that are consistent with published values. A PNNL-developed pore-scale model of broadband properties correctly predicted the electrical response using known clay content and particle size distributions. These results validate the consistency of the approach and provide a basis for investigating the effects of several system parameters on the electrical response for providing new insights into constitutive relationships for use at the field scale.

## **Pore-Scale Investigation of Microenvironments and Coupled Physical and Biogeochemical Processes Controlling Contaminant Reactive Transport**

Principal Investigators: C.I. Pearce, M.J. Wilkins, C. Zhang  
External Collaborators: S. Heald (ANL)

### Project Summary

Biogeochemical reactions at transition zones and within microenvironments, coupled with physical process (i.e., advection, diffusion) play a significant role in the cycling of both dominant terminal electron acceptors such as Fe(III), and contaminant metals such as U and Tc. Our Theme Area 2 research objective is to understand these biogeochemical and physical processes and how they affect contaminant reactive transport at the pore scale. The research approach involves the use of microfluidic pore structures etched into silicon (i.e., micro-models) to control and measure physical, chemical and biological conditions at the pore-scale. We investigate how the fate and transport of U(VI) and Tc(VII) are affected by (i) bacterial growth and distribution in transition zones (e.g. oxic/anoxic interface), (ii) Fe-bearing mineral precipitation in pore structures representing different microenvironments, and (iii) bacterial growth on structured Fe-bearing mineral surfaces (e.g. hematite).

To date, we have used photolithography to fabricate micro-models with a range of pore structures and multiple inlet/outlet ports. We have shown that the micro-model surface can be modified by sputter coating with iron oxide and confirmed the presence of a hematite surface coating (XANES, XRD) with a surface roughness of ~70nm (AFM). Using micro-models with multiple inlets/outlets, we have generated geochemical gradients between aerobic/anaerobic zones, and between high and low electron donor/acceptor zones, and demonstrated that the extent of mixing between different zones can be governed by controlling flow rate. We have conducted micro-model experiments to study the growth of an anaerobic Fe(III)-reducing bacteria, *Geobacter sulfurreducens*, across both an oxic/anoxic interface, and across a gradient of varying electron donor and acceptor concentrations. Growth has been demonstrated in pore spaces of 180  $\mu\text{m}$  via light and fluorescence microscopy, while effluent geochemistry has shown the complete consumption of electron donor (acetate) across the anaerobic zones. We are simulating Fe-cycling in the micro-model by creating a mixing zone between aerobic and anaerobic groundwater containing aqueous Fe(II). The effect of oxidation and precipitation of mixed Fe(II)/Fe(III) oxide phases on microbial growth and contaminant transport will be monitored. We are using the hematite-coated micro-model to study the impacts of pore-scale Fe(III) reduction on biomass growth and contaminant reactive transport.

During our APS beam-time (July 2010), we will use the X-ray microprobe capabilities on ID20 to analyze the structure and distribution of mixed Fe(II)/Fe(III) oxide phases, and the subsequent microbial reductive dissolution of these phases, on a 5  $\mu\text{m}$  scale. We will also investigate the localization and redox state of uranium in micro-models where simulated U(VI)-containing groundwater has been introduced. This will allow us to determine whether biosorption of U(VI) or reduction of U(VI) to U(IV) occur in regions of reduced flow due to accumulation of biomass. Research in FY2011 will focus on the proteogenomic signatures (in collaboration with Lipton) of biomass grown within the micro-model. It is hypothesized that a comparison of these signatures between micromodel-grown cells and planktonic biomass from static batch cultures will reveal proteins important in the attachment to mineral surfaces, and other proteins involved in subsurface growth. Finally, we will enrich key bacterial species from Hanford groundwater using micromodels. By flowing groundwater through an Fe(III)-coated micromodel, we aim to enrich strains that carry out Fe(III)-reduction in the Hanford subsurface. Subsequent molecular analysis of enriched biomass will aid the identification of such species.

## Microbial Ecology: Structure and Function of Subsurface Microbial Communities

Principal Investigator: A.E. Konopka

Internal Participants: X. Lin (Post-doc), A.E. Plymale, D.W. Kennedy, M. Lipton, J.-H. Lee.

