



U.S. DEPARTMENT OF
ENERGY

PNNL-SA-89078

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

PNNL Scientific Focus Area: Role of Microenvironments and Transition Zones in Subsurface Reactive Contaminant Transport

Principal Investigators:

J.M. Zachara J.K. Fredrickson

Laboratory Research Manager:

H. Bolton, Jr.

July 2012



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PNNL SBR Scientific Focus Area Annual Report FY2012

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

**2012 Annual Report
July 10, 2012**

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I. Program Overview

The PNNL SFA is investigating biogeochemical transport and microbiological processes in a hydrologically dynamic and interactive groundwater-river system within the 300 A at the southern end of the Hanford site. Research is directed at elemental biogeochemical processes and cycles including those of Fe, Mn, S, N, C, U, Tc, and Pu* that undergo significant reaction and transformation in certain system compartments. We emphasize a holistic understanding of the groundwater-river interaction zone with applicability to other watersheds of differing scales. A guiding scientific theme over the past three years has been the influence of microenvironments and redox transition zones on field scale reactive transport behavior.

Field investigations including microbial sampling and genetic analysis, down-well microcosm studies, and time series monitoring of key hydrologic and chemical parameters in different system compartments seek to identify biotic and abiotic variables diagnostic of system scale behaviors. The system is scientifically rich and includes an oxic uranium plume, an underlying stratigraphic sequence of naturally reduced sediments, oxic and anoxic groundwater-river mixing zones, and a biologically active hyporeic zone with oscillatory flow vectors. The surface footprint of the field site is approximately 2.3 km².

Contaminant uranium is a reactive hydrochemical tracer in the oxic zone and underlying redox transition zone sediments, and its complex hydrochemical behavior provides unique insights on in-situ coupled processes. The in-situ microbiologic community, and its function and response to dynamic hydrochemical conditions, is investigated through a combination of 16S-RNA sequencing and single cell genomics, with exploratory metagenomics and proteomics investigations underway. Field observations of spatiotemporal trends in solute, stable isotope, terminal electron acceptor, and dissolved U concentrations as linked to Columbia River stage inform hypotheses on biogeochemical processes, coupled process interactions, and important molecular and microscopic reactive transport mechanisms that are evaluated in the laboratory using site-derived microorganisms, subsurface sediments, and abstracted model biochemical and mineral systems.

Integrative field data assimilation methods that identify and propagate uncertainty, multi-scale stochastic biogeochemical transport modeling, and statistically-based microbial ecologic modeling are applied iteratively with field and laboratory experimentation to build integrated system simulators of increased accuracy and a scientific understanding of hierarchical interactions controlling system behavior. The development of an improved biogeochemical transport model that integrates molecular information on microorganism phylogeny and function with community spatial distribution and ecology is a long-term goal. Models are applied in the design of field experiments to investigate system behavior, to integrate multi-process information and characterization data, and to understand and predict large-scale behaviors of the 300 A groundwater-river interaction zone. Our integrated multi-scale experimental and modeling approach, driven by field scale observations and the identification and prediction of system scale diagnostic variables using process models with mechanistic integrity, fully supports the four long term goals (7-10 y) of the recent CESD Strategic Plan (2012).

The PNNL SFA has been in a state of transition over this reporting period, responding first to the results of the March 2011 Peer Review and second to reprogramming directives from SBR beginning in January 2012. These directives have included the termination of the 300 A IFRC which functioned as a field laboratory for the PNNL SFA.

- * Note the studied aquifer system contains local U, $^3\text{H}_2\text{O}$, and TCE/PCE contamination. Tc will pass through these same aquifer sediments further north in the Hanford site in the future, immediately before potential discharge to the Columbia River. Plutonium is not present in the 300 A field site, but exists in comparable Hanford and Ringold formation sediments in the 200A.

II. Goals and Scientific Objectives

Goals: i.) To understand the holistic biogeochemical functioning of an unconfined/semi-confined aquifer system that is in hydraulic continuity with a major river (Columbia River); and how aquifer hydrophysical, microbiologic, and mineralogic properties interact to control local and global redox status and reactivity, and ii.) To develop a modeling approach that describes and predicts microbiologic and geochemical variables that are diagnostic of system behavior at the deca- and kilo-meter scale in a subsurface water system influenced by groundwater-river water exchange, microenvironments, and redox transition zones.

The project is divided into three theme areas with the following objectives:

Theme Area I: Field Scale Biogeochemistry

Objectives: Quantify the biogeochemical functioning of oxic and reduced aquifer zones through time series measurements of solutes and microorganisms in groundwater as a function of depth, distance from the river, and river stage. Determine microbial community structure and function through sequencing, clone library, and genomics approaches; and establish relationships to diagnostic variables and aquifer properties. Conduct microbial cultivation to obtain isolates of representative functional guilds for physiology and genomic analyses to complement community level analyses and for Theme Area (TA) II and III research. Employ other field experiments to assess in-situ activities, functionality, and biogeochemical process rates.

Theme Area II: Coupled Process Integration and Multi-Scale Modeling

Objectives: Investigate the coupling of transport and biogeochemical reaction processes from the microenvironment scale (e.g., grain) to the field to identify the factors responsible for process and parameter scale dependency and to develop meaningful predictive relationships for heterogeneous field settings. Apply new data assimilation methods to integrate multi-disciplinary field data and molecular microbiologic analyses, and their uncertainties, into a biogeochemical transport model for iterative experimental design and multi-scale/field system predictions of decreasing uncertainty.

Theme Area III: Biogeochemical Electron Transfer

Objectives: Through laboratory study, identify the mechanisms and fundamental reaction rates of key biologic, geochemical, and biogeochemical redox reactions operative in different redox regimes and compartments of the studied unconfined/semi-confined aquifer system using advanced molecular spectroscopic and modeling approaches, model experimental systems, and microorganisms and sediments from the natural system. Link microscopic findings to the macroscopic scale through more accurate, but pragmatic process representations in biogeochemical transport models.

III. Program Structure

SFA Management

Harvey Bolton – Laboratory Research Manager. Communication and coordination of overall research directions and scientific impact with SBR/BER management. Resolution of staffing issues.

Jim Fredrickson – Scientific manager. Set research directions, milestones, and funding in alignment with SBR strategic plans and guidance. Encourage P.I. collaborations and synergies through interaction with theme area leads. Lead on all biologic research.

John Zachara – Scientific manager. Set research directions, milestones, and funding in alignment with SBR strategic plans and guidance in collaboration with JF. Encourage P.I. collaborations and synergies through interaction with theme area leads. Lead on all chemical and physical sciences research.

Theme Area I: Field Biogeochemistry

Allan Konopka – Co-theme area coordinator. Lead microbiologist on field studies of the 300 A microbial ecology. Identify key theme area hypotheses, milestones, field campaigns, and required staffing. Lead scientist for theme area publication.

Jim McKinley – Co-theme coordinator. Lead field geochemistry including analytical and sampling methodologies. Assist in identification of theme area hypotheses, milestones, field campaigns, and required staffing. Co-lead scientist for theme area publication.

Jim Fredrickson – Contributing P.I. with focus on biogeochemistry and elemental transformations across 300 A redox transition zones.

Mike Wilkins – Contributing young scientist in field biogeochemistry, proteomics, and single-cell genomics.

Theme Area II: Coupled Process Integration and Multi-Scale Modeling

Chongxuan Liu – Theme area coordinator. Research lead on biogeochemical transport modeling and model scaling relationships between the lab to field. Identify key theme area hypotheses, milestones, and publication targets.

Xingyuan Chen – Contributing young scientist in data assimilation, uncertainty analysis, stochastic transport modeling, and complex systems models.

Glenn Hammond – Contributing P.I. with expertise in high performance computing, PFLOWTRAN, hydrology, and large system simulations.

Tim Johnson – Contributing P.I. with expertise in field geophysical measurements and inversion modeling.

Chris Murray – Contributing P.I. with expertise in geostatistics

Tim Scheibe – Contributing P.I. with focus on pore scale modeling and upscaling.

John Zachara – Contributing P.I. with focus on laboratory experiments of coupled biogeochemical processes using field site materials and varied EMSL capabilities.

Theme Area III: Biogeochemical Electron Transfer

Liang Shi – Co-theme coordinator. Lead on molecular biochemistry including protein expression, isolation, characterization, and mechanistic reaction studies in collaboration with external P.I. Richardson. Identifies theme area hypotheses, milestones, experimental campaigns, and staffing in collaboration with KR.

Kevin Rosso – Co-theme coordinator. Lead on molecular biogeochemistry including electron transfer modeling in biotic and abiotic systems. Identifies theme area hypotheses, milestones, experimental campaigns, and staffing in collaboration with LS.

Andy Felmy – Contributing P.I. with focus on actinide biogeochemistry and project-wide applications of thermodynamic modeling.

Jenny Liu – Contributing young scientist with expertise in experimental studies of geochemical and biochemical redox reactions.

Carolyn Pearce – Contributing young scientist in molecular biogeochemistry with focus on the reactivity of iron and the application of synchrotron x-ray methods.

IV. Performance Milestones and Metrics

Scientific Progress

Here we summarize select progress for the three theme areas focusing on yearly productivity metrics. Size constraints preclude a comprehensive report.

