Advances in Groundwater Remediation and Modeling for Mining-Related Contaminants

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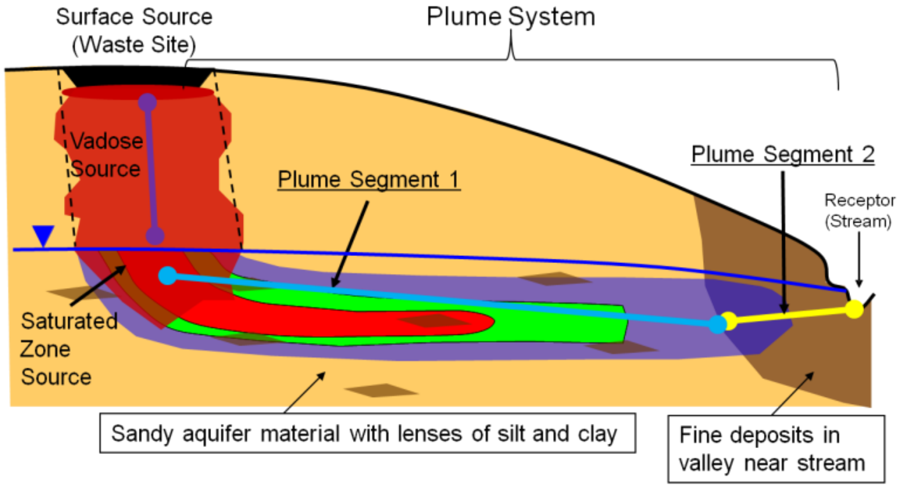
Introduction

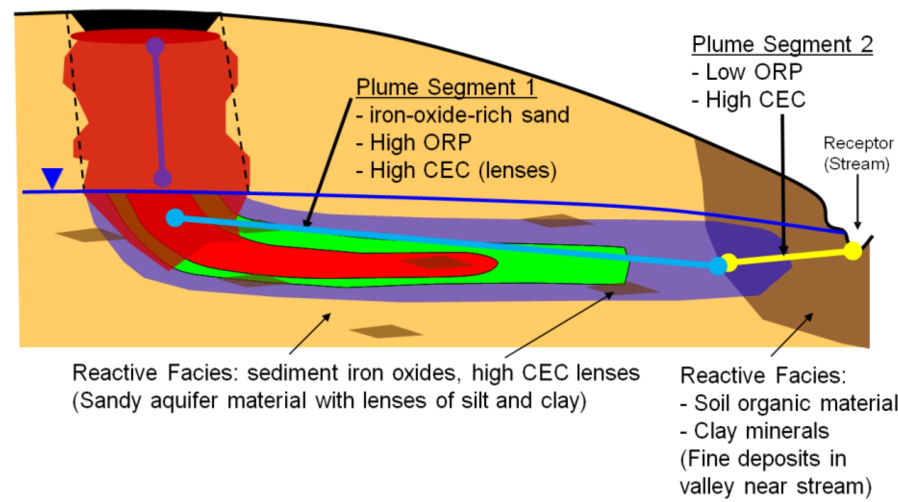
- Radionuclide and inorganic contaminants are issues at Department of Energy (DOE) sites and recent efforts have included
  - Approaches for conceptual models and attenuation assessment
  - Geochemical sequestration technologies
  - Modeling tools for remediation
  - Advances in remedy monitoring approaches.
- National efforts are also underway with respect to addressing complex sites.

Approaches for Conceptual Model and Attenuation Assessment

- The EPA MNA protocols for radionuclide and inorganic contaminants contain a significant amount of good information, but are limited in discussion of conceptual model development
- A conceptual model guidance document was prepared through a DOE program including elements of
  - Identifying controlling features and processes with some emphasis on reactive facies
  - Considering geochemical conditions and their evolution of over time naturally or due to remediation actions

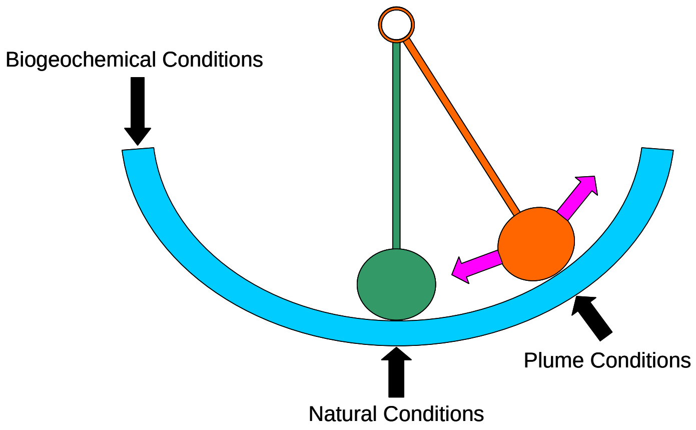
Controlling Features and Processes

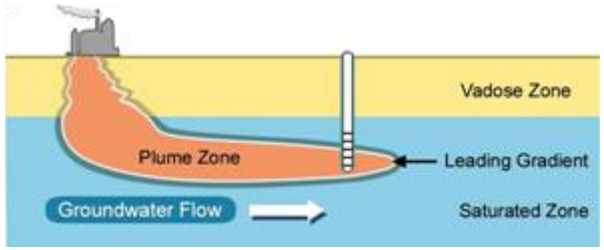


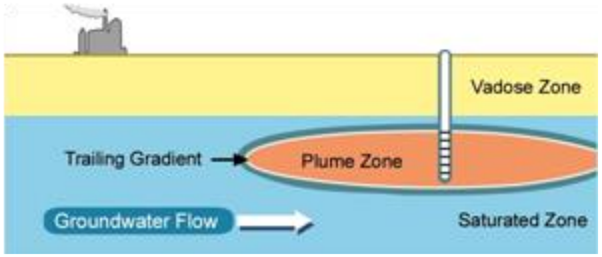


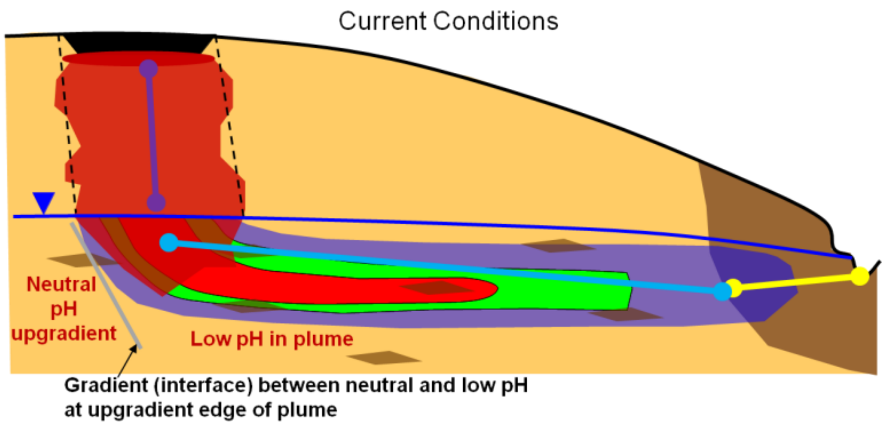
Truex, MJ, PV Brady, CJ Newell, M Rysz, M Denham, and K Vangelas. 2011.
The Scenarios Approach to Attenuation Based Remedies for Inorganic and Radionuclide Contaminants.
SRNL-STI-2011-00459, Savannah River National Laboratory, Aiken, SC