External Collaborators: R. Knight (UC)

### Project Summary

The objectives of this Theme Area 3 project are to: (a) carry out a census of Hanford subsurface microbial communities and (b) employ experimental manipulations of microbial communities under simulated natural conditions or *in situ*, to determine the rates of microbial processes and elucidate their limiting factor.

The initial project approach has been weighted toward in-depth molecular ecology analyses of organisms present in the subsurface. This has included analyses of both phylogenetic (small subunit ribosomal RNA via full-length and pyro-sequencing) and functional gene markers in DNA extracted from subsurface sediments (provided by Hanford IFRC). We have initiated in-situ incubation experiments in which the natural microflora colonize deployed substrata. We are developing flow cytometric approaches to identify and sort metabolically-active microbes for subsequent characterization.

Twenty-one sediment samples were analyzed from the Hanford 300 Area, from depths that ranged from 9 to 52 m. Microbial biomass was within a range of  $1\text{-}274 \times 10^5$  per g, with the highest numbers found in the Hanford formation. Approximately 8000 non-chimeric Bacterial and Archaeal 16S rRNA gene sequences were analyzed across geological strata that contained a natural redox transition zone. We detected 1233 and 120 unique bacterial and archaeal OTUs (Operational Taxonomic Units). Microbial community structure and richness varied substantially across the different geological strata. Bacterial OTU richness was highest (>700) in the upper Hanford formation, and declined to about 120 at the bottom of the Hanford formation. The Bacterial community in the oxic Hanford and Ringold Formations contained members of 9 major well-recognized phyla as well as unusually high proportions of 3 candidate divisions (GAL15, NC10, and SPAM). The deeper Ringold strata were characterized by low OTU richness and a very high preponderance (ca. 90%) of Proteobacteria. These subsurface sediments have been shown to contain a large number of phylogenetically novel microbes, with substantial heterogeneities between sediment samples from the same geological formation. High abundances of a denitrification gene marker (*nosZ*) were found below 18.3 m and most were affiliated with *Ochrobactrum anthropi*. A sulfate reducer gene marker (*dsrA*) was most abundant in Ringold sediments near the interface with the Hanford formation.

In FY2011, we will complete analysis of the spatial and temporal heterogeneities in groundwater community composition, via pyrosequencing analysis of 16S rRNA genes, in samples collected twice weekly from 9 Hanford IFRC wells (3 depths X 3 spatial clusters), over a 5 month period. We are collaborating with the Fredrickson project to carry out analysis of microbial activity rates, both in situ and in column studies. We will also finalize development of our flow cytometry protocols and deploy them to identify (and physically enrich) metabolically-active microbes; these data will be invaluable in collaborating with those engaged in molecular-scale biogeochemical research.

## **Pore- and Field-Scale Biogeochemical Processes Controlling Contaminant Fate & Transport: Characterization of Biogeochemical Redox Transformations in Hanford 300 Area Subsurface Sediments**

Principal Investigator: J.K. Fredrickson

Internal Participants: J.-H. Lee (Post-doc), A.E. Plymale, D.W. Kennedy, A. Dohnalkova, X. Lin, R. Kukkadapu, C.T. Resch, D. Moore

External Collaborators: E. Roden (UWM), K. Kemner (ANL), S. Heald (ANL), H. Beyenal (WSU via independent SBR project)

### Project Summary

This SFA research is defining the nature and distribution of biogeochemical processes in Hanford's near river shore unconfined aquifer in the 300 A. Important objectives are to: i.) determine the potential for native microbes to utilize various terminal electron acceptors (EAs: oxygen; nitrate; ferric iron; sulfate) present in groundwater and associated sediment, and ii.) assess the identity, rates, and reaction products of U & Tc biogeochemical redox reactions. Research utilizes sediments and groundwater from the Hanford 300A IFRC (coarse Hanford formation, and fine-grained Ringold Formation) in batch and column laboratory experiments, and down-hole microcosms deployed in the IFRC well-field. Advanced spectroscopies and microscopies (EMSL, APS) are used to probe biogeochemical reaction products.