Theme Area I: Field Biogeochemistry

Metric 1: Evaluate the potential for microbial redox cycling of Fe and S in Hanford 300 A sediments.

Progress – A collection of solid-phase Fe redox cycling organisms was isolated from Hanford 300 Area subsurface sediments. A Fe(III) phyllosilicate/Fe(III) oxide-reducing strain of *Geobacter* closely related to *G. bremensis* was isolated from conventional enrichment cultures initiated with Fe(III) phyllosilicate-bearing Ringold formation sediments. Four different solid-phase Fe(II)-oxidizing isolates including *Bradyrhizobium* sp., *Cupriavidus* sp., *Dechloromonas* sp., and *Nocardioides* sp. were derived from in situ “i-chip” deployments (containing either reduced smectite or biotite as Fe(II) sources) in Hanford formation sediments. Multiple *Bradyrhizobium* isolates were obtained from the i-chip deployments, which was consistent with their presence in clone libraries from Hanford 300 Area sediments at depths where sharp gradients in oxygen and nitrate have been documented. *Bradyrhizobium* might play a significant role in situ Fe(II) oxidation in the Hanford subsurface. The physiologic and genetic properties of one Hanford *Bradyrhizobium* isolate (strain 22) has been studied in detail, including the acquisition of a draft whole genome sequence. A proposal for sequencing the *Geobacter* isolate and a selection of the other Fe(II)-oxidizing organisms has been submitted to the JGI Microbial Isolates sequencing program, with these organisms representing targets for future SFA biogeochemical research.

Microcosm experiments were conducted to investigate the potential for oxidation of solid-phase Fe(II) and reduced S compounds by microorganisms from within and below the redox transition zone. The potential for oxidation of both native reduced Ringold formation mineral phases and exogenous solid-phase Fe(II) and reduced S compounds in response to addition of O₂ or nitrate was evaluated. Barcode pyrosequencing of the V4 region of the 16S rRNA gene was conducted on selected time course samples from the microcosms for which PCR-competent DNA could be recovered. All non-sterile reactors consumed > 15 mM nitrate over a 226 day incubation period; uninoculated reactors failed to consume nitrate. However, there was no systematic decline in HCl-extractable Fe(II) concentration in either the nitrate or air-amended reactors, indicating resistance of the natural Fe(II) mineral phases

to bacterial oxidation. Reactors to which no oxidant was added consumed sulfate after a 1-4 month lag period. The source of inoculation had little effect on these patterns. In all reactors, sequences related to *Pseudomonas fluorescens* initially dominated, but the composition shifted to the known nitrate-reducing organism *P. stutzeri* after several weeks of incubation. Many OTUs showed close matches to other organisms found in the SFA phylogenetic census of the saturated zone. Ringold sediments from below the redox transition zone exhibited significant oxidant consumption tied to the metabolism of detrital organic matter. A notable result of the microcosm experiments was the acquisition of four different aerobic framboidal pyrite-oxidizing enrichment cultures that were derived from pyrite-amended reduced Ringold sediments with oxygen as the electron acceptor. Pyrosequence libraries are being developed for two of the enrichments, with the results used to establish a strategy for isolating the organism(s) responsible for pyrite oxidation.

Metric 2: Analyze the effects of spatial and temporal variability on the microbiologic composition and functional potential of the Hanford unconfined aquifer near the Columbia River shoreline.

Progress – Temporal shifts in microbial community composition in the high conductivity zone of the aquifer were determined by high density well-water sampling and 16s-RNA sequencing during the late winter and spring. Significant observed shifts were related to changes in groundwater geochemistry and water table elevation, revealing that subsurface microbial communities were considerably more dynamic over short intervals of time and space than anticipated. There were also significant (>10X) dynamic changes in the abundance of microbial protists signifying that a predation event may be a consequence of river water intrusion. Statistical analyses and transport modeling is underway on the data set to identify correlated properties and variables, and to simulate the hydrologic (river water) intrusion event. Microbes associated with methane oxidation and metal reduction located at the base of this hydrologic unit varied markedly in abundance through time and space, suggesting dynamic changes in fluxes of electron donors and acceptors over an annual cycle. Furthermore, the seasonal rise in the Columbia River causes river-water intrusion that carries novel microbes into the shallow regions of the subsurface.

A novel statistical framework was developed for the unconfined and semi-confined aquifer sequence that quantitatively estimates ecological processes and characterizes important environmental features even when key features are unknown and unmeasured. Drift consistently governed ~25% of spatial turnover in community composition; selection dominated (governing ~60% of turnover) across spatially-structured habitats with low permeability sediments; and dispersal limitation was most influential (governing ~40% of turnover) across spatially-unstructured habitats with highly-permeable sediments. Quantitative influences of ecological processes may therefore be predictable from hydrophysical or geologic structure. The conceptual model is characterized by three vertical zones among which there is limited exchange of microbes, an unmeasured environmental variable in the Ringold that strongly determines microbial community composition, and spatially random environmental conditions in the Hanford that govern community composition to a moderate degree.

Metric 3: Explore the interdependence of the subsurface microbial community and its geochemical and physical environment. Determine whether stratigraphic boundaries harbor

significant microbial communities because of favorable physical conditions and cross formational hydrologic gradients and nutrient fluxes.

Progress – A passive multi-level sampler (MLS) was deployed in two wells to investigate geochemical gradients across the Hanford-Ringold redox boundary in the presence (3-27) and absence (1-57) of the fine-grained Ringold facies that serves as an aquitard. Well screens at both locations span the Hanford-Ringold contact: 3-27 is in the IFRC well-field while 1-57 is closer to the river and north of the IFRC site. Results suggested that the biogeochemical gradients changed with season, perhaps in response to variations in river stage. In November 2010, when groundwaters were flowing toward the Columbia River, profiled methane concentrations reached 100 ppmv at the oxidation-reduction boundary (Well 3-27) approximately 0.25 m below the contact. In May of 2011, when the hydrologic gradient was affected by high stage in the adjacent Columbia river, profiled methane concentrations were at a maximum of 370 ppmv at this same location. Other redox sensitive components showed gradients in concentration across the contact, including increasing H_2 , HS^- , Fe^{2+} , and Mn^{2+} with depth accompanied by abrupt decreases in O_2 and NO_3^- . In contrast, methane concentrations measured across the contact in Well 1-57 in May 2012 reached a staggering 18,000 ppmv, indicating much higher methane fluxes to the oxic, lower Hanford formation aquifer in the absence of the aquitard. These findings suggested that the Ringold formation, which contains significant concentrations of detrital organic matter, could function as a biogeochemical source of reactive electron donor to the lower U plume in areas where the fine-grained Ringold facies is absent. Microbial sampling and analysis was performed at Well 3-27 using sterile quartz sand as a colonization medium. Sequencing results showed a significant shift in microbial populations across the Hanford-Ringold boundary, with a significant concentration of methanotrophs populating the oxidation-reduction boundary in the Ringold formation just below the interface. An additional experiment is ongoing, in which MLS sample cells were inoculated with a sterile sand-biotite mixture to test whether Fe(II) oxidizing bacteria could be stimulated in the presence of a mineralogic source of Fe(II).

A comparative study of microbial community structure and geochemical variation was begun using intact core samples from the Ringold fine-grained facies collected from new IFRC corner wells installed in FY 2011. These four new wells sampled upper Ringold sediments with a range of properties and detrital organic matter. Intact sediment subsamples from cores were imaged by micro-tomography at $7\mu\text{m}$ resolution to define the nature of inter-connected pore-space accessible to microorganisms, and spatial relationships to mineral and organic phases hosting essential nutrients. Initial results showed significant differences in micro-scale texture within the nominally homogeneous Ringold fine-grained facies, with some samples exhibiting well developed μm -scale fracture systems and others displaying significant pore space with minimal connectivity. These significant physical differences are expected to influence solute, nutrient, and dissolved gas transport, and the functional characteristics and size of the microbiologic community. Metagenomics analyses of co-sampled sediments have been performed but have not yet been processed and interpreted. There was a significant variation in the phylogeny of the microbial community across the range of samples investigated (e.g., dissimilarity indices across OTU abundances varied from 0.6 to 0.99), consistent with the hypothesis that textural variation within the nominally homogeneous strata could control microbial population dynamics. This experiment is ongoing with multiple microbiologic analyses underway and the details of image processing

under development. When tomographic analyses are optimized and complete, pore structure characterization will be combined with metagenomics results to determine whether a clear relationship exists between the microbial community and its physical environment.

Metric 4: Monitor the dynamics and spatial locations of spring river water intrusion in the Hanford formation saturated zone using electrical geophysical methods to support robust modeling of temporal, time series measurements of groundwater microbiology and chemical composition.

Progress – Time-lapse electrical resistivity tomography (ERT) was used to image the inland intrusion of river water during high Columbia River stage conditions in spring and summer of 2011. The survey was made up of 3 ERT lines located between the IFRC site and the Columbia River. The easternmost line was referred to as line 1 and the westernmost as line 3. Lines 1 and 2 were each composed of 60 electrodes at 4 m separation, while line 3 was made up of 64 electrodes at 3 m separation. Identical Wenner and dipole-dipole surveys were collected along each line on a repeating schedule throughout the four-month monitoring period, producing at least three surveys per line per day. In addition, contact resistance and reciprocal data sets were collected daily for noise analysis. The ERT data were filtered before inversion to yield a common set of measurements for the entire survey period. This resulted in a set of measurements that contained identical electrode configurations and, therefore, the same number of measurements in each inversion. Water levels, temperature, and specific conductance were continuously monitored in nearby wells. River stage measurements were acquired throughout the monitoring period by a gage located adjacent to the 300 Area.