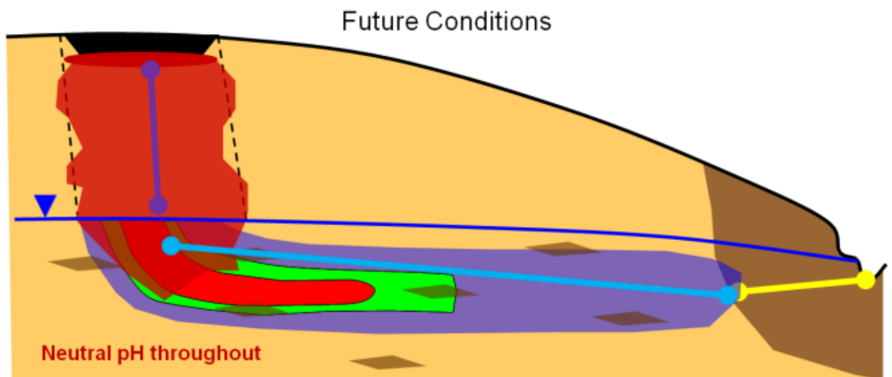
Geochemical Gradients





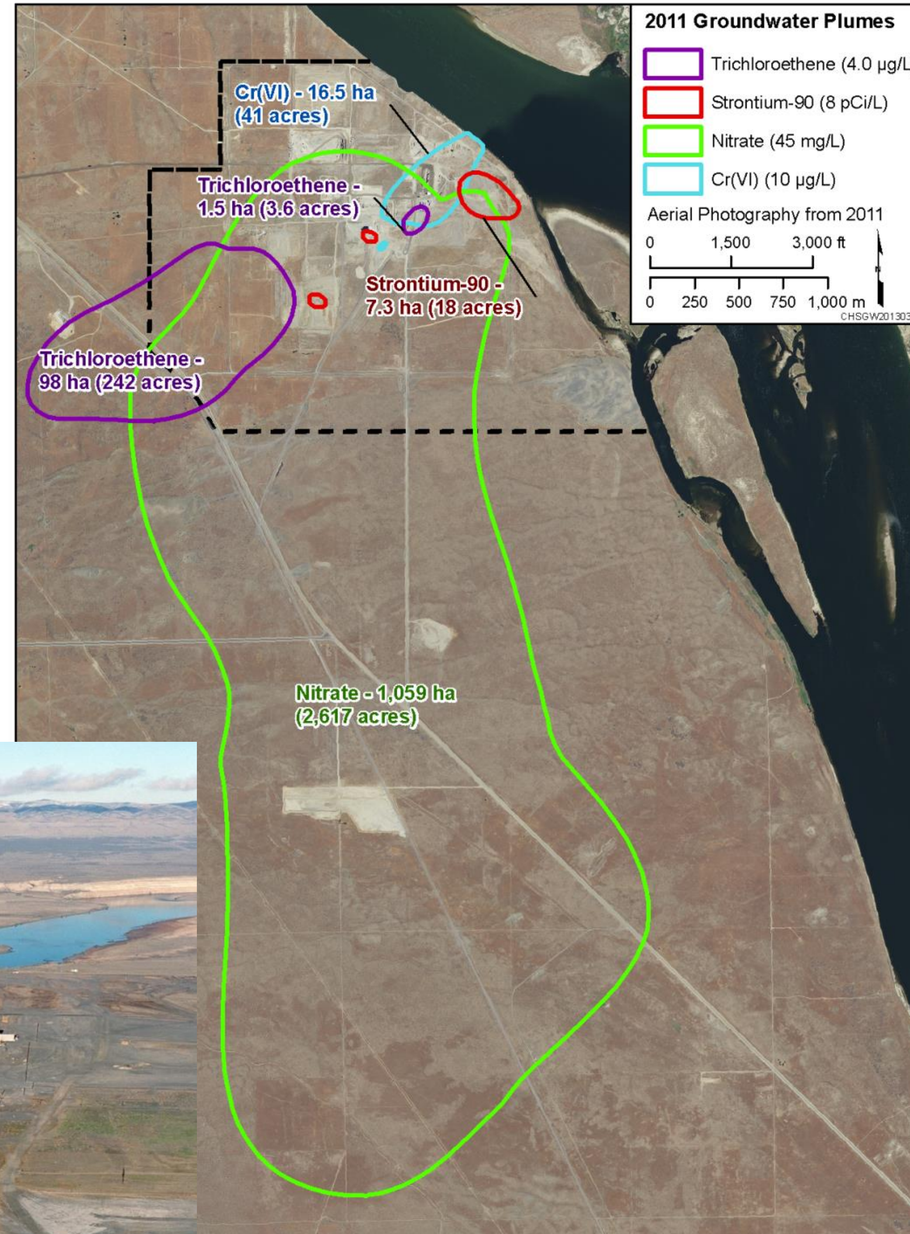






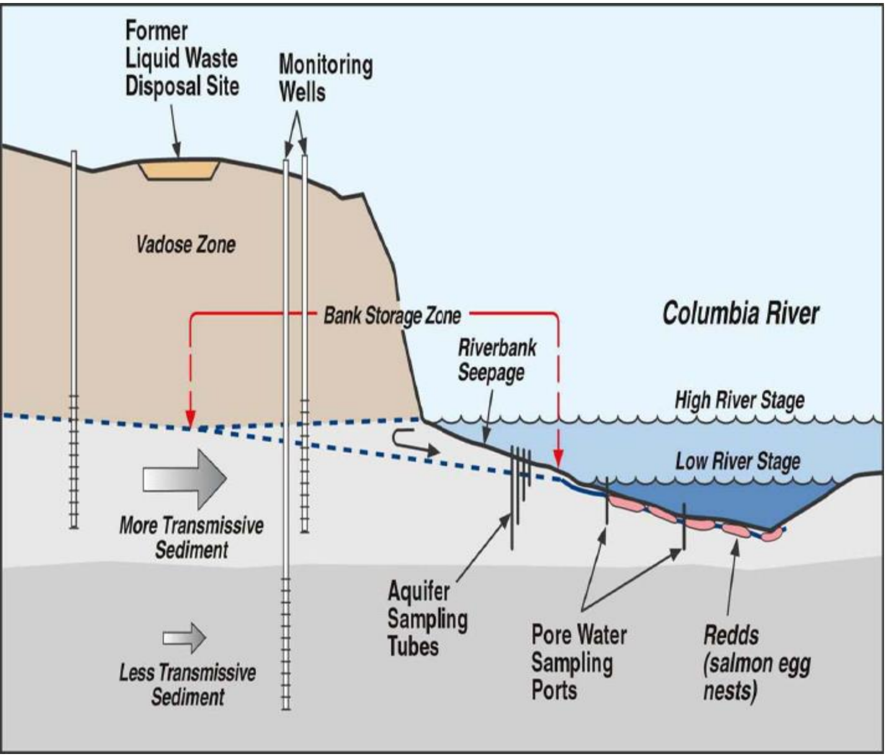
100-F/IU Area at Hanford

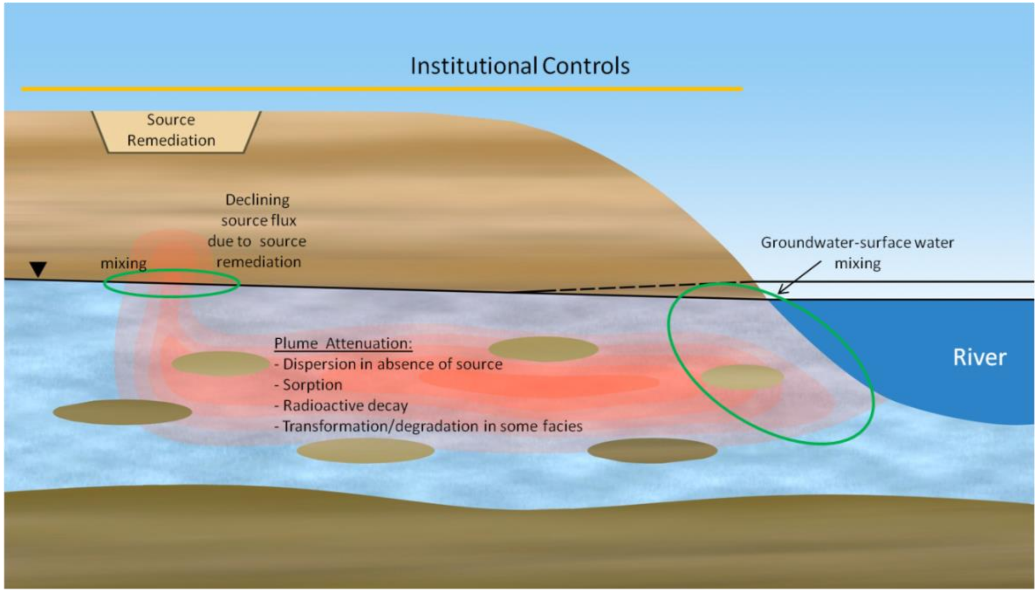
- MNA lines of evidence based on reactive facies for attenuation processes.



100-F/IU Natural Attenuation