In FY2011, Hanford formation sediment was incubated with and without sulfate at a concentration equivalent to that in 300A groundwater (0.63 mM). Biogenic reduction of sediment Fe(III) was faster with sulfate than without, suggesting that reduction was facilitated by abiotic reaction with biogenic sulfide. The heat-treated sediments did not show any obvious Fe reduction either with or without sulfate. Fine-grained Ringold oxidized and reduced sediments did not exhibit Fe or sulfate reduction under the specific experimental conditions. Sulfate was reduced in Hanford sediment and the sediment-associated sulfide accounted for 63% of the initial sulfate-sulfur. Mössbauer analysis revealed that changes in native Fe were subtle; and indicative of a minor decrease in an oxide component and an increase in phyllosilicate and sulfide Fe(II). Nitrate was also reduced in all three sediments, albeit at different rates. Microbial U(VI) reduction was observed in the Hanford formation sediments both with and without sulfate, while Ringold oxidized and reduced sediments showed adsorption of U(VI), but no obvious microbial reduction. Microbial reduction was not observed above a concentration of 120  $\mu\text{M}$  U(VI), while the lower concentrations of 20 and 60  $\mu\text{M}$  U(VI) were reduced in Hanford formation sediments regardless of organic carbon stimulation although at different rates. There was no detectable Tc(VII) reduction in Ringold oxidized sediment, while Tc(VII) was reduced to Tc(IV) in the organic carbon-stimulated Hanford formation sediments.

Tc(VII) reduction experiments were also performed using the bioreduced Hanford formation sediments to probe the redox reactivity of biogenic Fe(II). The reduction rates of Tc(VII) increased with increasing sediment mass [i.e., Fe(II)] concentrations. In general, sediments exhibiting sulfate and Fe(III) reduction exhibited slightly higher rates of Tc(VII) reduction compared to those where only Fe(III) was reduced. X-ray spectroscopy of the bioreduced sediments indicated the presence of Tc-Fe and Tc-S bonding in sediments incubated with sulfate.

In FY2011, we will complete research on U and Tc bioreductive transformations in Hanford 300A subsurface sediments and Tc reduction by sulfide and synthetic iron sulfides. New studies will begin on microbial metabolic activity rates (including the use of resazurin for  $\text{O}_2$  respiration), both in-situ and in laboratory batch and column studies in collaboration with Konopka SFA and the Hanford IFRC. Oxidation rates will be measured for bioreduced Fe and Tc phases in Hanford formation sediments. Explorative research will begin on biogeochemical reactions in the unconfined aquifer between the 300A IFRC and the Columbia River where there is significant seasonal intrusion of river water if appropriate samples can be obtained.

## 5 Staffing and Budget Summary

Funding allocations by project, technical lead, and collaborator for FY 2010 and proposed for 2011 are provided in Table 1. The funding distribution between internal and external participants remains unchanged from FY2009. Also noted are post-docs shared between project activities to foster collaboration. Further changes to our internal funding model are expected in FY 2011 as we continue to implement the scientific theme areas. Our intent is to move away from specifically funded projects like those in Table 1 to a modular/task funding structure based on the theme areas. The theme areas would be allocated budget that is distributed within area to theme participants by the coordinators to perform collaborative research that closely aligns with theme needs and desired scientific impacts. The theme participants would consequently be working on individual tasks within the theme area and not projects. Any given PNNL-SBR investigator could work on multiple tasks in multiple theme areas if sufficiently skilled and productive. It will take another year before this model can be implemented in full.

The PNNL scientific staff participating in the SFA continues to evolve. There are several reasons for this including the personal preference and expertise of the staff members, and their ability to meet necessary responsibilities of a PNNL-SBR-SFA investigator in terms of scientific innovation and productivity, and ability or desire to engage in highly collaborative research. The PNNL SFA is not for every investigator, and the management team is committed to making necessary changes to assure that the scientific achievements of the SFA are as strong as they can be. Don Baer and Andy Ward will no longer be functioning as PNNL-SFA P.I.s after FY 2010. Part of their research scope will remain as components of other tasks.

Our listing of external collaborators has remained relatively stable over the past two years. We will be reviewing our external collaborator program next year for its effectiveness. Some of the collaborations are highly effective, while others are not so. Distance and separation can be problematic. A successful collaboration requires continued engagement between a PNNL SFA contact and the external investigator, and efforts are underway within the SFA to strengthen these interactions for each collaborator.