A modified time-lapse inversion approach was developed, whereby the transient water table elevation was explicitly modeled by removing regularization constraints across the water table boundary. This implementation was critical for producing meaningful imaging results. Approximately 1200 data sets (400 per line over 3 lines) were inverted using high performance computing resources to produce a time-lapse sequence of changes in bulk conductivity caused by river water intrusion during the 2011 spring runoff cycle over approximately 125 days. The resulting time series for each mesh element was then analyzed using common time series analysis to reveal the timing and location of river water intrusion beneath each line. The results revealed non-uniform flows characterized by preferred flow zones where river water enters and exits quickly with stage increase and decrease, and low permeability zones with broader bulk conductivity ‘break through’ curves and longer river water residence times. The results are being integrated within and modeled with our plume-scale PFLOWTRAN hydro-biogeochemical model to provide insights on, and simulations of the temporal trends and changes in groundwater microbiology and composition observed in IFRC cluster wells during and after river water intrusion (Metric 2).

Theme Area II: Coupled Process Integration and Multi-Scale Modeling

Metric 1: Develop a biogeochemical model from experimental laboratory observations that can systematically integrate cross-scale data and its uncertainty, and has a scalable structure to incorporate subgrid coupling of reactions with diffusive mass transfer in heterogeneous porous media.

Progress – Various numeric and experimental approaches including molecular dynamics simulations, pore network models, experimental and numerical micro-models, and multi-species reactive diffusion models have been used to validate process concepts and to develop models for reactive transport processes at the subgrid scale. The results have shown that U(VI) surface complexation (the process responsible for in-situ adsorptive retardation at the 300 A field site) is a fast process at the molecular scale, but is rate-limited by coupled diffusion in intra- and inter-granular domains of the sediments. Adsorbed water density and mobility in nano-sized pores, pore connectivity and diffusion path tortuosity, species-specific diffusivity and charge coupling, local chemical composition, and surface site saturation levels all affect the macroscopic manifestation of surface complexation. However the most influential factor on reaction kinetics was the deviation of the surface complexation reaction from the equilibrium state. Consequently a multi-rate model with multiple first-order rates driven by the deviation from local equilibrium well approximates the complex kinetic behavior of U observed in sediment.

A multi-domain framework has been developed to integrate subgrid reactive transport properties and processes in macroscopic reactive transport models, and to scale geochemical/biogeochemical reactions from the pore to the numerical grid scale. The model operationally divides the porous medium within a numerical grid into multiple, interactive subgrid domains that have distinctive reactive transport properties. These domains could be facies as described in Metric 2, below. Each domain is treated as a homogeneous system with specific reaction properties, reactants (abiotic, biotic), and pore-scale processes. The subgrid domains are linked through physical mass exchange that can be characterized using non-reactive tracers. The model concept was systematically evaluated using a comprehensive data set on U(VI) adsorption/desorption and reactive transport in 300 A sediments. For this specific case, a reactive transport model that incorporated multi-rate U(VI) surface complexation reactions (SCR) in the intra-granular domain, and multi-species reactive transport processes in dual inter-granular domains (mobile and immobile) at the subgrid scales accurately simulates U(VI) reactive transport at millimeter to meter experimental scales using the same set of geochemical reactions and reaction parameters. The model is ready for field application.

Metric 2: Develop conceptual and numeric approaches for system-level integration of disparate, multi-scale data types in complex environments, and utilize these approaches in plume scale models to elucidate processes and mechanisms controlling microorganism community structure and solute migration.

Progress – The first integration approach evaluated was for indicator or categorical data that are discrete or discontinuous in space. Subsurface features such as gravel channels or sand and silt lenses represent a type of categorical data that are referred to as facies. Facies can be delineated according to physical, hydrologic, or geochemical properties, or based on a combination of properties using multivariate analysis methods. Cluster analysis was applied to borehole geophysical data (spectral gamma logs) from the 300 A IFRC site to identify physical lithofacies. The three dimensional spatial distribution of lithofacies throughout the IFRC site was then simulated using transition probability geostatistics. These distinct lithofacies will be assigned specific hydrologic and chemical parameters within our site transport model and used to simulate the various field experiments within the IFRC. Another methodology currently being developed is based on a combination of level set methods,

which are used to delineate facies boundaries, and optimization methods which are used to estimate parameters within facies.

The Ensemble Kalman filter (EnKF) method is being applied to properties that vary continuously in space such as hydraulic conductivity. This data assimilation method, which has been used in meteorology, oceanography, and petroleum engineering, provides an efficient tool for sequentially assimilating multi-type and multi-scale data and also for uncertainty quantification. The EnKF method is being used in conjunction with the PFLOTRAN subsurface transport simulator to assimilate new hydrologic data collected from the IFRC site, and to simulate a series of four closely-spaced field injection experiments performed in late CY 2011. The iterative methodology computes the uncertainty in model simulations prior and posterior to the assimilation of new/improved parameters, charting the sequential improvement in model accuracy that results from continued research. Ongoing collaborative research between TAI and TAII seeks to integrate assimilation techniques for categorical data and continuous variables as needed to define relationships between lithofacies, abiotic sediment properties, and the composition and function of microbial communities within the 300 A aquifer system.

Theme Area III: Biogeochemical Electron Transfer

Metric 1: Determine the primary biochemical mechanisms through which Hanford-derived microorganisms influence the valence and speciation (e.g., oxidation and reduction) of extracellular Fe, with emphasis on mineral-bound Fe forms.

Progress – The protein complex MtrABC in the Mtr pathway of metal reducing bacteria is responsible for transferring electrons from the periplasm, across the outer membrane, to the surfaces of extracellular Fe(III)-containing minerals. MtrABC was incorporated into proteoliposomes in an attempt to provide the first direct measurements of the interfacial electron transfer rates of this protein complex to Fe(III)-containing mineral phases. This experimental system has taken years to perfect. Immunogold localization and proteolytic digestion experiments confirmed the exposure of MtrC on the surfaces of the proteoliposomes indicating that at least some of the incorporated complexes were in the proper orientation. MtrABC in proteoliposomes mediated electron transfer between reduced methyl viologen inside the proteoliposomes, which serves as an electron donor, to hematite (α -Fe₂O₃), goethite (α -FeOOH) and lepidocrocite (γ -FeOOH) external to the proteoliposomes at physiologically relevant rates confirming their hypothesized role in extracellular electron transfer to solids. The recently solved crystal structures (by this project) of analogous *c*-cyts MtrF and UndA (Appendix A) confirm that these surface-localized proteins transfer electrons directly to the surface of Fe(III) oxides via their solvent-exposed hemes, with secreted flavins functioning as co-factors. The organizational and electron transfer characteristics of the Mtr pathway may be shared by other microorganisms for exchanging electrons with their extracellular environment. Our results suggest that sequence-based approaches (e.g., metagenomics and functional gene arrays) can be used to better assess the potentials of the electron transfer processes mediated by the Mtr pathways in environmental samples and to explore the natural diversity of these pathways.

Microbial census in conjunction with cultivation and physiology studies in the 300 A (TAI) suggest that bacterial Fe(II) oxidation is an important in-situ process. A survey of sequenced microbial genomes has identified homologues of the Mtr pathway (responsible for

Fe(III) reduction) in the Fe(II)-oxidizing bacteria *Dechloromonas aromatica* RCB (RCB), *Gallionella capsiferriformans* ES-2 (ES-2) and *Sideroxydans lithotrophicus* ES-1 (ES-1). This putative Mtr pathway is named Mto (i.e., metal-oxidizing). The *mtoABCD* and *cymA* genes of the Mto pathways identified from the Fe(II)-oxidizing bacteria ES-1, ES-2 and RCB were cloned for heterologous expression, and subsequent characterization and reactivity studies. MtoA is believed to be inserted into MtoB to mediate electron transfer across the outer membrane between extracellular Fe(II) and MtoD in the periplasm. Consistent with this prediction, cloned *mtoA* of ES-1 partially complements an MR-1 mutant lacking MtrA with regard to ferrihydrite reduction. Purified MtoA of ES-1 is a 10-heme *c*-Cyt that oxidizes soluble Fe(II). Oxidation of Fe(II) by MtoA is pH- and complexing ligand-dependent. Thermodynamic modeling revealed that redox reaction rates for the different Fe(II)-complexes correlated with their respective reaction-free energies. Fe(II) oxidation by ES-1 MtoA was rapid and involved all of its ten hemes. Results suggest that MtoABD and CymA operate in a direction reverse to the Mtr pathway, transferring electrons from extracellular Fe(II) across the bacterial cell envelope to the quinone/quinol pool in the inner-membrane.

Metric 2: Determine the rates, mechanisms, and molecular-level properties controlling heterogeneous redox transformations of Tc and U by Hanford subsurface Fe(II)-bearing mineral phases under groundwater representative conditions and develop process models.