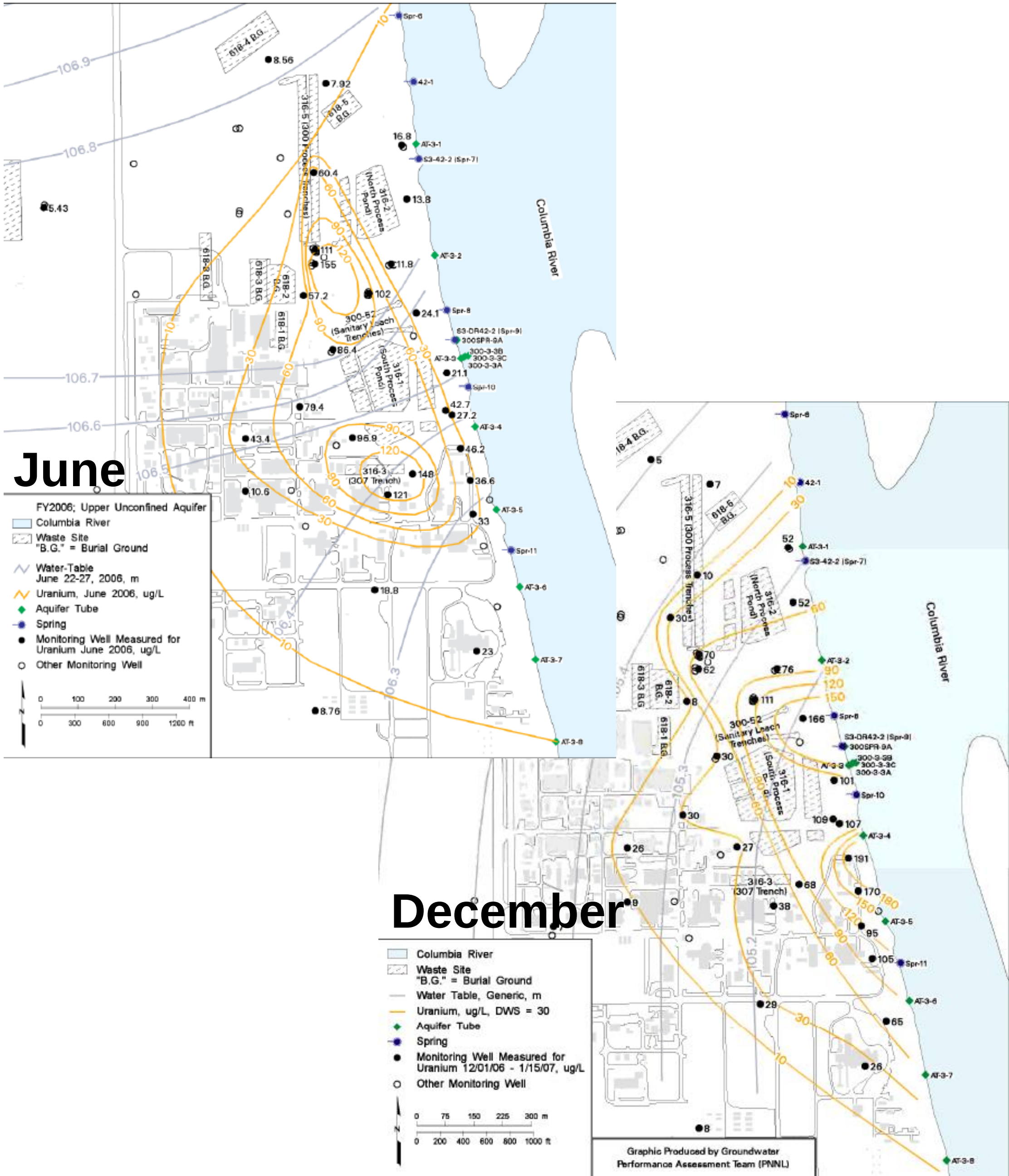
- Understand system and interaction with river
- Transition of plumes to declining condition in absence of source and with attenuation processes in reactive facies
- Predictive assessment of protectiveness, monitoring verification over time
- Conceptual model as technical and communication tool



