Role of Microenvironments and Transition Zones in Subsurface Reactive Contaminant Transport: The PNNL SFA

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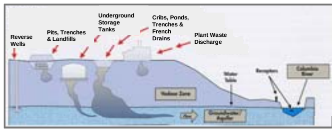
CONCEPT

The PNNL-SFA will significantly advance understanding of Hanford-inspired subsurface science issues that are timely and that align with PNNL technical expertise and capabilities. Important goals are to develop: 1) an integrated conceptual model for microbial ecology in the Hanford subsurface and its influence on biogeochemical reactions impacting contaminant migration; 2) a fundamental understanding of chemical reaction, biotransformation, and physical transport processes in microenvironments and transition zones of documented field or conceptual importance, and 3) biogeochemical reactive transport models for Tc, U, and Pu integrating multi-process coupling at different spatial scales. Targeted contaminant chemical reaction and biotransformation processes include heterogeneous and biologic electron transfer, precipitation and dissolution, and surface complexation. The research program is supported by lab- and field investigations, and coupled computation and experimentation to explore molecular, grain/pore, and mesoscopic processes operative in complex field-scale biogeochemical systems. Geophysical techniques and modeling approaches are being evaluated to define, characterize, and map spatial structures and reactive transport properties of microenvironments and transition zones in the field. Research is conducted by collaborative teams of PNNL and external investigators focused on three impactful science themes.



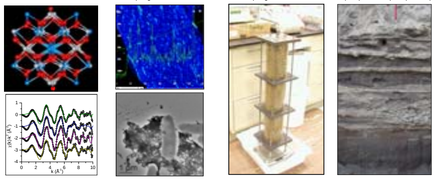
Common fundamental science questions are associated with different Hanford waste sites. SFA research will provide the scientific basis for more applied S&T research.

EMPHASIS

- Hanford-inspired subsurface science issues with long-term implications.
- Hanford risk drivers (U, Tc, and Pu) exhibiting complex biogeochemistry and significant inventory (U=202,700 kg, ^{99}Tc=1390 Ci, Pu=400 kg).
- River corridor (300 A with shallow vadose zone) and interior plateau sites (200 A with deep vadose zone).
- Close alignment with Hanford Integrated Field Research Challenge (IFRC) and Environmental Molecular Sciences Laboratory (EMSL) capabilities.
- Projects integrated across scales from the molecular to field with focus on three science themes.
- Fundamental science emphasis for application of findings to other sites and environments.

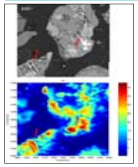
Different Scales, Issues, and Science

Molecular	Grain/pore	Mesoscopic	Field-plume
Bonding environment & local structure; Fundamental mechanisms; Energetics & structural controls; Solvation effects	Mineral residence phase identity & composition; Reaction networks & kinetics; Morphologic & surface issues; Fundamental process coupling	Rate processes (Chemical; Microbiologic; Mass transfer); Advection effects; 1-D scaling issues; Pore-scale process coupling	Physical heterogeneity (Water velocities, directions; Reactants); Multi-scale mass transfer; Mixing & averaging; Distributed properties; Seasonal issues (temperature, precipitation)



MICROENVIRONMENTS AND TRANSITION ZONES

Microenvironments are submicron to meter scale domains that exert strong influence on water and sediment chemistry of larger vadose or aquifer zones because of integrated microbial, geochemical, and hydrophysical processes that occur at dissimilar or accelerated rates within them.



Electron micrograph and Fe concentration map of a Hanford lithic fragment. Fe(II) is a key reactant and lithogenic energy source for microorganisms. It exists in restricted spaces (microenvironments).

Common silt-textured stringers containing phyllosilicates with high cation exchange capacity and water retention properties at Hanford have dramatically different reaction properties than co-associated sands.

Transition zones are field-scale features through which chemical, physical, or microbiological properties change over relatively short distances (e.g., <1 m) to influence, or in response to, contaminant migration.

Biogeochemical redox boundary in 300 A Ringold sediments ~2.5 m below Hanford-Ringold contact. The genesis and chemical/mineralogic characteristics of this zone are under investigation.

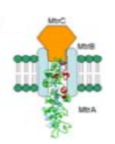
Research in out-years will expand to investigate the region of groundwater-river interaction associated with and beyond the IFRC as a complex system. This domain contains multiple transition zones including a seasonally dynamic water table and region within the aquifer where groundwater and river-water mix, and a hyporheic zone at the groundwater-river interface where flux vectors and redox state change frequently in response to river discharge. Understanding and describing the microbial ecology, coupled biogeochemical processes, and hydrophysical controls over the system scale will be a goal. The Hanford IFRC site is circled in red.

SCIENCE THEME 1: BIOGEOCHEMICAL ELECTRON TRANSFER REACTIONS

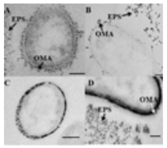
Scope and Research Examples:

- Developing a molecular-level understanding of key microbial and abiotic 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).
  - Enzymatic reduction of relevant forms of Fe(III), such as Fe(III)-oxides and oxyhydroxides, and oxidation of aqueous Fe(II), Fe(II) sorbed on mineral matter, or Fe(II)-bearing mineral phases.
  - Reaction rate and extent of heterogeneous U(VI) and Tc(VII) reduction by structural mineralogic Fe(II), and the effects of impurities, surface oxidation or co-precipitation, and Fe(II) resupply on mineral reduction potential.
  - Competitive oxidation and release rates of abiotic or biomineralized pure or iron-coprecipitated U(IV) and Tc(IV) phases in the presence of dissolved oxygen and mineral/microbiologic reductants, and reduction of Pu(IV) phases and associated remobilization potential by Fe(II).