Progress – Hanford 300 A sediments contain a magnetic mineral fraction (~2 wt%) composed of 90% titanomagnetite ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$; where $X \sim 0.15$). Because whole sediment studies imply that this phase is reactive with Tc(VII), this fraction was isolated and subject to laboratory experimentation. Solid-phase Fe(II), measurable within 5 nm of the mineral surface using *L*-edge XAS and XPS (at the ALS), was found to be highly responsive to changes in the aqueous environment, e.g., exposure to 300A groundwater taken above and below the redox boundary. Reaction with a 10 μM Tc(VII) solution showed that the natural magnetic isolates were able to reduce Tc(VII) with concurrent oxidation of Fe(II) to Fe(III) at the mineral surface, as were compositionally pristine synthetic micro-particle and nano-particle analogue phases. When differences in experimental conditions, specifically the particle surface area to solution volume ratio, were taken into consideration, measured Tc(VII) reduction rates for natural material, synthetic bulk powder, and nano-particles were within an order of magnitude of each other suggesting kinetic scalability. These results provide a credible explanation for the curious mass loss of Tc(VII) in Ringold aquifer sediments of the Hanford central plateau that also contain a magnetic mineral fraction.

The heterogeneous reduction of Tc(VII) and U(VI) by synthetic $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ phases representative of those in 300 A sediment was investigated with mass and electron balanced tracking of reactive Fe(II) at the solid-liquid interface. Reaction with Tc(VII) solution yielded fast exponentially decaying reduction kinetics with rates that increased with increasing solid-state Fe(II)/Fe(III) ratio in the nanoparticles. A mechanistic reaction model was developed involving reduction of Tc(VII) to form Tc(IV)/Fe(III) solids by structural Fe(II) resupplied and sustained by outward migration of Fe(II) from the particle interior. End member magnetite ($\text{Fe}^{2+}/\text{Fe}^{3+} = \sim 0.5$) reduced U^{VI} to uraninite ($\text{U}^{\text{IV}}\text{O}_2$) nanoparticles, whereas titanomagnetite nanoparticles with $x \leq 0.5$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios between 0.5 and 1.2 reduce U^{VI} to a non-uraninite U^{IV} species, as indicated by EXAFS measurement (at the APS). This work highlights previously unexplored thermodynamic and geochemical factors that influence the speciation and solubility of Tc and U in the subsurface.

Metric 3: Determine the kinetics, mechanisms, and products of the reaction of Fe(II)_{aq} with PuO_{2+x}.

Progress – The primary Pu solid phase found in subsurface environments is PuO_{2+x}, owing to its very low solubility over a broad range of pH. Important science questions exist on the stability of this phase in microenvironments where Fe(II)_{aq} may be released from the weathering of basaltic lithic fragments, or from bacterial action in domains of elevated detrital organic matter or residual organic processing chemicals. Recent laboratory studies of PuO_{2+x} suspensions prepared using either ²³⁹Pu or ²⁴²Pu have shown dramatic differences in reduction rates by aqueous Fe(II). Specifically, in the case of ²⁴²PuO₂/Fe(II) suspensions the dominant oxidation state in solution has been shown to be Pu(V) whereas in ²³⁹PuO₂/Fe(II) suspensions the dominant oxidation state is Pu(III). This finding demonstrates the key role played by radiolysis reactions in PuO₂ reduction, and draws into question the mechanism of surface mediated reduction of PuO₂ by aqueous Fe(II). An additional important observation was that the introduction of competing ions (trivalent lanthanides) to ²³⁹PuO₂/Fe(II) suspensions displaces reduced Pu(III) from the dominantly +4 oxide. This is the first observed release of soluble Pu from PuO_{2+x} suspensions at pH values >6. Surface complexed Pu(III), resulting from redox reactions at the surface of PuO_{2+x}, may be displaced to the aqueous phase by exchange reactions with common groundwater ions (i.e. Ca²⁺, Mg²⁺).

Science Highlights

Here we highlight five publications published or submitted during the reporting period. Please note **Appendix A** for full listing.

Theme Area I

Lin X., McKinley J., Resch C.T., Kaluzny R., Lauber C.L., Fredrickson J., Knight R., and Konopka A. (2012) Spatial and temporal dynamics of the microbial community in the Hanford unconfined aquifer. *ISME Journal*, doi:10.1038/ismej.2012.26.

Aquifer microbes perform critical biogeochemical functions, but their diversity and population dynamics have not been extensively analyzed. We used multivariate statistical techniques to analyze 200,000 gene sequences of groundwater Bacteria and Archaea from nine wells in the Hanford IFRC experimental well field over a 10-month period. The microbial community composition was not static over the monitored period, but changed both temporally and spatially in the physically heterogeneous Hanford aquifer. The rate of change accelerated when Columbia River water intruded more than 200 m into the well field, and some microbes were uniquely found only in this period. This was one of the first demonstrations that riverine water inputs may impact the biogeochemistry and microbial ecology of subsurface sediments. This stimulates a "whole systems" analysis of the hydrodynamics, geochemistry, and microbial functionality in the Columbia River's hyporheic zone to determine how these dynamics affect not just the composition of the microbial community but also its activity.

Wallin E. L., Johnson T. C., Greenwood W. J., and Zachara J. M. (2012) Imaging high stage river-water intrusion into a contaminated aquifer along a major river corridor using 2D time-lapse surface electrical resistivity tomography. *Water Resources Research*, Submitted.

Stage-driven river water-groundwater exchange has a governing influence on both the physical and biogeochemical mechanisms governing uranium behavior in the Hanford 300 Area. However, information on hydrodynamics at the system scale is limited to sparsely spaced boreholes, resulting in uncertainty concerning the nature of hyporheic exchange. Based on the contrast in specific conductance between river water and groundwater, we developed and demonstrated a capability to image inland river water intrusion and retreat from the 300 Area during spring runoff using surface-based time-lapse electrical resistivity tomography (ERT). We generated approximately 400 time-lapse images on each of three ~250 m cross-sections to reveal spatial and temporal changes in saturated zone electrical conductivity associated with corresponding changes in pore fluid composition. Successful application of the approach depended critically on the ability to leverage high-performance computing resources and the development of a modeling technique to explicitly handle changes in smear zone saturation associated with the time-varying water table. Time-series analysis revealed a complex pattern of river water intrusion and retreat dominated by a high velocity flow channel. Also evident were zones of lower permeability characterized by delayed river water intrusion and retreat. This application is well suited for 3D time-lapse imaging and provides a method for non-invasive and cost effective mapping of groundwater-river exchange zones that influence watershed biogeochemistry and transport processes.

Theme Area II

Zhang X., Liu C., Hu B. X., and Zhang G. (2012) Uncertainty analysis of multi-rate kinetics of uranium desorption. *Environmental Science & Technology*, Submitted.

Kinetic models of geochemical/biogeochemical reactions contain both model structure and parameter uncertainties that inherit from fundamental kinetic assumptions, errors in experimental data used to calibrate model parameters, and limitations of experimental conditions for model extrapolation. Credible application of kinetic models for process understanding and reactive transport simulations requires quantification of both model and parameter uncertainties. This research used a modified Bayes-based, Markov Chain Monte Carlo (MCMC) approach to quantify both parameter and model uncertainties using multi-rate U(VI) surface complexation reaction kinetics as an example. This was the first literature demonstration of the use of a statistics-based approach to quantify the uncertainties of a kinetic model with a large number of rate parameters. A computationally efficient and numerically robust algorithm was developed to address multiple model parameters with poor a priori knowledge of parameter statistics. The results confirmed previous speculation that the multi-rate model contained uneven uncertainties in its rate constants, and that model prediction uncertainties increase with time. Also revealed was that the model structure uncertainty was much larger than previously realized when extrapolating the model to different chemical conditions. Our new approach can be readily used to analyze uncertainties for other geochemical and biogeochemical models, and for multiple, coupled reactive process models in complex systems.

Theme Area III

Liu J., Pearce C. I., Qafoku O., Rosso K. M., Arenholz E., Heald S. M., and Peretyazhko T. S. (2012) Tc(VII) reduction kinetics by magnetite and titanomagnetite ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$) nanoparticles: A tunable Fe(II)/Fe(III) redox potential system. *Geochimica et Cosmochimica Acta*, In Press.

Fe(II)-bearing minerals such as spinel-type iron oxides are key mineral phases in sediments because of stored reducing equivalents capable of participating in biogeochemical redox reactions. However, this reactivity depends in poorly understood ways on the density and accessibility of the Fe(II) in the lattice, properties sensitive to mineral structure, composition, pre-oxidation, and aqueous redox conditions at the mineral-water interface. We investigated these relationships using a novel and well-characterized set of titanium-doped magnetite nanoparticles, structurally and chemically analogous to titanomagnetites naturally present in Hanford sediments, using reduction of Tc(VII) as a probe of redox reactivity. A heterogeneous electron transfer model was developed involving reduction of Tc(VII) to form Tc(IV)/Fe(III) solids by lattice Fe(II) enriched at the nanoparticle surface, a reactive Fe(II) pool that during reaction is resupplied and sustained by outward migration of Fe(II) from the mineral interior. The study provides new mechanistic insights into solid-state and interfacial factors controlling the contribution of mineralogic Fe(II) to redox transformations important in the biogeochemistry of the subsurface.