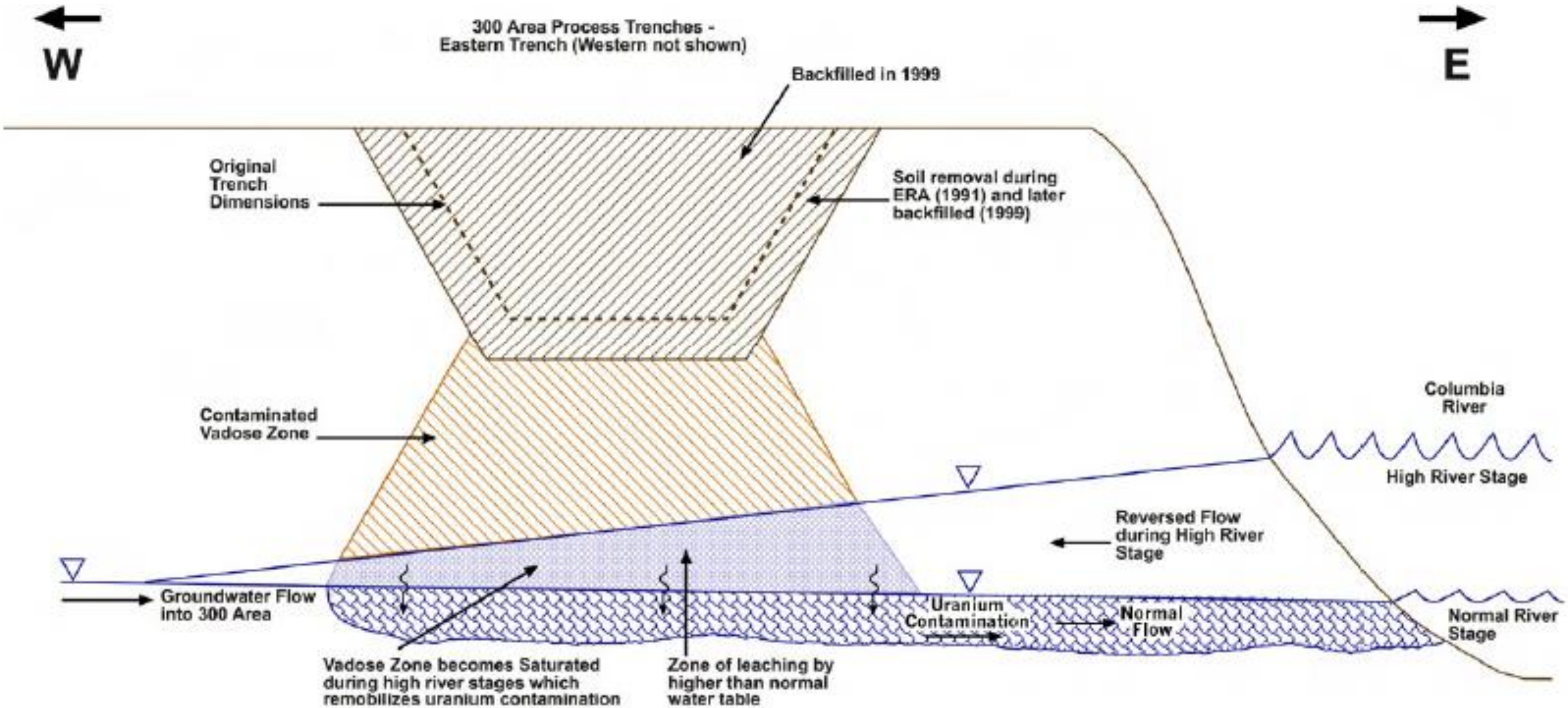


Persistent Uranium Plume

- Hanford 300 Area Example
  - Uranium waste solutions discharged to surface
  - Uranium plume adjacent to Columbia River
- Remedy History
  - Surface sites excavated and MNA selected as plume remedy
  - Plume is persistent and varies over time
  - Remedial investigation and re-evaluation of conceptual model
    - Uranium source present in lower vadose zone contacted by seasonal water table rise