Capital equipment requests for FY2011 will be developed at the annual year-end PNNL SFA workshop in October 2010 and submitted to CESD immediately thereafter.

Table 1. FY2010 SFA financial information.

FY10 - FY11 SBR - Scientific Focus Area (SFA) - Budget Summary				
Project #	Project Title	Co-Principal Investigator	FY10 Actual	FY11 Proposed
Project 1	ERSP Management	John Zachara/Jim Fredrickson	\$383,681	\$383,681
Project 2	Structure and Chemical Properties of Nanoparticulates	Don Baer	\$54,050 <sup>1</sup>	
Project 3	Biomolecular Studies of Microbiological Processes Controlling Contaminant Fate and Transport	Matthew Marshall	\$279,450	\$279,450
Project 4	The Chemical Form and Transformation Reactions of Plutonium in Hanford Soils and Sediments	Andy Felmy	\$404,450	\$379,450
Project 5	Pore to Field Scale Biogeochemical Processes Controlling Contaminant Fate & Transport	Jim Fredrickson	\$517,500	\$517,500
Project 6	Microbial Ecology	Alan Konopka	\$400,000	\$400,000
Project 7	Microscopic Mass Transfer of U and Tc in Subsurface Sediments	Chongxuan Liu	\$388,125	\$388,125
Project 8	Molecular Scale Mechanisms of Biogeochemical Electron Transfer	Kevin Rosso	\$485,500	\$485,500
Project 9	Multiscale Reactive Transport Modeling	Tim Scheibe	\$365,750	\$365,750
Project 10	Functional Characterization of Microbial Macromolecules	Liang Shi	\$310,500	\$310,500
Project 11	Facies-based Characterization of Hydrogeologic Structures and Reactive Transport Properties	Andy Ward	\$385,538 <sup>2</sup>	\$385,538
Project 12	Reactive Transport of U and Tc in Sediments Containing Microenvironments and Transition Zones	John Zachara	\$552,500	\$552,500
Project 13	New Post Doc's	New Post Doc's	\$54,536 <sup>3</sup>	\$171,000
Project 14	Proteome Analyses of Subsurface Microbial Systems	Mary Lipton	\$186,300 <sup>4</sup>	\$186,300
Project 15	Young Investigator	Wilkins, Pearce, Zhang	\$284,567	\$284,567
	<b>Total SFA internal funds</b>		<b>\$5,052,447</b>	<b>\$5,089,861</b>
<b>Collaborators</b>				
Project 3	University of Tennessee	Frank Loffler		\$100,000
Project 4	Los Alamos National Laboratory	Steve Conradson	\$100,000	\$100,000
Project 5	University of Wisconsin-Madison	Eric Roden	\$90,890	\$90,890
Project 5	Argonne National Laboratory	Ken Kemner	\$150,000	\$150,000
Project 6	University of Colorado	Rob Knight	\$90,890	\$90,890
Project 7	Stanford University	Scott Fendorf	\$90,890	\$90,890
Project 9	Oregon State University	Brian Wood	\$110,000	\$110,000
Project 10	University of East Anglia	David Richardson	\$184,706	\$184,706
Project 11	Idaho National Laboratory	Roelof Versteeg	\$100,000 <sup>5</sup>	\$0
Project 12	USGS	James Davis	\$136,340 <sup>6</sup>	\$136,340
Project 12	Oak Ridge National Laboratory	Scott Brooks	\$200,000	\$200,000
	Other Subcontracts (i.e. Univ of Texas - Arlington, Iowa State Univ)		\$94,600 <sup>7</sup>	\$57,186
	<b>Total University and/or private sector funds (includes USGS)</b>		<b>\$798,316</b>	<b>\$860,902</b>
	<b>Total other National Laboratory funds</b>		<b>\$550,000</b>	<b>\$450,000</b>
		Subcontract overheads	\$99,237	\$99,237
		<b>Total</b>	<b>\$6,500,000</b>	<b>\$6,500,000</b>
	<sup>1</sup> Project discontinued			
	<sup>2</sup> New P.I. and workscope anticipated for FY11			
	<sup>3</sup> Post-Docs shared between projects			
	<sup>4</sup> Project under internal review			
	<sup>5</sup> Collaborator has left INL			
	<sup>6</sup> May change to LBNL along with Davis move			
	<sup>7</sup> Subcontracts with Jochen Blumberger, and Alexandra Navrotsky to be initiated in FY2011.			

