INTEGRATED FIELD CHALLENGE SITE
Hanford 300 Area
U.S. Department of Energy Office of Science
Environmental Remediation Sciences Program


Hanford 300 Area

Multi-Scale Mass Transfer Processes Controlling Natural Attenuation and Engineered Remediation: An IFC Focused on Hanford's 300 Area Uranium Plume

J. Zachara*, *PNNL*; M. Freshley, *PNNL*; D. DePaolo, *LBNL*; J. Fredrickson, *PNNL*; R. Haggerty, *Oregon State U*; D. Kent, *USGS*; A. Konopka, *Purdue U*; P. Lichtner, *LANL*; C. Liu, *PNNL*; J. McKinley, *PNNL*; M. Rockhold, *PNNL*; Y. Rubin, *U CA/Berkeley*; J. Szecsody, *PNNL*; R. Versteeg, *INL*; A. Ward, *PNNL*; B. Williams, *PNNL*; C. Zheng, *U. Alabama*; and Mike Thompson, DOE 300 A Site Steward

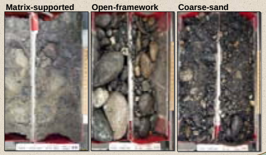
SCIENCE THEMES

Overall
Multiscale, multi-rate mass transfer influencing field-scale contaminant migration and remediation

Secondary
- Physical, chemical, and microbiologic factors controlling field-scale mass transfer
- Transferring laboratory kinetic data to field
- Kinetic effects of transients in water chemistry
- Microbiologic stability of remediation products
- Process evolution along flow paths
- Characterization and modeling approaches for mass-transfer dominated field systems
- Fundamental to applied science transfer

South Process Pond Excavation

IFC Hanford Formation Cores



ANTICIPATED OUTCOMES

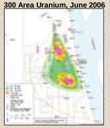
- Outstanding, multidisciplinary collaborative effort that significantly advances science
  - Characterization, experiment design, interpretation
  - Basic underpinnings of EM-20 activities
- Enduring and accessible field experiment data sets for hypothesis and model testing
- Improved linked multi-scale mass transfer/biogeochemical models for reactive contaminants
- New conceptual understanding of mass transfer processes at different scales influencing field behavior
  - Desorption, dissolution, dissipation
  - Effective reaction kinetics
  - Contaminant immobilization

BACKGROUND

History
- Site received effluents from REDOX and PUREX process development (1944-1954) and N-reactor fuels fabrication (1976-1986)
- Neutralized U(VI)-Cu(II) nitric acid solutions were primary waste stream
- 37,000 – 65,000 kg of U and 265,000 – 300,000 kg of Cu

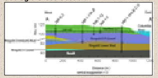
300 Area Uranium, Dec. 2005

300 Area Uranium, June 2006

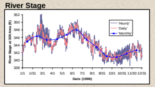


Hydrology
- Linked groundwater – river system
- Groundwater trajectory and composition shifts between fall/winter and spring/summer
- Sediments vary from open-framework to matrix-supported gravels to coarse sands
- Upper portion (Hanford formation) of aquifer (~3-7 m) carries U(VI) contamination
- Generally high hydraulic conductivity (> 1000 m/d)

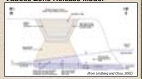
Geologic Cross Section



River Stage

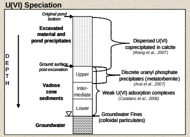


Vadose Zone Release Model

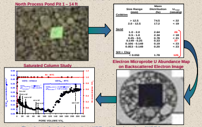


Science
- Significant ERSP (EMSP), EM-30, and EM-20 research performed on site
- Hydrology, geochemistry, U(VI) speciation, and microscopic mass transfer characterization studies performed
- Initial hydrologic and multi-component reactive transport models developed
- Limited microbiologic information, *Shewanella* in the hyporeic zone

U(VI) Speciation

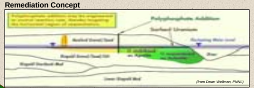


Mass Transfer Effects



The release of sorbed contaminant U(VI) and the adsorption of U(VI) from contaminated groundwater both show strong kinetic behavior

Remediation Concept

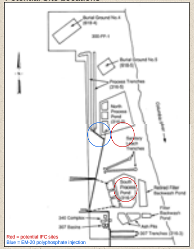


Remediation
- MNA IROD issued 12 years ago, but U(VI) concentrations have not decreased as predicted
- EM-20 is testing a polyphosphate remediation strategy at the site (see left) in response to regulatory (EPA) demands

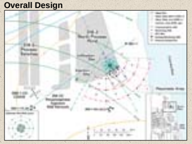
PROPOSED EXPERIMENTAL PROGRAM & SCHEDULE

Field Site
The field site will include an injection and monitoring array and an infiltration cell. Two potential site locations are being considered (see below left).