Source and Boundary Conditions Control the Plume

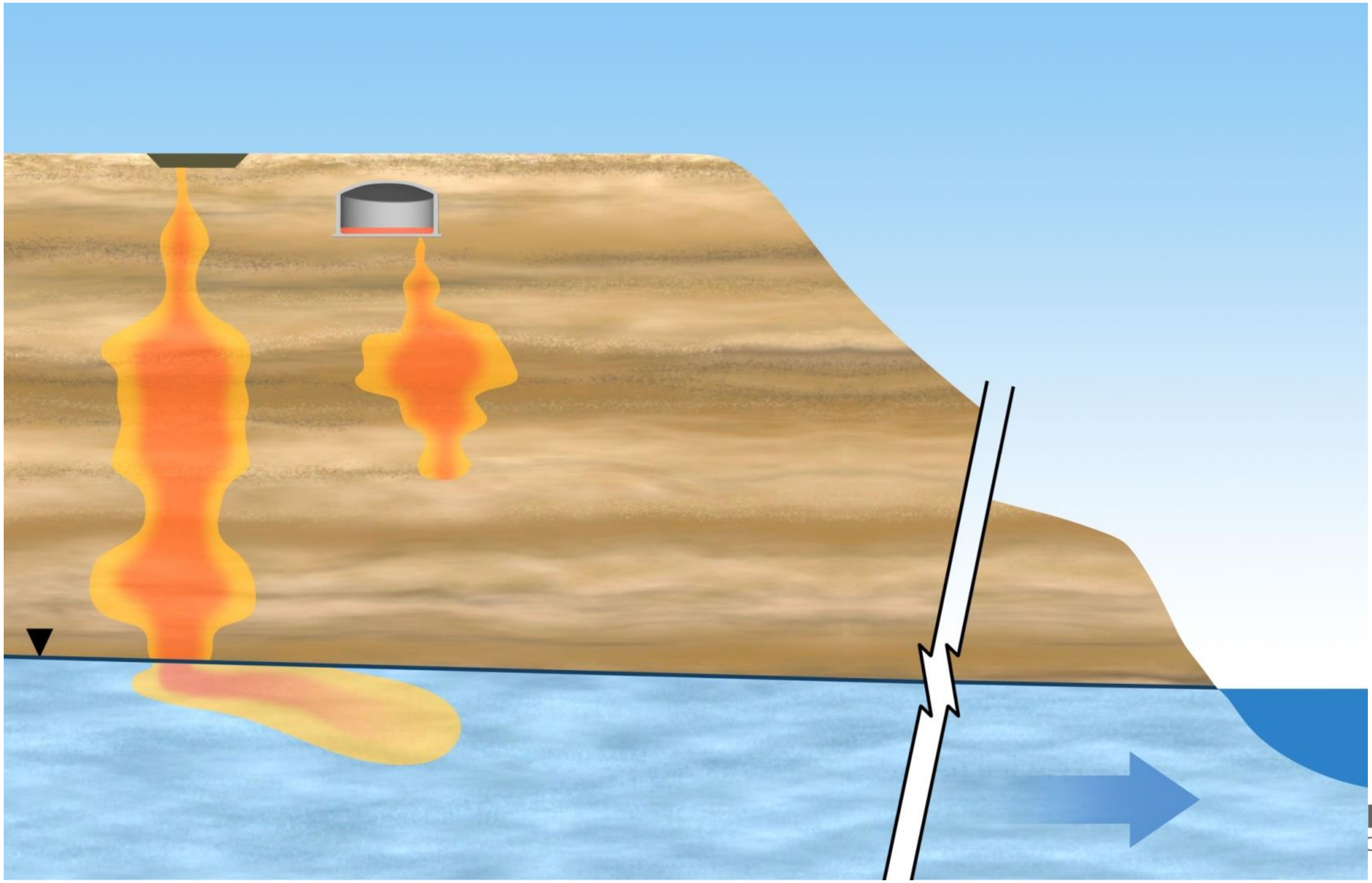


Geochemical Sequestration

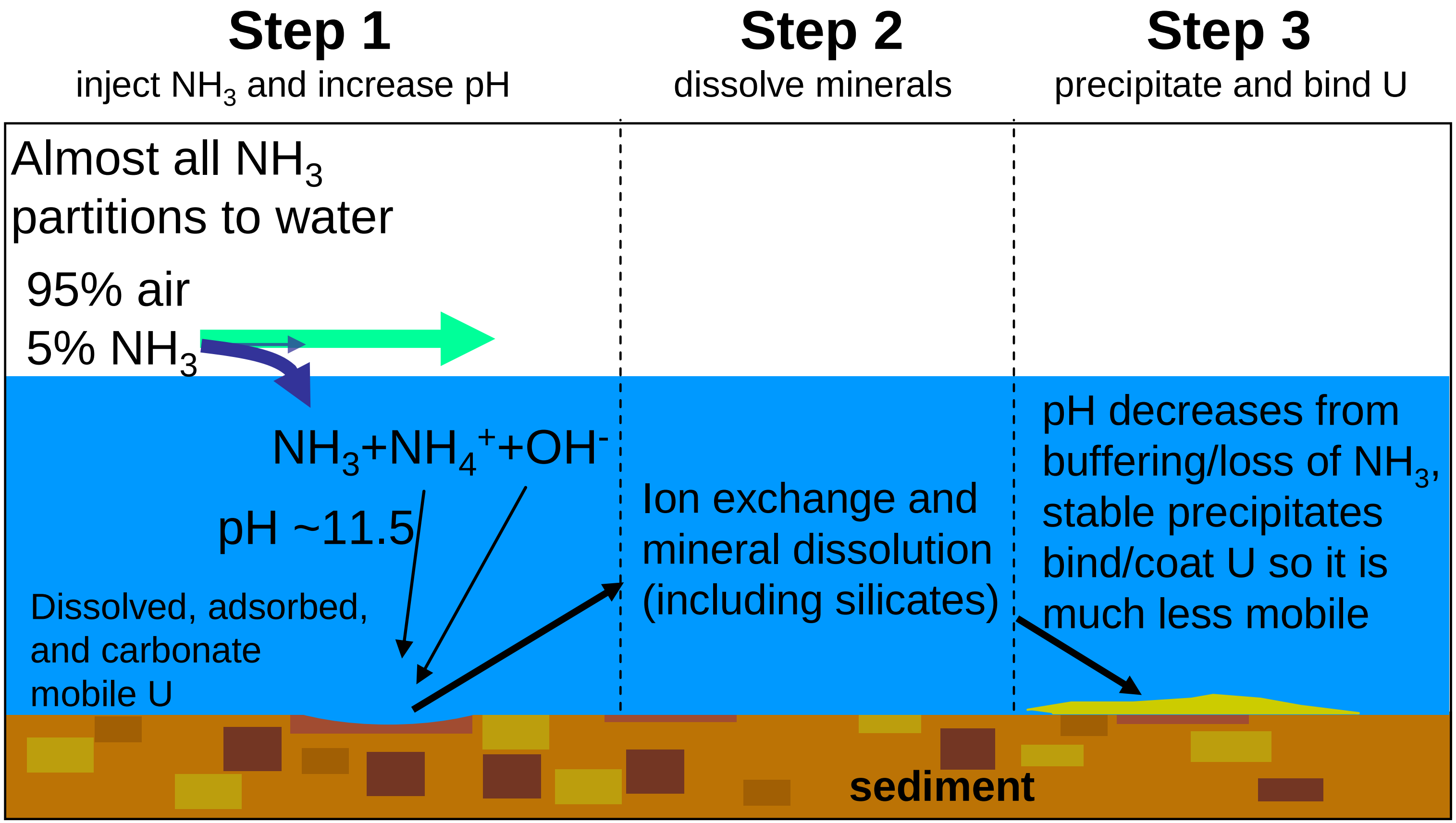
- Geochemical manipulation in the subsurface is being investigated as a means to reduce mobility of radionuclide and inorganic contaminants
  - Reduction processes
  - Geochemical sequestration
- Example of a vadose zone technology
  - Uranium in the vadose zone at Hanford is a long-term source to groundwater
  - Ammonia treatment has the potential to reduce uranium flux to the groundwater