Liu J., Wang Z., Belchik S. M., Edwards M. J., Liu C., Kennedy D. W., Merkley E. D., Lipton M. S., Butt J. N., Richardson D. J., Zachara J. M., Fredrickson J. K., Rosso K. M., and Shi L. (2012) Identification and characterization of MtoA: A decaheme c-Type cytochrome of the neutrophilic Fe(II)-oxidizing bacterium *Sideroxydans lithotrophicus* ES-1. *Frontiers in Microbiology*, 3.

The electron transfer mechanisms for microbial Fe(II) oxidation are much less characterized than those for Fe(III) reduction. To this end, we identified homologues of MtrA, MtrB, and CymA, proteins that are central to the electron transfer pathway for extracellular Fe(III) reduction in Shewanella in the genome of the Fe(II)-oxidizing bacterium Sideroxydans. The identified homologues were named MtoAB and CymA_{ES-1} to distinguish them from those involved in Fe(III) reduction. Characterization of purified MtoA showed that it was a Fe(II)-oxidizing cytochrome with 10 hemes that collectively participated in electron transfer during Fe(II) oxidation. Experimentation revealed that changes in pH and aqueous speciation caused by complexing ligands significantly influenced the rate and extent of Fe(II) oxidation by MtoA. The initial reaction rates of Fe(II) oxidation by MtoA were very sensitive to reaction-free energy. This was the first detailed study of a cytochrome from an Fe(II)-oxidizing bacterium. Our results indicate that, by working in concert with MtoB and CymA_{ES-1}, MtoA oxidizes Fe(II) at the bacterial surface and transfers released electrons across the bacterial cell envelope to the quinone pool in the inner membrane. The direction of electron transfer conducted by MtoAB-CymA_{ES-1} is opposite to that mediated by MtrAB-CymA of Shewanella. The involvement of homologous protein complex pathways in both Fe(II)-oxidation and Fe(III)-reduction (MtoAB-CymA_{ES-1}/MtrAB-CymA) implies the generality of these reaction mechanisms in metal oxidizing and reducing bacteria.

Publication Venues

SFA investigators published in the following journals during the reporting period that spans calendar years 2011-2012 (note **Appendix A** for citations). Our scientific impact has been large over an impressive disciplinary space, and addressing a range of spatial and temporal scales. Journal impact factors are noted in parentheses.

Acta Crystallographica Section F – Structural Biology and Crystallization Communications, American Mineralogist (2.026), Analytical Chemistry (5.874), Applied and Environmental Microbiology (3.778), Biochemical Journal (5.016), Biochemical Society Transactions (3.989), Biochemistry (3.226), Bio Techniques, Ecological Letters, Environmental Microbiology (5.537), Environmental Science and Technology (4.827), Frontiers in Microbiology, Geochimica et Cosmochimica Acta (4.101), ISME Journal (6.153), Journal of the American Chemical Society (9.023), Journal of Biological Chemistry (5.328), Journal of Colloid and Interface Science (3.068), Journal of Contaminant Hydrology (2.124), Mineralogical Magazine (0.949), Molecular Microbiology (4.819), Physical Chemistry Chemical Physics (3.454), Physical Reviews, Proceedings of the National Academy of Sciences (USA, 9.771), Structure (6.337), and Water Resources Research (2.737).

Future Scientific Vision and Goals

Funding reductions in FY 2012 and FY 2013, the termination of the Hanford IFRC project, and SBR demands for changes in SFA research scope to new, but as yet undefined science goals have placed the SFA in a state of transition and uncertainty. High quality SFA research personnel, who have distinguished themselves and the project through active publication of world-class science, are now looking for new opportunities internally and externally as SBR programmatic directions appear to be away from their areas of expertise. It is difficult for the PNNL SFA to articulate a rational future scientific vision at this time when the science goals and drivers for new BER/SBR research are not clear.

The PNNL SFA will consequently continue to pursue the research agenda that it presented to BER staff in August 2011 in response to the March 2011 peer review, until new science goals are articulated for SBR that allow a rational transition in research scope. That research agenda, which included a complex systems approach to investigate biogeochemical grand challenges in Hanford's groundwater-river interaction zone including the concept of "hot spots and hot moments", was accepted by BER/SBR in a letter sent to PNNL SFA management in Oct. 2011. Current research in the SFA is driven by field observations in the 300 A as requested by SBR, with the ultimate goal to develop coupled process models with mechanistic integrity that predict complex field system behavior. We request an additional 2 year period (FY 2013 and 2014) to bring these important investigations to a satisfying scientific completion.

Changes to the SFA research portfolio and the internal funding distribution will occur in FY 2013 when select components of the terminated IFRC project are integrated into the SFA. The SFA will have greater focus on the field after that integration. Significant activities being transferred include IFRC infrastructure maintenance (including continual hydrologic monitoring of river stage and well water levels), time-series monitoring of key diagnostic water quality variables to enable complex systems analysis of the U-plume, and field scale reactive transport model development and parameterization. Financial estimates have been made for IFRC site closure, but it has been decided to maintain the IFRC site in its current configuration for at least two years to complete impactful scientific studies of the groundwater-river interaction zone.

Additional changes in SFA research scope and direction will be made in FY 2013 in response to recent SBR comments to: i.) increase the scale of research beyond the 1600 m² IFRC site and ii.) align SFA science with an evolving SBR science goal to develop approaches to understand the biogeochemical structure and function of watersheds. The 300 A field site exists within the enormous Columbia River watershed, and it is consequently impractical to propose a watershed

study of this system. The Hanford Columbia River corridor does, however, display an extended and dynamic groundwater-river interaction zone that offers unique opportunities to study biogeochemical processes that occur within a critical watershed compartment at a very large scale. Fundamental research on this zone also provides important information to Hanford site managers and stakeholders on the environmental compartment that regulates off-site release. Impactful natural processes occur in the groundwater-river interaction zone that influence the terrestrial carbon cycle, moderate environmental responses to climate change, and regulate elemental biogeochemical cycles that control water quality at the watershed scale. Approaches developed to study this dynamic system will have wide applicability elsewhere. Our initial transition plan, to be submitted in Power-Point format during Aug. 2012 will further elaborate on these concepts.

Broad goals for research over the next year (FY 2013) that incorporate the above changes are as follows:

- Initiate spatiotemporal genomic and proteomic studies of microorganisms in different system compartments (groundwater and aquifer sediments at different depths, GW-R mixing zone, hyporeic zone, and river). Link to robust in-situ investigations of biogeochemical function and rates, and biogeochemical model development.
- Extend the current partial plume model funded by SciDAC to the full plume scale and integrate available hydrogeologic data and multi-disciplinary information on the groundwater-river interaction zone to yield a system scale model. Document model accuracy and initiate steps for sequential improvement to include microbial ecology, community structure, and biogeochemical processes.
- Refine the current SFA statistical model of the role of deterministic and stochastic processes on subsurface microbial ecology through additional site investigations and genomic analyses, and integrate with the stochastic system-scale reactive transport model for interactive, heuristic simulations. Develop and demonstrate suitable data assimilation methods and uncertainty analysis for biotic and abiotic data of very different type and temporal resolution. Conceptualize the linkage of biogeochemical process and molecular microbiologic data within a stochastic format.
- Perform hydrobiogeochemical studies of the U-plume utilizing unique multi-dimensional attributes of contaminant U as a tracer of system scale coupled processes and fluxes, and the influences of heterogeneities of different form. Focus on hotspot locations including zones of: i.) dynamic U accumulation and release, ii.) accelerated electron donor supply and microbial utilization, and iii.) methane upwelling into the lower oxic aquifer. Develop approaches to characterize, understand, and model the contributions of these local zones of accelerated activity to overall system response.
- Use focused laboratory investigations with site sediments, microorganisms, mineral phases, and dissolved constituents to develop understandings and microscopic models of functional biogeochemical processes (emphasizing C, N, S, Fe, and P) controlling system behavior whose importance has been informed by genomic and proteomic analyses of field system compartments and biogeochemical field investigations. Included are fundamental genomic, physiological, biochemical and genetic investigations of Hanford microbes representing key functional guilds to underpin field biogeochemical processes and inform metagenomic/proteomic datasets.

New Scientific Research that May Shift Focus

None to report.

Collaborative Research

The PNNL SFA has maintained an active program of collaborative research. These collaborators have worked closely with PNNL research teams; complementing expertise, enriching research results, and enhancing impact (note co-authors in SFA publications, **Appendix A**). Funding provided to external collaborators (**Section V.**) has supported students and post-docs, and enabled specialized analyses beyond the expertise of PNNL staff. Funds to collaborators in FY 2012 were cut by 15% over those provided in FY 2011. The PNNL SFA expects to end most funded collaborations after FY 2012 because of funding limitations. The collaborators have been notified of these plans. The collaborators, their expertise, and theme area of contribution are noted immediately below.