## **Appendix A. Publications and Presentations**

### ***Publications***

- Armstrong, C. R., A. R. Felmy and S. B. Clark. 2010. Solubility of triuranyl diphosphate tetrahydrate (TDT) and Na autunite at 23°C and 50°C. *Radiochimica Acta* (In press).
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- Ewing, R., Q. Hu, and C. Liu. 2010. Scale dependence of intra-granular porosity, diffusivity, and tortuosity. *Water Resour. Res.* 46:W06513, doi:10.1029/2009WR008183.
- Felmy, A. R., K. J. Cantrell, and S. D. Conradson. 2010. Plutonium contamination issues in Hanford soils and sediments; discharges from the Z-Plant (PFP) complex. *Chemistry and Physics of the Earth* (In press).
- Greenwood, J. W., and A. L. Ward. 2010. Characterizing anisotropy and heterogeneity in a fluvial aquifer with azimuthal resistivity soundings. *Journal of Applied Geophysics* (Submitted).

- Harrington, S. J., B. D. Wood, and R. Haggerty. 2010. Effects of equilibrium pH and inorganic carbon on uranium transport in Hanford sediment. *Journal of Contaminant Hydrology* (In review).
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### **Presentations**

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- Belchik, S. M., D. W. Kennedy, A. Dohnalkova, H. Wu, Y. Lin, J. K. Fredrickson, and L. Shi. 2010. "Extracellular Reduction of Hexavalent Chromium by MtrC and OmcA of *Shewanella oneidensis* MR-1." Presented at ASM General Meeting 2010, San Diego, CA on May 25, 2010.

Davis, J. A. 2009. "Case Studies of Uranium Transport and Retardation in Unconsolidated Aquifers." Distinguished Science Seminar Series, CSIRO Land and Water, Perth, Australia, June 2009.

Davis, J.A. 2009. "Processes Controlling Uranium Transport in Groundwater at Three Contaminated DOE Sites." Distinguished Speaker Series, Lawrence Berkeley National Laboratory, November 2009.

Felmy, A. R., K. J. Cantrell, and S. D. Conradson. 2009. "Plutonium Contamination Issues in Hanford Soils and Sediments: Discharges from the Z-Plant Complex." Presented at MIGRATION 2009, the 12<sup>th</sup> International Conference On the Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere, Kennewick, WA on September 20-25, 2009.

Fredrickson, J. K., J. P. McKinley, C. T. Resch, J. H. Lee, X. Lin, D. W. Kennedy, A. Konopka, C. I. Pearce, K. M. Rosso, B. N. Bjornstad, T. Peretyazhko, and J. M. Zachara. 2010. "Biogeochemical Redox Transition with Depth in the Hanford 300 Area Subsurface." Presented at the DOE-ERSP 5th Annual PI Meeting, Washington DC on March 29, 2010.

Fredrickson, J. K. 2009. "Electron Transfer at the Microbe-Mineral Interface." Presented at the University of Nebraska, NE on December 10, 2009.

Fredrickson, J. K. 2010. "Microbial Metal Reduction." Presented at Portland State University, Portland, OR on January 22, 2010.

Hay, M. B., D. L. Stoliker, J. A. Davis, and J. M. Zachara. 2010. "Understanding Grain-Scale Diffusion Processes and Quantifying Mass Transfer Parameters in Hanford 300A Sediments." Presented at the DOE-ERSP 5th Annual PI Meeting, Washington, DC on March 29, 2010.

Hay, M. B., J. A. Davis, and J. M. Zachara. 2010. "Sorption of Uranium on Synthetic Porous Phases as a Model for Understanding Grain-Scale Diffusion Kinetics in Contaminated Sediments." Presented at the Goldschmidt Conference, Knoxville, TN, June 13-18, 2010.

Konopka, A. 2010. "Underfoot and Underappreciated – Subsurface Microbial Communities at an Experimental Field Research Site in Hanford's 300 Area." Presented at Argonne National Lab, Argonne, IL on March 18, 2010.