Hanford Subsurface Contaminant Plumes

- Address source flux and plume issues

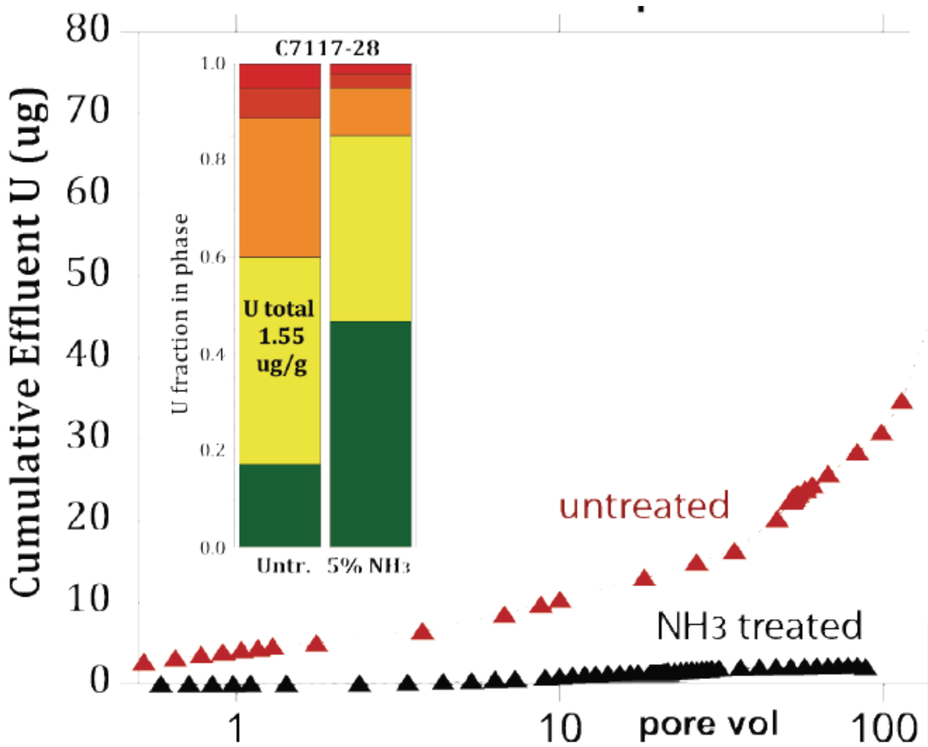


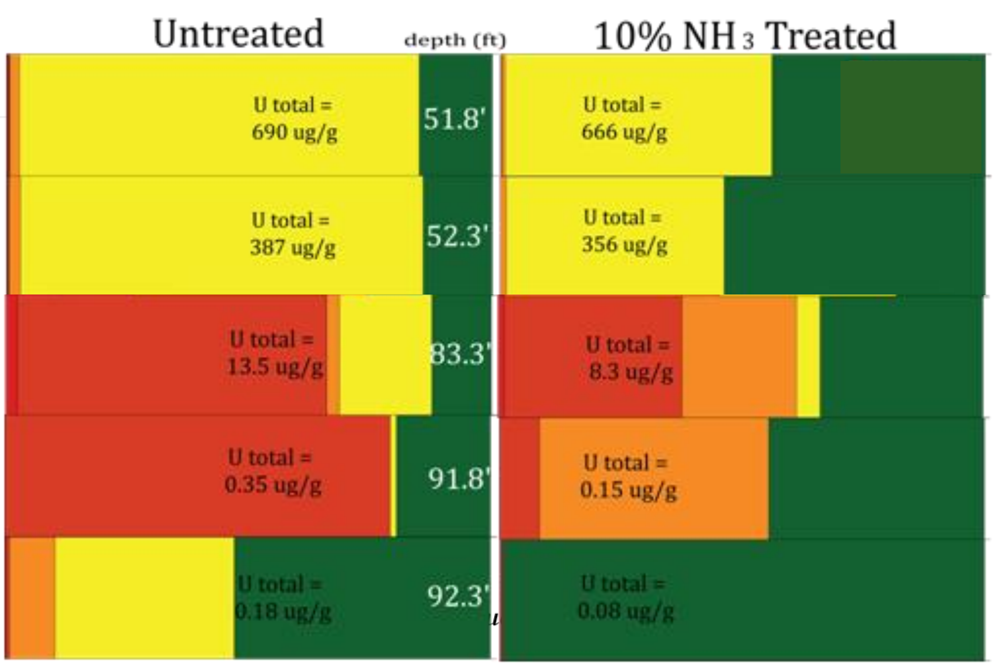
Geochemical Sequestration by Ammonia Gas Treatment



Extraction Solution	Hypothesized targeted sediment components	Interpreted uranium mobility of extracted fraction	Color Code
1. Aqueous: uncontaminated Hanford groundwater	Uranium in pore water and a portion of sorbed uranium	Mobile phase	
2. Ion Exch.: 1M Mg-nitrate	Readily desorbed uranium	Readily mobile through equilibrium partitioning	
3. Acetate pH5: 1 hour in pH 5 sodium acetate solution	Uranium associated with surface exposed carbonate precipitates, including uranium carbonates, or other readily dissolved precipitates	Moderately mobile through rapid dissolution processes	
4. Acetate pH 2.3: 1 week in pH 2.3 acetic acid	Dissolution of most carbonate compounds, including uranium carbonates, and sodium boltwoodite	Slow dissolution processes are associated with uranium release from this fraction such that uranium mobility is low with respect to impacting groundwater	
5. 8M HNO_3: 2 hours in 8M nitric acid at 95°C	Dissolution of most minerals expected to contain uranium, considered to represent total uranium extraction for this study[1]	Very slow dissolution processes are associated with uranium release from this fraction such that uranium mobility is very low with respect to impacting groundwater	

Example Results

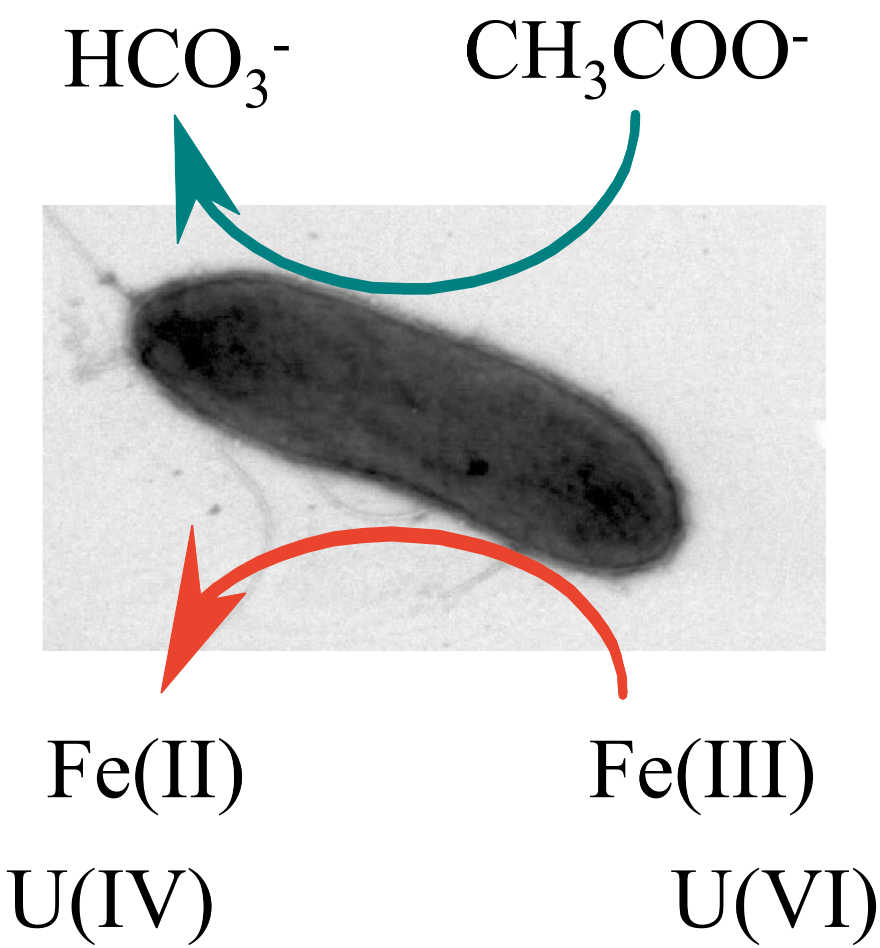




Modeling Tools

- Radionuclide and inorganic transport are impacted by multiple features and processes, especially during remediation
  - Conceptual model importance
  - Role of numerical modeling
- Example of a uranium bioremediation study at a former mill site