- J. Blumberger (*University of London*) – Molecular modeling of heme motifs, Theme Area III
- H. Beyenal (*Washington State University*) – Biofilm characterization, Theme Area I
- S. Conradson (*LANL*) – X-ray absorption spectroscopy of plutonium, Theme Area III
- J. Davis (*LBNL*) – Surface chemical reactions and modeling, Theme Area II
- S. Fendorf (*Stanford University*) – Reactive diffusion, Theme Area II
- R. Ewing (*University of Iowa*) – Pore network modeling, Theme Area II
- A. Hunt (*Wright State University*) – Upscaling theory, Theme Area II
- K. Kemner (*ANL*) – Synchrotron x-ray science, Theme Area II
- A. Navrotsky (*University of California, Davis*) – Mineral thermochemistry, Theme Area III
- D. Richardson (*University of East Anglia*) – Molecular microbiology, Theme Area III
- E. Roden (*University of Wisconsin*) – Bacterial N, Fe, and S cycling, Theme Areas I and III
- B. Wood (*Oregon State University*) – Volume average upscaling, Theme Area II

V. Staffing and Budget Summary

Funding Allocation by Program Element and Individual Researcher

Information is provided below on the manner in which SFA funding from SBR was distributed to PNNL staff and external collaborators in FY 2012. We report funding allocations for SFA Management, Theme Area I, Theme Area II, Theme Area III, and external collaborators. The total allocated budget for FY 2012 was \$6,641,805 which includes \$1,116,806 in carryover from FY 2011, and \$5,525,000 in new FY 2012 funds. We also note post-docs and other post-graduate student appointees associated with Theme Area Research. We expect minimal carryover from FY 2012 to FY 2013.

SFA Management

NAME	FTE's	FY12 Budget
Zachara, John M	0.32	
Fredrickson, Jim K	0.24	
Project Specialists	0.45	
Other Labor	0.11	
Total	1.11	685,051

Theme I - Field Scale Biogeochemistry

NAME	FTE's	FY12 Budget
Fredrickson, Jim K	0.14	
Konopka, Allan E	0.16	
McKinley, James P	0.17	
Wilkins, Michael J	0.19	
Other Labor	2.36	
Post Doc / Post Bac	1.29	
Total	4.31	1,456,296

Theme I - Post Doc / Post Bac / Students		
NAME	FTE's	Student Type
Lee, Ji-Hoon	1.00	Post Doc II
Lund, Rachael M	0.20	Post Bac & Masters
Ramanathan, Ramya	0.09	Post Doc III
Total	1.29	

Theme Area II - Coupled Process Integration and Multi-Scale Modeling

NAME	FTE's	FY12 Budget
Chen, Xingyuan	0.44	
Hammond, Glenn E	0.10	
Johnson, Tim	0.05	
Liu, Chongxuan	0.56	
Murray, Christopher J	0.08	
Scheibe, Timothy D	0.23	
Zachara, John M	0.09	
Other Labor	1.32	
Post Doc / Post Bac	3.78	
Total	6.66	1,396,657

Theme II - Post Doc / Post Bac / Students		
NAME	FTE's	Student Type
McKinley, Matthew I	0.67	Post Bac & Masters
Shang, Jianying	0.75	Post Doc I
Shi, Zhi	0.61	Post Doc I
Singh, Abhas	1.00	Post Doc I
Yang, Xiaofan	0.75	Post Doc III
Total	3.78	

Theme III - Biogeochemical Electron Transfer

NAME	FTE's	FY12 Budget
Felmy, Andrew R	0.27	
Liu, Juan	0.29	
Pearce, Carolyn I	0.91	
Rosso, Kevin M	0.28	
Shi, Liang	0.42	
Other Labor	2.13	
Post Doc / Post Bac	1.24	
Total	5.55	1,571,802

Theme III - Post Doc / Post Bac / Students		
NAME	FTE's	Student Type
Anderson, Brian J	0.25	Post Bac & Masters
Chatman, Shawn M E	0.23	Post Doc I
Liu, Ying	0.56	Post Doc I
Merkley, Eric D	0.20	Post Doc II
Total	1.24	

Funding Allocations to External Collaborators

NAME		FY12 Budget
J. Blumberger (<i>University of London</i>)		19,148
H. Beyenal (<i>Washington State University</i>)		40,000
S. Conradson (<i>LANL</i>)		85,000
J. Davis (<i>LBNL</i>)		127,500
S. Fendorf (<i>Stanford University</i>)		75,000
R. Ewing (<i>University of Iowa</i>)		50,000
A. Hunt (<i>Wright State University</i>)		55,000
K. Kemner (<i>ANL</i>)		127,500
A. Navrotsky (<i>University of California, Davis</i>)		25,500
D. Richardson (<i>University of East Anglia</i>)		187,253
E. Roden (<i>University of Wisconsin</i>)		160,510
B. Wood (<i>Oregon State University</i>)		93,500
Subcontracting Fees		110,113
Total		1,156,024

Personnel Actions and Procedures

BER supported projects within PNNL's Biologic Sciences Division (BSD) have recently hired Dr. William Nelson from the Wrigley Marine Science Center of the University of Southern California. His expertise is in the analysis of microbial genomics emphasizing bioinformatics. The recommendation to hire a staff member with this expertise was made by SBR management to PNNL SFA management in Oct. 2011 in response to our March 2011 SFA peer review. Dr. Nelson will begin work at PNNL in September 2012 and spend approximately 0.5 FTE on the PNNL SFA project in Theme Area I working on metagenomics analyses of the varied compartments of the 300 A groundwater-river interaction zone. He will also join our SFA research team that is working to conceptualize a new biogeochemical reactive transport model that integrates dynamic molecular information on microbial ecology and community function with geochemical reaction and hydrologic transport. We do not expect any additional new hires until the future direction of the SBR program is clear.

Currently, the SFA supports five newly hired young scientists (see **Section III**). Funding levels range from ~35% to 100% depending on individual and their other commitments. Rapid and dramatic changes to the SBR program including budget cuts and redirection have caused stress among this group who are concerned over their future prospects and the nature of science that BER/SBR will choose to pursue

The PNNL SFA had a young investigators project underway in FY 2010 and FY2011 to enhance the integration of new staff into the BER research system. That project was dissolved in FY 2012 as a result of budget cuts and the staff integrated within research projects led by more experienced P.I.s. Integration of key IFRC activities into the SFA, a new hire, and redirection to focus on larger scale systems will reduce the level of support that the SFA can provide to

younger staff in general. SFA management is seeking to identify alternate internal funding sources for those short on funding, but prospects are not optimistic. Some may have to leave the lab in search of employment elsewhere.

National Lab Investments in Program

None to report.

Appendix A: SFA Journal Publications

2012

Ahmed B., Cao B., McLean J. S., Ica T., Dohnalkova A., and Fredrickson J. K. (2012) Fe(III) reduction and U(VI) immobilization by *Paenibacillus* sp. 300A isolated from Hanford 300A subsurface sediments. *Applied Environmental Microbiology*, Submitted.

Batuk O. N., Conradson S. D., Boukhalfa H., Burakov B. E., Clark D. L., Czerwinski K. R., Felmy A. R., Lezama-Pacheco J. S., Kalmykov S. N., Moore D. A., Myasoedov B. F., Reilly D. D., Roback R. C., Vlasova I. E., Webb S. M., and Wilkerson M. P. (2012) Environmental and forensic chemistry of U and Pu at Chernobyl, McGuire AFB, Mayak, Rocky Flats, Hanford, and Los Alamos. *Nature*, Submitted.

Breuer M., Zarzycki P., Blumberger J., and Rosso K. M. (2012) Thermodynamics of electron flow in the bacterial deca-heme cytochrome MtrF. *Journal of the American Chemical Society*, In Press.

Breuer M., Zarzycki P., Shi L., Clarke T. A., Edwards M. J., Butt J. N., Richardson D. J., Fredrickson J. K., Zachara J., Blumberger J., and Rosso K. M. (2012) Molecular structure and free energy landscape for electron transport in the deca-heme protein MtrF. *Biochemical Society Transactions*, In Press.

Chen X., Murakami H., Hahn M., Hammond G. E., Rockhold M., Rubin Y., and Zachara J. (2012) Three-dimensional Bayesian geostatistical aquifer characterization at the Hanford 300 Area using tracer test data. *Water Resources Research* 48, W06501, doi:10.1029/20911WR010675.

Edwards M. J., Hall A., Shi L., Fredrickson J., Zachara J. M., Butt J. N., Richardson D. J., and Clarke T. A. (2012) The crystal structure of the extracellular 11-heme cytochrome UndA reveals a conserved 10-heme motif and defined binding site for soluble iron chelates. *Structure*, In Press.

Ewing R. P., Liu C. X., and Hu Q. H. (2012) Modeling intragranular diffusion in low-connectivity granular media. *Water Resources Research* 48, W03518, doi:10.1029/2011WR011407.

Felmy A. R., Moore D. A., Pearce C. I., Conradson S., Qafoku O., Buck E. C., Rosso K. M., and Ilton E. S. (2012) The reactivity of plutonium in PuO₂/magnetite suspensions: Identification of a new source of soluble plutonium. *Environmental Science & Technology*, In Review.

Fonseca B. M., Tien M., Rivera M., Shi L., and Louro R. O. (2012) Efficient and selective isotopic labeling of hemes to facilitate the study of multiheme proteins. *Bio Techniques*, In Press.

Kerisit S. and Liu C. X. (2012) Diffusion and adsorption of uranyl carbonate species in nanosized mineral fractures. *Environmental Science & Technology* 46, 1632-1640.

Konopka A. and Wilkins M. (2012) Application of meta-transcriptomics and -proteomics to analysis of *in situ* physiological state. *Frontiers in Microbiology* 3.