Konopka, A. 2010. "Underfoot and Underappreciated – Subsurface Microbial Communities at an Experimental Field Research Site in Hanford's 300 Area." Presented at the University of Wisconsin-Madison, Madison, WI on March 19, 2010.

Konopka, A., X. Lin, D. W. Kennedy, A. E. Plymale, J. K. Fredrickson, M. S. Lipton, A. D. Peacock, and R. Knight. 2009. "Microbial Ecology in Subsurface Sediments from Hanford 300A Area." Presented at the ERSP Internal SFA Meeting, Richland, WA on October 28, 2009.

Lee, J. H., X. Lin, D. W. Kennedy, A. E. Plymale, A. Konopka, R. K. Kukkadapu, J. M. Zachara, J. K. Fredrickson, K. M. Kemner, and S. M. Heald. 2010. "Biogeochemical Activities and Microbial Community Diversity associated with Hanford 300 Area Subsurface Sediments." Presented at the DOE-ERSP 5th Annual PI Meeting, Washington, DC on March 29, 2010.

Lin, X., D. W. Kennedy, A. E. Plymale, J. H. Lee, B. N. Bjornstad, J. K. Fredrickson, and A. Konopka. 2010. "Microbial Community Structure, Diversity, and Heterotrophic Activity within the

Saturated Zone of the 300 Area, Hanford Site.” Presented at the DOE-ERSP 5th Annual PI Meeting, Washington, DC on March 29, 2010.

Lin, X., D. W. Kennedy, A. E. Plymale, B. N. Bjornstad, J. H. Lee, J. K. Fredrickson, and A. Konopka. 2010. “Microbial Diversity, Community Composition, and Functional Potential in the Subsurface of Hanford Site 300 Area, Washington USA.” International Symposium on Microbial Ecology-ISME13, Seattle, WA in August 2010.

Liu, C., Z. Shi, N. Qafoku, Z. Wang, A. Reed, and J. M. Zachara. 2009. “Scale-Dependent Contaminant Desorption Rates in Sediments.” Presented at 2009 AGU Fall conference, San Francisco, CA on December 15, 2009.

Liu, C., S. N. Kerisit, R. Ewing, S. Fendorf, and J. M. Zachara. 2009. “Microscopic Mass Transfer of U and Tc in Porous Media.” Presented at the ERSP Internal SFA Meeting, Richland, WA on October 28, 2009.

Liu, C., S. N. Kerisit, J. M. Zachara, R. Ewing, B. D. Kocar, and S. Fendorf. 2010. “Microscopic Reactive Transport and Its Effect on Scale-Dependency of Geochemical and Biogeochemical Reaction Rates in Subsurface Porous Media.” Presented at the DOE-ERSP 5th Annual PI Meeting, Washington, DC on March 29, 2010.

Liu, C., J. M. Zachara, and J. P. McKinley, 2010. “Scale-Dependent Rates of Geochemical and Biogeochemical Reactions: Role of Pore-Scale Mass Transfer.” Invited presentation by Chongxuan Liu to Battelle Conference 2010, Remediation of Chlorinated and Recalcitrant Compound, 7th International Conference, Monterey, CA on May 25, 2010.

Liu, C., J. M. Zachara, and C. Zhang. 2010. “The Role of Pore-Scale Reactive Mass Transport in the Scale-Dependency of Geochemical and Biogeochemical Reaction Rates: A Uranyl Desorption Case.” Presented at the DOE-ERSP 5th Annual PI Meeting, Washington, DC on March 29, 2010.

Liu, J., C. I. Pearce, O. Qafoku, E. Arenholz, S. M. Heald, T. Peretyazhko, and K. M. Rosso. 2010. “Reduction of Contaminant Tc(VII) by Magnetite ( $\text{Fe}_3\text{O}_4$ ) and Titanomagnetite ( $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ ) Nanoparticles.” Presented at the Goldschmidt Meeting, Knoxville, TN on June 14, 2010.

Marshall, M. J., A. Dohnalkova, B. W. Arey, K. H. Williams, and J. K. Fredrickson. 2010. “Visualization of Hydrated Bacterial Structures by Complementary Electron Microscopy Techniques.” Presented at the DOE-ERSP 5th Annual PI Meeting, Washington, DC on March 29, 2010.