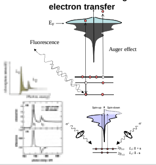
Fundamental protein interactions



Molecular bio(geo)chemistry of Hanford microorganisms



Molecular controls on heterogeneous electron transfer

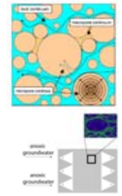


SCIENCE THEME 2: PORE SCALE REACTIVE TRANSPORT AND UPSCALING

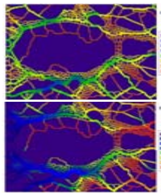
Scope and Research Examples:

- Experimental and theoretical investigations of coupled geochemical, biological, and transport processes at the pore and grain scale that control contaminant fate, and innovative concepts for their application to the meter-scale and above.
  - New approaches for pore scale experimental studies, and improved multi-species reactive transport theory and computational tools for simulation and numerical experiments.
  - Redox (and pH) transition front migration, and intra-grain electron (and proton) transfer in poorly poised subsurface sediments.
  - Effect of pore size, structure, connectivity, and diffusivity on microbiologically driven reactions including electron transfer and dissolution/precipitation.
  - Upscaling concepts, relationships, and models for coupled process and hierarchical systems.

Micromodels for pore scale biogeochemical research



Linkage of pore scale & continuum models to understand transport controls on reaction rates



Transport experiments of different type and scale

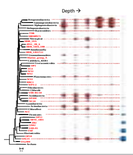
SCIENCE THEME 3: BIOGEOCHEMICAL/MICROBIAL COMMUNITY SPATIAL & TEMPORAL DYNAMICS

Scope and Research Examples:

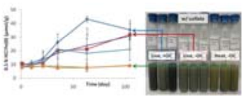
- Investigations of coupled microbiological-geochemical-physical properties and processes controlling field scale (sub-cm to m) subsurface microbial community structure-function, and causal connections between the identity and diversity within specific microbial functional groups and the stability of biogeochemical process rates.
  - Multi-level *in situ* microbial colonization of artificial substrates (e.g., Biosep beads) and geochemistry across subsurface transition zones to simultaneously define microbial community structure and biogeochemical processes as a function of local chemical & hydrologic environment.
  - Core and groundwater sampling (~cm scale resolution) to define microbial community structure and function across key Hanford subsurface transitions zones & interfaces including: saturated-unsaturated (vadose) 300A IFRC "smear" zone; lower Hanford formation-Ringold redox transition; Ringold rip-up clasts within the Hanford.
  - Community composition and functional responses of constructed subsurface communities in microfluidic devices of defined physical structure and natural communities associated with 300A subsurface sediment in laboratory columns to environmental perturbations (e.g., chemical/nutrient concentration gradients).
  - Assay of phylogenetic vs. functional heterogeneity of subsurface microbial communities – dual analysis of functional genes (e.g., terminal electron acceptor utilization, carbon catabolism) and phylogenetically informative genes (e.g., 16S) to complement analysis of biogeochemical activity rates.

In-well multi-level experiments

Microbial community structure



Microbial community function



ANTICIPATED SCIENCE ACCOMPLISHMENTS

Science Theme - 1

- Fundamental understanding of the redox properties of structural Fe(II)/Fe(III) in different mineral environments and factors (interfacial, thermodynamic) controlling reaction kinetics with contaminant (U, Tc, Pu) and natural oxidants/reductants of different molecular form.
- Nature, properties and structure, and reaction pathways of proteins and protein complexes responsible for electron transfer reactions (oxidation and reduction) with both solids and solutes in Hanford-relevant and model microorganisms.

Science Theme - 2

- New conceptual and numeric models of pore/grain scale microbiologic and biogeochemical processes mediated by diffusive and advective transport based on experimental observation for both redox and non-redox sensitive systems.
- Understanding scaling relationships of Hanford-specific, hierarchical, coupled process systems from the grain to field scale based on up-scaling and down-scaling perspectives.

Science Theme - 3

- A holistic understanding of microorganism community structure and dynamics within the Hanford formation saturated and temporally saturated vadose (smear) zone, and controlling factors.
- Biogeochemical function (e.g., reactions and their rates) and in-situ activities of microorganisms in the river corridor unconfined aquifer; and key systems level energy, carbon, and other nutrient balances.

CONTRIBUTIONS TO HANFORD CLOSURE

- Improved biogeochemical reaction models for U, Tc, and Pu relevant to Hanford geochemical and sediment mineralogic conditions, including Hanford speciation states and reaction networks.
- Knowledge of the complex functioning of the unconfined aquifer – Columbia River system where Hanford contaminants will potentially cross site boundaries.
- Understanding the role of Hanford specific transition zones on water and contaminant migration.
- New ways to characterize the in-situ structure and reactive transport properties of subsurface domains of different types.
- Fundamental basis for natural attenuation decisions, and documented ways to use laboratory derived information for field scale predictions.
- Insights for long term stewardship in terms of potentials for future mobilization or immobilization.

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