Potential Site Locations

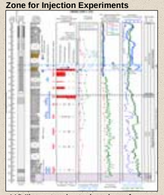


Overall Design

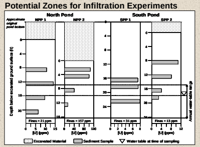


- The field site will include a spatially proximate infiltration plot (blue) and saturated zone injection gallery and monitoring array.
- Injection experiments will be performed in the U(VI)-contaminated region of the aquifer (see red) that lies within the highly permeable Hanford formation.
- The radial monitoring array that includes wells with multi-level sampling and continuous measurements of water level and specific conductance, will allow experiments to exploit seasonal changes in groundwater composition, flow directions and flowpaths, and U[VI] concentration.

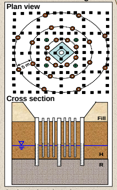
Zone for Injection Experiments



Potential Zones for Infiltration Experiments



Infiltration Cell Design



- The infiltration plot will be situated within U(VI)-contaminated vadose zone sediments of either the North or South process ponds and its associated, dynamic capillary fringe region.
- Disturbed, uncontaminated fill will be excavated during site development to expose undisturbed, contaminated sediments.
- An extensive geophysical monitoring array (above) will be established that will be augmented with spatially/vertically distributed tensiometers, wick and suction samplers, and piezometers for direct sampling of moisture content and porewaters.

Characterization
- A 3-D geostatistical model of the experimental domains will be established in terms of lithofacies, chemofacies, biofacies, and U distribution.
- The model will include the spatial distributions of the different facies types and contaminant U, their properties relevant to water and solute migration, and uncertainty.
- Various measurements derived from state-of-the-art downhole logging, laboratory investigations of borehole sediments, and surface and cross-borehole geophysical techniques will be integrated and correlated within the model.

Primary Science Questions
- Can experimental domains be sufficiently characterized to quantify the influence of spatially variable: sorbent, sorbate, and microbe concentrations; rate processes; and hydraulic conductivity on U(VI) water concentrations influenced by desorption, adsorption, and/or precipitation with phosphate?
- What is the dominant mass transfer scale or process controlling vadose zone porewater or groundwater U(VI) concentrations under natural and remedial conditions? Can strategies be devised to overcome mass transfer limitations that may compromise remedial actions?
- What are the relationships between laboratory mass transfer rates and those measured in the field? Can differences be reconciled and sufficiently understood to allow defensible field-scale modeling and reasonable projections of future behavior?

Experiment Types
- Infiltration experiments in a U(VI) contaminated vadose zone where water application rate, volume, and composition (HCO_3/pH; Na/Ca; PO_4) are varied to investigate mass transfer, geochemical kinetic (e.g., dissolution/desorption), and water pathway effects on U(VI) fluxes to the capillary fringe and groundwater.
- Injection experiments in the U(VI)-contaminated saturated zone where HCO_3 and U(VI) concentrations, and U(VI) isotopic ratios are varied to investigate scale-dependent mass transfer involved in forward (adsorption); backward (desorption), and steady-state (isotopic exchange) U(VI) reaction processes in flow paths with different trajectories.
- Injection and in-situ reaction experiments to evaluate the role of mass transfer and microbiological processes in controlling the efficiency of various phosphate forms [e.g., polyphosphate, Ca-citrate/PO_4, organic P in presence and absence of desorption agents (HCO_3)] to precipitate and immobilize contaminant U(VI) as a remedial strategy.

Models and Modeling Strategy
- STOMP as the primary project model that integrates site-wide hydrogeochemical results of different types and newly developed process models for 3-D, reaction-based reactive transport calculations used in experiment planning, interpretation, and evaluation of future remediation actions.
- Other codes developed by project participants with different and/or special capabilities for individual experiment interpretation and hypothesis evaluation (e.g., FLOTRAN for multi-continuum, mass-transfer limited geochemical calculations; and MODFLO for multi-scale mass transfer).
- Stochastic modeling of hydraulic conductivity, sorbent, mass transfer rate, and sorbed U(VI) distributions (e.g., hydro- and chemo-facies) by project experts, as well as spatial moment analyses of plumes resulting from different subsurface manipulations.