Marshall, M. J., A. Dohnalkova, B. W. Arey, K. H. Williams, and J. K. Fredrickson. 2010. “Visualization of Hydrated Bacterial Structures by Complementary Electron Microscopy Techniques.” Presented at the Goldschmidt 2010, Knoxville, TN on June 15, 2010.

Marshall, M. J., D. W. Kennedy, A. Konopka, J. K. Fredrickson, and A. S. Beliaev. 2010. “Isolation and Characterization of Metal- and Radionuclide-Reducing Microorganisms from 300 Area Sediments within the Hanford Site.” International Symposium on Microbial Ecology-ISME13, Seattle, WA in August, 2010.

Pearce, C. I., O. Qafoku, J. Liu, E. Arenholz, S. M. Heald, A. R. Felmy, C. M. B. Henderson, and K. M. Rosso. 2010. “Characterization of Reactive Ferrous Iron in Titanomagnetite ( $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ )

Nanoparticles for Contaminant Reduction.” Presented at the Goldschmidt Meeting, Knoxville, TN on June 15, 2010.

Peretyazhko, T., J. M. Zachara, R. K. Kukkadapu, C. Liu, S. M. Heald, C. T. Resch, B. W. Arey, C. M. Wang, and A. E. Plymale. 2010. “Reactions of Tc with Fe(II) and O<sub>2</sub> in Hanford Redox-Sensitive Sediments.” Presented at the DOE-ERSP 5th Annual PI Meeting 2010, Washington, DC on March 29, 2010.

Peretyazhko, T., J. M. Zachara, R. K. Kukkadapu, C. Liu, S. M. Heald, C. T. Resch, B. W. Arey, C. M. Wang, and A. E. Plymale. 2010. “Reactions of Tc with Fe(II) and O<sub>2</sub> in Hanford Redox-Sensitive Sediments.” Presented at the Goldschmidt 2010, Knoxville, TN on June 18, 2010.

Plymale, A. E., J. H. Lee, S. M. Heald, J. P. McKinley, C. T. Resch, D. W. Kennedy, and J. K. Fredrickson. 2010. “Biogeochemical Transformations of Technetium-99 in Hanford 300 Area Subsurface Sediments.” International Symposium on Microbial Ecology-ISME13, Seattle, WA in August 2010.

Rosso, K. M., C. I. Pearce, O. Qafoku, J. Liu, T. Droubay, T. Peretyazhko, E. S. Ilton, E. Arenholz, S. M. Heald, and A. R. Felmy. 2010. “Rates and Mechanisms of Heterogeneous Per technetate Reduction by Mixed Valent Iron Oxides.” Presented at the DOE-ERSP 5th Annual PI Meeting 2010, Washington, DC on March 28, 2010.

Rosso, K. M. 2010. “Electron Transfer and the Biogeochemistry of Iron: A Frontier in Environmental Chemistry.” Presented at the Chemistry Department Seminar Series, University of Loyola, Chicago, IL on February 25, 2010.

Scheibe, T. D., A. M. Tartakovsky, and B. J. Palmer. 2009. “Pore-Scale Simulation and Upscaling of Solute Transport in Groundwater Incorporating Intra-Grain Mass Transfer Processes.” Presented at AGU, San Francisco, CA on December 18, 2009.

Scheibe, T. D. 2010. “Quantifying Flow and Reactive Transport in the Heterogeneous Subsurface Environment: From Pores to Porous Media and Facies to Aquifers.” Henry Darcy Distinguished Lectures (Invited) given at multiple institutions throughout the calendar year, sponsored by the National Ground Water Association.

Scheibe, T. D. 2010. “Quantifying Flow and Reactive Transport in the Heterogeneous Subsurface Environment: From Pores to Porous Media and Facies to Aquifers.” Invited Keynote Lecture given at Computational Methods in Water Resources (CMWR 2010), Barcelona, Spain on June 21, 2010.

Shelobolina, E. S., M. Blothe, H. Xu, H. Konishi, R. Kukkadapu, and E. Roden. 2010. “Microbial Oxidation and Mineralogical Alteration of Biotite.” Invited (Plenary) presentation at the Goldschmidt Conference, Knoxville, TN on June 18, 2010.