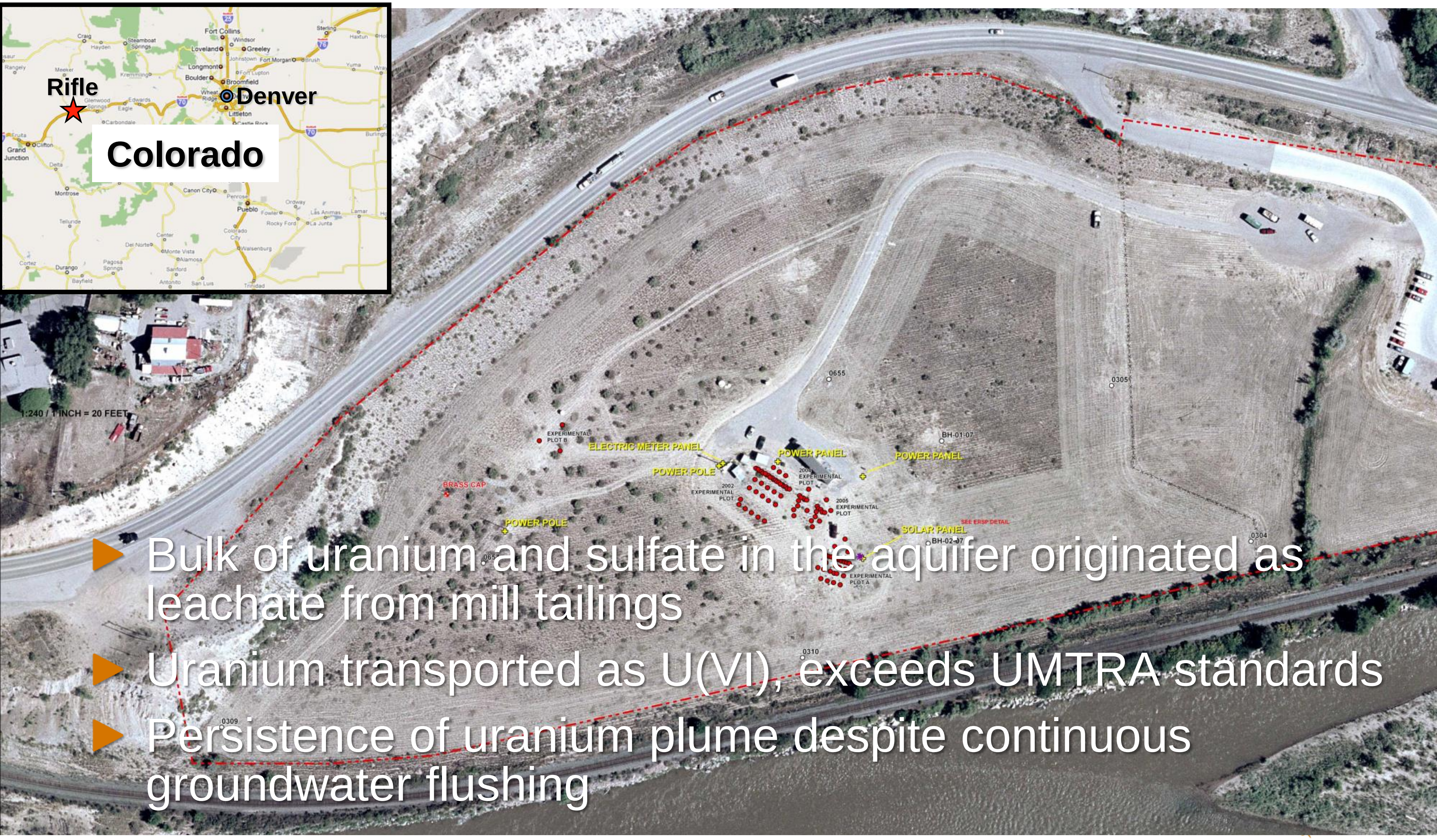
Metal Reducing Bacteria



Geobacter uraniireducens, Isolated from the Rifle Site and a Member of the Subsurface Clade I *Geobacter*

- U(VI) is the mobile valence state of uranium
- Reduced uranium, U(IV), is in mineral or sorbed form
- Reduction of U(VI) to U(IV) within aquifers could immobilize uranium
- Lovley et al. 1991 lab studies suggest simple strategy to promote U(VI) reduction in contaminated aquifers:
  - add acetate as an electron donor to stimulate indigenous dissimilatory metal-reducing bacteria (DMRB)
  - U(VI) is reduced concurrently with Fe(III)

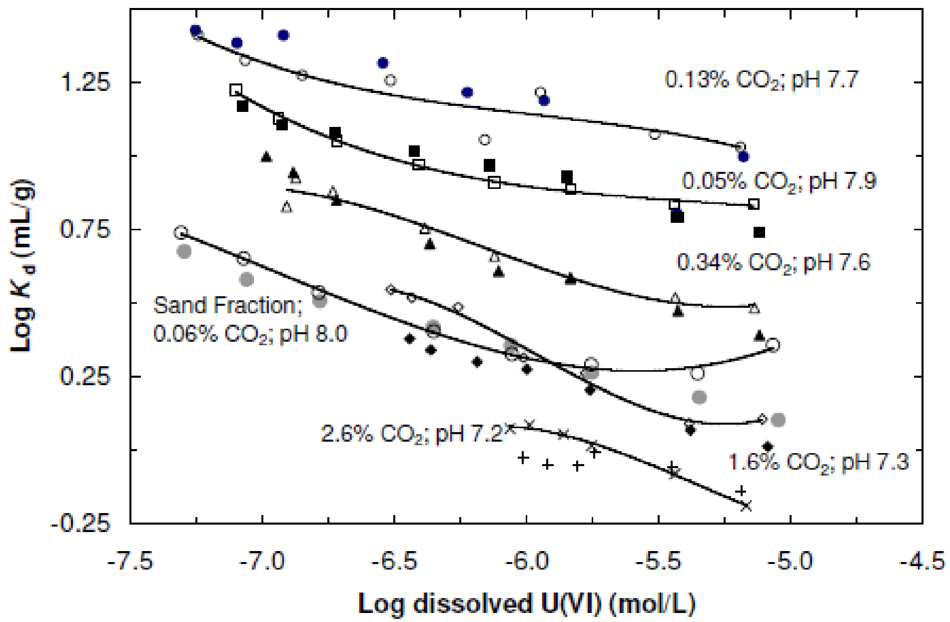
Old Rifle Uranium Mill Site, CO



- Bulk of uranium and sulfate in the aquifer originated as leachate from mill tailings
- Uranium transported as U(VI), exceeds UMTRA standards
- Persistence of uranium plume despite continuous groundwater flushing