EXAMPLE OPPORTUNITIES FOR COLLABORATIVE RESEARCH

- In-situ adsorption/desorption experiments of various types
- Laboratory to field comparisons
- Evaluation of geophysical methods and inversion techniques
- Mass transfer processes of different types at different scales
- Microbiology of linked groundwater-river systems of low to high transmissivity
- Geologic, hydrologic, geochemical, and biogeochemical modeling of different types
- Microbiology and geochemistry of phosphate amended systems

MATERIALS AVAILABLE TO EXTERNAL INVESTIGATORS

- Historic U(VI)-contaminated source term materials (limited)
- Contaminated U(VI) vadose zone materials whose geochemical speciation and mass transfer properties have been determined (limited)
- Uncontaminated vadose zone and aquifer sediments from various locations
- Circumneutral site groundwaters with variable U(VI), HCO_3, and Ca concentrations
- Core materials from vadose zone and aquifer experimental plots (TBC, limited)
- Aseptic samples of vadose zone and Hanford and Ringold formation aquifer sediments (for microbiological studies TBC, limited)

* TBC = to be collected

LINKAGE TO SITE REMEDIATION, CLOSURE AND MONITORED NATURAL ATTENUATION

- Operational model for infusion of DOE science into site remediation and closure decisions
  - Lab to field
  - Concept to application
  - Evaluation and testing of new models and measurement techniques
- 300 A site is representative of Hanford River Corridor locations
  - Applicability of conceptual and numeric models to other locations
- Scientific context for evaluation of remediation strategies and concepts
  - MNA versus active approaches
  - Optimization strategies
  - Expectations for remediation efficiency

INFORMATION SOURCES & KEY PUBLICATIONS

Arai, Y., M. A. Marcus, N. Tamura, J. A. Davis, and J. M. Zachara. 2007. Spectroscopic evidence for uranium bearing precipitates in vadoze zone sediments at the Hanford 300-Area site. *Environmental Science & Technology* (Accepted).

Bond, D. L., J. A. Davis, and J. M. Zachara. 2007. Uranium(VI) dissolution and desorption from contaminated vadose zone sediments. *Geochimica et Cosmochimica Acta* (Accepted).

Williams, B. A., C. F. Brown, W. Um, M. J. Nimmons, R. E. Peterson, B. N. Bjornstad, D. C. Lanigan, R. J. Serne, F. A. Spane, and M. L. Rockhold. 2007. Draft Limited Field Investigation Report for Uranium Contamination in the 300 Area, 300-FF-5 Operable Unit, Hanford Site, Washington, *PNNL-16435*, Pacific Northwest National Laboratory, Richland, WA

Catalano, J. G., J. P. McKinley, J. M. Zachara, S. C. Smith, and G. E. Brown, Jr. 2006. Changes in uranium speciation through a depth sequence of contaminated Hanford sediments. *Environ. Sci. Technol.,* 40(8):2517-2524.

Peterson, R. E., E. J. Freeman, C. J. Murray, P. D. Thorne, M. J. Truex, V. R. Vermeul, M. D. Williams, S. B. Yabusaki, J. M. Zachara, J. L. Lindberg, and J. P. MacDonald. 2005. Contaminants of Potential Concern in the 300-FF-5 Operable Unit: Expanded Annual Groundwater Report for FY2004. *PNNL-15127*. Pacific Northwest National Laboratory, Richland, WA.

Qafoku, N. P., J. M. Zachara, C. Liu, P. L. Gassman, O. S. Qafoku, and S. C. Smith. 2005. Kinetic desorption and sorption of U(VI) during reactive transport in a contaminated Hanford sediment. *Environ. Sci. Technol.,* 39:3157-3165.

Wang, Z., J. M. Zachara, J. P. McKinley, S. C. Smith, and S. M. Heald. 2005. Cryogenic laser induced U(VI) fluorescence studies of a U(VI) substituted natural calcite: Implications to U(VI) speciation in contaminated Hanford sediments. *Environ. Sci. Technol.* 39:2651-2659.

Zachara, J. M., J. A. Davis, C. Liu, J. P. McKinley, N. P. Qafoku, D. M. Wellman, and S. B. Yabusaki. 2005. Uranium Geochemistry in Vadose Zone and Aquifer Sediments from the 300 Area Uranium Plume. *PNNL-15121*. Pacific Northwest National Laboratory, Richland, WA.

Hanford IFC Website ~ Currently password protected. A tiered-access web-site is in preparation that will include comprehensive background information available to all, as well as new measurements and data generated with ERSD support.