- Lee J. H., Fredrickson J. K., Kukkadapu R. K., Boyanov M. I., Kemner K. M., Lin X. J., Kennedy D. W., Bjornstad B. N., Konopka A. E., Moore D. A., Resch C. T., and Phillips J. L. (2012) Microbial reductive transformation of phyllosilicate Fe(III) and U(VI) in Fluvial subsurface sediments. *Environmental Science & Technology* 46, 3721-3730.
- Lilova K. I., Pearce C. I., Gorski C. A., Rosso K. M., and Navrotsky A. (2012) Thermodynamics of the magnetite-ulvöspinel ($\text{Fe}_3\text{O}_4\text{-Fe}^{2+}\text{TiO}_4$) solid solution. *American Mineralogist*, In Press.
- Lilova K. I., Xu F., Rosso K. M., Pearce C. I., Kamali S., and Navrotsky A. (2012) Oxide melt solution calorimetry of Fe^{2+} -bearing oxides and application to the magnetite-maghemite ($\text{Fe}_3\text{O}_4\text{-Fe}_{8/3}\text{O}_4$) system. *American Mineralogist* 97, 164-175.
- Lin X. J., Kennedy D., Peacock A., McKinley J., Resch C. T., Fredrickson J., and Konopka A. (2012) Distribution of microbial biomass and potential for anaerobic respiration in Hanford Site 300 Area subsurface sediment. *Applied and Environmental Microbiology* 78, 759-767.
- Lin X., Kennedy D., Fredrickson J., Bjornstad B., and Konopka A. (2012) Vertical stratification of subsurface microbial community composition across geological formations at the Hanford Site. *Environmental Microbiology* 14, 414-425.
- Lin X., McKinley J., Resch C.T., Kaluzny R., Lauber C.L., Fredrickson J., Knight R., and Konopka A. (2012) Spatial and temporal dynamics of the microbial community in the Hanford unconfined aquifer. *ISME Journal*; doi:10.1038/ismej.2012.26.
- Liu J., Pearce C. I., Qafoku O., Rosso K. M., Arenholz E., Heald S. M., and Peretyazhko T. S. (2012) Tc(VII) reduction kinetics by magnetite and titanomagnetite ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$) nanoparticles: A tunable Fe(II)/Fe(III) redox potential system. *Geochimica et Cosmochimica Acta*, In Press.
- Liu J., Wang Z., Belchik S. M., Edwards M. J., Liu C., Kennedy D. W., Merkley E. D., Lipton M. S., Butt J. N., Richardson D. J., Zachara J. M., Fredrickson J. K., Rosso K. M., and Shi L. (2012) Identification and characterization of MtoA: A decaheme c-type cytochrome of the neutrophilic Fe(II)-oxidizing bacterium *Sideroxydans lithotrophicus* ES-1. *Frontiers in Microbiology* 3.
- Marritt S. J., Lowe T. G., Bye J., McMillan D. G., Shi L., Fredrickson J., Zachara J., Richardson D. J., Cheesman M. R., Jeuken L. J., and Butt J. N. (2012) A functional description of CymA, an electron-transfer hub supporting anaerobic respiratory flexibility in *Shewanella*. *Biochemical Journal* 444, 465-74.
- Pearce C. I., Qafoku O., Liu J., Arenholz E., Heald S. M., Kukkadapu R. K., Gorski C. A., Henderson C. M. B., and Rosso K. M. (2012) Synthesis and properties of titanomagnetite ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$) nanoparticles: A tunable solid-state Fe(II/III) redox system. *Journal of Colloid and Interface Science*, In Press.
- Pearce C. I., Wilkins M., Zhang C. C., Heald S. M., Fredrickson J. K., and Zachara J. M. (2012) Pore-scale imaging and characterization of biogeochemical controls on iron and uranium speciation under flow conditions. *Environmental Science & Technology*, In Press.

Peng S., Hu Q. H., Ewing R. P., Liu C. X., and Zachara J. M. (2012) Quantitative 3-D elemental mapping by LA-ICP-MS of a basaltic clast from the Hanford 300 Area, Washington, USA. *Environmental Science & Technology* 46, 2025-2032.

Peretyazhko T. S., Zachara J. M., Kukkadapu R. K., Heald S. M., Kutnyakov I. V., Resch C. T., Arey B. W., Wang C. M., Kovarik L., Phillips J. L., and Moore D. A. (2012) Pertechneate (TcO_4^-) reduction by reactive ferrous iron forms in naturally anoxic, redox transition zone sediments from the Hanford Site, USA. *Geochimica et Cosmochimica Acta*, In Press.

Plymale A. E., Bailey V. L., Fredrickson J. K., Heald S. M., Buck E. C., Shi L., Wang Z. M., Resch C. T., Moore D. A., and Bolton H. (2012) Biotic and abiotic reduction and solubilization of $\text{Pu(IV)O}_2 \cdot x\text{H}_2\text{O}_{(\text{am})}$ as affected by anthraquinone-2,6-disulfonate (AQDS) and ethylenediaminetetraacetate (EDTA). *Environmental Science & Technology* 46, 2132-2140.

Richardson D. J., Butt J. N., Fredrickson J. K., Zachara J. M., Shi L., Edwards M. J., White G. F., Baiden N., Gates A. J., Marritt S. J., and Clarke T. A. (2012) Porin-cytochrome' model for microbe-to-mineral electron transfer. *Molecular Microbiology*, In Press.

Richardson D. J., Edwards M. J., White G. F., Baiden N., Hartshorne R. S., Fredrickson J., Shi L., Zachara J. M., Gates A. J., Butt J. N., and Clarke T. A. (2012) Exploring the biochemistry at the extracellular redox frontier of bacterial mineral Fe(III) respiration. *Biochemical Society Transactions* 40, 493-500.

Roden E. E. and Shelobolina E. (2012) Microbial iron redox cycling in subsurface environments. *Biochemical Society Transactions*, In Press.

Roden E., McBeth J. M., Blöthe M., Percak-Dennett E. M., Fleming E. J., Holyoke R. R., Luther G. W., and Emerson D. (2012) The microbial ferrous wheel in a neutral pH groundwater seep. *Frontiers in Microbiology* 3.

Shelobolina E. S., Konishi H., Xu H., Benzine J., Xiong M. Y., Wu T., Blöthe M., and Roden E. (2012) Isolation of phyllosilicate-iron redox cycling microorganisms from an illite-smectite rich hydromorphic soil. *Frontiers in Microbiology* 3.

Shelobolina E., Xu H., Konishi H., Kukkadapu R. K., Wu T., Blöthe M., and Roden E. E. (2012) Microbial lithotrophic oxidation of structural Fe(II) in biotite. *Applied Environmental Microbiology*, In Press.

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Appendix B: SFA Presentations

2012

Breuer M., Zarzycki P. P., Rosso K. M., and Blumberger J. (2012) "Thermodynamics of electron flow in the bacterial decaheme cytochrome MtrF." Presented at the Biochemical Society Electron Transfer at the Microbe-Mineral Interface, Norwich, United Kingdom on April 2-3, 2012.

Latta D., Pearce C. I., Gorski C. A., Rosso K. M., O'Loughlin E. J., Kemner K. M., Scherer M., and Boyanov M. I. (2012) "Reactivity of UVI with pure, oxidized, and Ti-substituted magnetites." Presented at the 22nd Annual Goldschmidt Conference, Montreal, PQ, Canada.

Liu C., Zhang C., Shi Z., and Zachara J. M. (2012) "Effect of pore-scale processes coupling on hematite reduction rate in subsurface porous media." Invited presentation at the ACS Spring Meeting, San Diego, CA on March 26, 2012.

Marshall M. J., Plymale A. E., Wilkins M. J., Kennedy D. W., and Konopka A. (2012) "Isolation and characterization of metal redox-transforming microorganisms from the Hanford 300 Area." Invited presentation at the ACS National Spring Meeting, San Diego, CA on March 26, 2012.

Richardson D. J., Edwards M., White G. F., Baiden N., Hartshorne R. S., Fredrickson J. K., Shi L., Zachara J. M., Gates A. J., Butt J. N., and Clarke T. (2012) "Exploring the biochemistry at the extracellular redox frontier of bacterial mineral Fe(III) respiration." Invited presentation at the Biochemical Society Annual Symposium - Frontiers in Biological Catalysis, Robinson College Cambridge, UK on January 10-12, 2012.

Roden E. E. and Shelobolina E. (2012) "Microbial iron redox cycling in subsurface environments." Presented at the Biochemical Society Electron Transfer at the Microbe-Mineral Interface, Norwich, United Kingdom on April 2-3, 2012.

Rosso K. M., Breuer M., Blumberger J., Zarzycki P. P., Smith D. M. A., Shi L., Richardson D., Clarke T. A., Edwards M., Butt J. N., Zachara J. M., and Fredrickson J. K. (2012) "Molecular structure and electron transfer in microbial cytochromes." Presented at the Biochemical Society Electron Transfer at the Microbe-Mineral Interface, Norwich, United Kingdom on April 2-3, 2012.

Rosso K. M. (2012) "Electron transfer and the biogeochemistry of iron." Invited Presentation as a Harvard Guest Lecturer on Advanced Topics in Environmental Chemistry, Cambridge, MA on February 29, 2012.