Shelobolina, E., T. Wu, D. Kennedy, and E. Roden. 2010. “Microbial Fe-Phyllosilicate Redox Metabolism in Hanford 300 Area Sediments.” Presented at the DOE-ERSP 5th Annual PI Meeting 2010, Washington, DC on March 28, 2010.

Shi, L., D. Richardson, T. A. Clarke, S. M. Belchik, D. W. Kennedy, A. Dohnalkova, A. E. Plymale, Z. Wang, M. J. Marshall, J. N. Adkins, K. M. Rosso, J. M. Zachara, and J. K. Fredrickson. 2010. “Functional Characterization of Microbial Proteins Involved in Biogeochemical Electron Transfer

Reactions.” Presented at the DOE-ERSP 5th Annual PI Meeting 2010, Washington, DC on March 28, 2010.

Shi, L., D. Richardson, T. A. Clarke, S. M. Belchik, D. W. Kennedy, A. Dohnalkova, A. E. Plymale, Z. Wang, M. J. Marshall, J. N. Adkins, K. M. Rosso, J. M. Zachara, and J. K. Fredrickson. 2010. “Functional Characterization of Microbial Proteins Involved in Biogeochemical Electron Transfer Reactions.” Presented at the DOE-ERSP 5th Annual PI Meeting 2010, Washington, DC on March 28, 2010.

Shi, L., S. M. Belchik, A. E. Plymale, S. M. Heald, T. C. Squier, and J. K. Fredrickson. 2010. “Purification and Characterization of [NiFe]-Hydrogenase of *Shewanella oneidensis* MR-1.” Presented at ASM General Meeting 2010, San Diego, CA on May 25, 2010.

Valdes-Parada, F. J., M. L. Porter, and B. D. Wood. 2009. “Should Tortuosity Still be used in Upscaling?” Presented at AGU, San Francisco, CA on December 18, 2009.

Ward, A. L., N. Hasan, A. Tartakovsky, and R. J. Versteeg. 2009. “A Pore-Scale Analysis of the Electrical Properties of Partially Saturated Porous Media and Implications for Scaling Reactive Transport.” Presented at the DOE-ERSP 5th Annual PI Meeting, Washington, DC on March 28, 2010.

Ward, A. L., R. J. Versteeg, T. Johnson, and W. J. Greenwood. 2010. “Integration of Core, Log, and Electrical Resistivity Tomography Data to Improve Hydrogeological Characterization of the Hanford 300 Area IFRC Site.” Presented at the DOE-ERSP 5th Annual PI Meeting, Washington, DC on March 28, 2010.

Wu, T., E. Shelobolina, H. Xu, R. Kukkadapu, and E. Roden. 2010. “Experimental Studies of Microbial Fe(III)-Phyllosilicate Reduction in Subsurface Sediments.” Invited presentation at the Goldschmidt Conference, Knoxville, TN on June 18, 2010.

Wu, T., E. Shelobolina, H. Xu, R. Kukkadapu, and E. Roden. 2010. “Microbial Fe(III)-Phyllosilicate Reduction in Subsurface Sediments.” Presented at the DOE-ERSP Annual PI Meeting, Washington, DC, on March 28, 2010.

Zachara, J. M., J. K. Fredrickson, H. Bolton, Jr., D. R. Baer, S. C. Brooks, S. Conradson, J. A. Davis, A. R. Felmy, S. Fendorf, K. M. Kemner, R. Knight, A. Konopka, M. S. Lipton, C. Liu, F. E. Loeffler, M. J. Marshall, D. Richardson, E. E. Roden, K. M. Rosso, D. Saffarini, T. D. Scheibe, L. Shi, R. J. Versteeg, and B. D. Wood. 2010. “Role of Microenvironments and Transition Zones in Subsurface Reactive Contaminant Transport: The PNNL SFA.” Presented at the DOE-ERSP 5th Annual PI Meeting, Washington, DC on March 28, 2010.

Zhang, C., M. J. Wilkins, C. I. Pearce, A. E. Franks, D. R. Lovley, S. Heald, J. K. Fredrickson, and J. M. Zachara. 2010. “Investigating the Impact of Microenvironments on Contaminant Biogeochemical Reactive Transport.” Presented at the DOE-ERSP 5th Annual PI Meeting, Washington, DC on March 28, 2010.