Scheibe T. D. (2012) "Overcoming the tyranny of scales in subsurface flow and reactive transport simulation," Invited presentation given at the 2012 Society for Industrial and Applied Mathematics (SIAM) Annual Meeting, Minneapolis, MN, on July 9-13, 2012.

Shi L., Liu J., Rosso K. M., Wang Z., Edwards M., Kennedy D. W., Byrne-Bailey K., Coates J. D., Butt J. N., Richardson D. J., Zachara J. M., and Fredrickson J. K. (2012) "Identification and characterization of Mtr homologues from the neutrophilic Fe(II)-oxidizing bacteria." Presented at

the Biochemical Society Electron Transfer at the Microbe-Mineral Interface, Norwich, United Kingdom on April 2-3, 2012.

2011

Belchik S. M., Liu J., Wang Z., Rosso K. M., Zachara J. M., Fredrickson J. K., and Shi L. (2011) "Purification and characterization of SL-MtrA, an iron oxidizing c-type cytochrome of *Sideroxydans lithotrophicus* ES-1." Presented at the ASM 111th General Meeting, New Orleans, LA on May 23, 2011.

Cao B., Belchik S. M., Marshall M. J., Dohnalkova A., Fredrickson J. K., and Shi L. (2011) "Functional analysis of PtpA, a low molecular mass protein tyrosine phosphatase of *Shewanella oneidensis* MR-1, in biofilm formation and extracellular polymeric substances biosynthesis." Presented at the ASM 111th General Meeting, New Orleans, LA on May 23, 2011.

Felmy A. R., Arey B. W., Ilton E. S., Rosso K. M., and Zachara J. M. (2011) "Interfacial reactivity: Emerging paradigms from molecular-microscopic level observations." Presented at the Frontiers in Geosciences Colloquia, Los Alamos, NM on February 28, 2011.

Felmy A. R., Rosso K. M., Conradson S. D., Buck E. C., Moore D. A., Pearce C. I., Qafoku O., Liu J., and Ilton E. S. (2011) "Redox transformations of PuO_2^{2+} and TcO_4^- induced by Fe(II): Impact of the formation of different Fe(III) containing reaction products." Presented by Carolyn Pearce at the Migration 2011, Beijing, China on September 18-23, 2011.

Fredrickson J. K., Lee J. H., Plymale A. E., Dohnalkova A., Heald S. M., Peretyazhko T., McKinley J. P., Kukkadapu R. K., and Zachara J. M. (2011) "Biogeochemical redox transformation of pertechnetate ($^{99}\text{TcO}_4^-$)." Invited presentation at the Goldschmidt 2011 Conference, Prague, Czech Republic on August 15, 2011.

Kerisit S. N., Liu C., Felmy A. R., and Ilton E. S. (2011) "Atomistic simulations of uranium in the environment: Diffusion, adsorption, and incorporation." Invited presentation at the Goldschmidt 2011 Conference, Prague, Czech Republic on August 15, 2011.

Konopka A. (2011) "Nature's pulsing paradigm." Invited presentation at the 3rd Annual Argonne Soil Metagenomics Workshop, Argonne, IL on October 7, 2011.

Liu C. "Pore-scale processes coupling and upscaling of geochemical reactions." (2011) Keynote presentation at the IPACES Annual Conference 2011, Guiyang, July 8, 2011.

Liu C. (2011) "Upscaling of geochemical and biogeochemical reactions." Invited at the International Groundwater Forum 2011, Wuhan, July 14, 2011.

Liu C., Kerisit S. N., and Zachara J. M. (2011) "Sub-grid reactive diffusion and apparent uranyl adsorption/desorption rates." Presented at the American Geophysical Union Fall 2011 Meeting, San Francisco, CA on December 5, 2011.

Liu C., Kerisit S. N., Shang J., Zachara J. M., Ma R., Zheng C., Greskowiak J., and Prommer H. (2011) "Importance of fundamental processes and upscaling to reactive transport prediction." Invited presentation at the Fragrant Hill Workshop: China's Groundwater Contamination, Beijing, China on September 27, 2011.

Liu C., Kerisit S. N., Ewing R. N., Hunt A., Shang J., and Zachara J. M. (2011) "Pore-scale process coupling and its effect on the apparent rates of uranyl surface complexation." Keynote presentation at the Goldschmidt 2011 Conference, Prague, Czech Republic on August 19, 2011.

McKinley J. P., Miller E. A., Miller M. D., and Liu J. (2011) "Microscale reconstruction of biogeochemical substrates." Presented by Micah Miller at the American Geophysical Union Fall 2011 Meeting, San Francisco, CA on December 9, 2011.

Merkley E. D., Wu S., Tolic N., Smith R. D., Lipton M. S., and Adkins J. N. (2011) "Determining cross-linking sites in a homodimer by peptide and intact protein LC-MS." Presented at Cascadia Proteomics Symposium, Seattle, WA on July 18, 2011.

Pearce C. I., Liu J., Qafoku O., Arenholz E., Heald S. M., and Rosso K. M. (2011) "Fe(II) exchange at titanomagnetite-water interfaces." Presented at the Goldschmidt 2011 Conference, Prague, Czech Republic on August 19, 2011.

Richardson D. J., Edwards M., White G. F., Baiden N., Hartshorne R. S., Fredrickson J. K., Shi L., Zachara J. M., Gates A. J., Butt J. N., and Clarke T. (2011) "Electron transfer to the microbe-mineral interface." Presented at the 7th European Workshop on Bacterial Respiratory Chains: Biochemistry, Genetics, Assembly and their Regulation, Backagården Kurs & Konferenscenter, Höör, Lund, Sweden on May 11-15, 2011.

Rockhold M. L., Chen X., Ramanathan R., Vermeul V. R., Johnson T. C., and Murray C. J. (2011) "Facies delineation using core, wireline log, and electromagnetic borehole flowmeter data." Presented at the American Geophysical Union Fall 2011 Meeting, San Francisco, CA on December 9, 2011.

Rosso K. M., Zarzycki P. P., Pearce C. I., Katz J., Gilbert B., Handler R., Scherer M., and Meakin P. (2011) "Reactive Fe(II) and electron exchange dynamics in iron oxides." Presented at the Goldschmidt 2011 Conference, Prague, Czech Republic on August 19, 2011.

Rosso K. M., Zarzycki P. P., Breuer M., Blumberger J., Shi L., Richardson D., Clarke T. A., Edwards M., Butt J. N., Zachara J. M., and Fredrickson J. K. (2011) "Large-scale simulation of molecular structure and electron transfer in microbial cytochromes." Invited presentation at the Goldschmidt 2011 Conference, Prague, Czech Republic on August 19, 2011.

Scheibe T. D. (2011) "Quantifying flow and reactive transport in the heterogeneous subsurface environment: From pores to porous media and facies to aquifers," Invited presentation at the Guy F. Atkinson Distinguished Lecture Series, University of Utah, Department of Geology, November 10, 2011.

Scheibe T. D., Palmer B. J., Tartakovsky A. M., Schuchardt K. L., Richmond M. C., Perkins W. A., Serkowski J. A., Jones C., and Ma K. L. (2011) "Visualization of pore-scale flow and

reactive transport processes." Invited presentation at ModelCARE 2011, Leipzig, Germany, September 18-22, 2011.

Scheibe T. D., Hou Z., and Palmer B. J. (2011) Pore-scale simulation of intragranular diffusion: Effects of incomplete mixing on macroscopic manifestations." Invited presentation by Tim Scheibe at the American Geophysical Union Fall 2011 Meeting, San Francisco, CA on December 9, 2011.

Shang J., Liu C., and Zachara J. M. (2011) "Pore-scale exploration of uranyl desorption." Presented at the American Geophysical Union Fall 2011 Meeting, San Francisco, CA on December 9, 2011.

Shelobolina E., Xu H., Konishi H., Wu T., and Roden E. E. (2011) "Lithotrophic oxidation of Fe(II)-silicates as the basis for a deep granitic biosphere." Presented at the Geological Society of American Annual Meeting, October 2011.

Smith J. N., Minard K. R., Hostetler K. E., Pearce C. I., and Pounds J. G. (2011) "A strategy for overcoming challenges associated with measuring nanoparticle biokinetics: titanomagnetite nanoparticle biokinetics in mice." Presented at the Society of Toxicology (SOT) Annual Meeting 2012, San Francisco, CA on March 11-15, 2012.

Wilkins M. J. (2011) "Investigating the impact of pore scale microenvironments on contaminant biogeochemical reactive transport." Presented at the American Geophysical Union Fall 2011 Meeting, San Francisco, CA on December 9, 2011.

Xiong M., Shelobolina E. S., Benzine J., Konishi H., Xu H., Roden E. E. (2011) "Isolation of iron cycling microorganisms from illite-smectite rich rhizosphere." Presented at the American Society for Microbiology General Meeting, May 21-24, 2011.

Zachara J. M., Szecsody J. E., and Liu C. (2011) "Lessons learned in the remediation of complex groundwater systems." Invited presentation at the Fragrant Hills Science Conference, Beijing, China on September 27, 2011.

Zachara J. M., Peretyazhko T., Kukkadapu R. K., McKinley J. P., Liu C., and Felmy A. R. (2011) "Challenges in the identification of redox reactive Fe(II) mineral phases in suboxic aquifer sediments." Invited presentation at the Goldschmidt 2011 Conference, Prague, Czech Republic on August 18, 2011.