Challenges

- Transient hydrology with physical and chemical heterogeneities
- Uranium has broad range of mobility sensitive to pH, alkalinity, U concentration, major ion chemistry, redox state and surface reactivity
- Biostimulation products (e.g., HCO_3^-, biomass, Fe(II), sulfide, S, CH_4) can alter hydrologic and geochemical conditions controlling uranium mobility

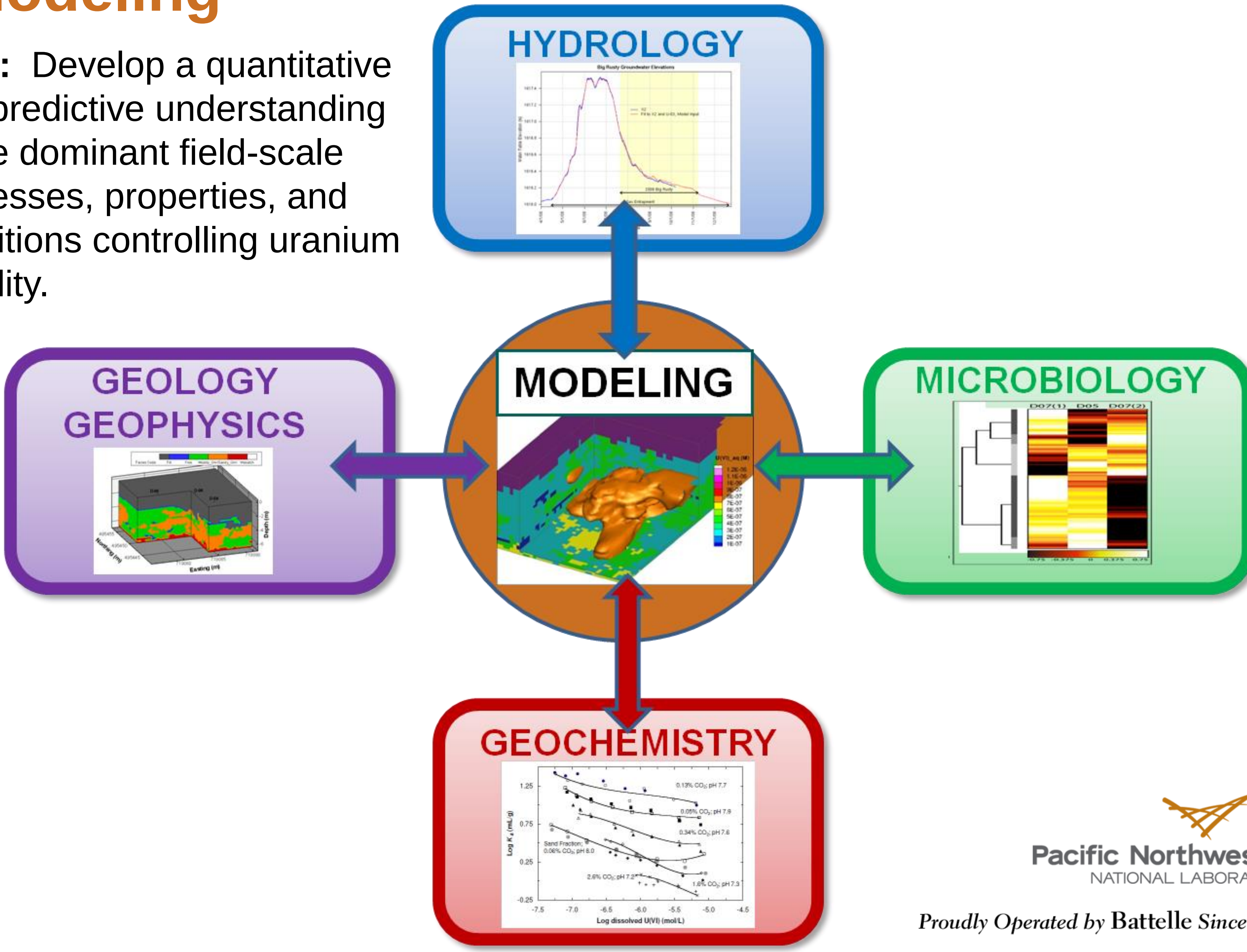


Hyun et al. 2009 ES&T

- Microorganisms controlling important terminal electron accepting process reactions are subject to evolving geochemistry and community interactions

Biogeochemical Reactive Transport Modeling

Goal: Develop a quantitative and predictive understanding of the dominant field-scale processes, properties, and conditions controlling uranium mobility.



Example Publications

U.S.NRC
United States Nuclear Regulatory Commission
Protecting People and the Environment

NUREG/CR-7014
PNNL-19026

Processes, Properties, and Conditions Controlling In Situ Bioremediation of Uranium in Shallow, Alluvial Aquifers

Manuscript Completed: March 2010
Date Published: July 2010

Prepared by
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U.S.NRC
United States Nuclear Regulatory Commission
Protecting People and the Environment

NUREG/CR-7167

Assessing the Potential for Biorestoration of Uranium In Situ Recovery Sites

Manuscript Completed: September, 2013
Date Published: February, 2014

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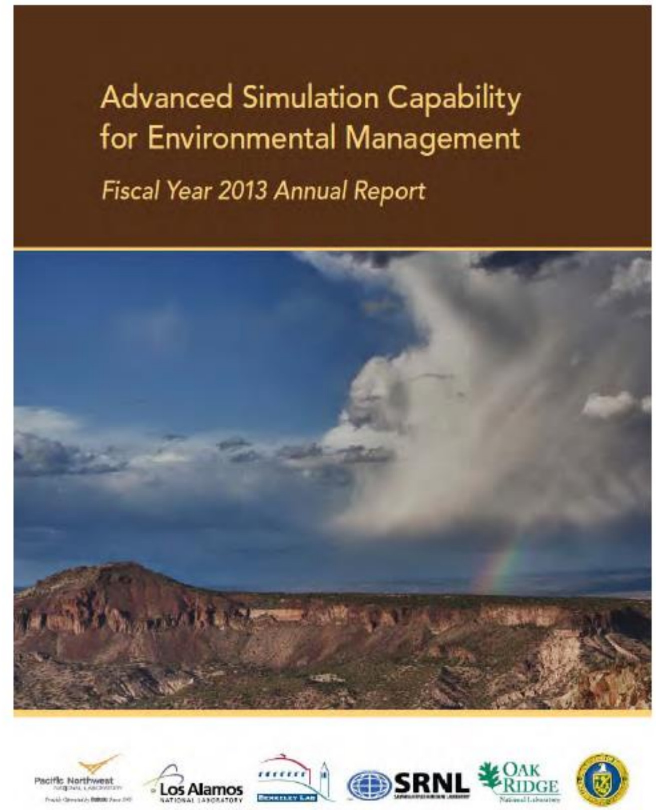
New DOE Modeling Tool

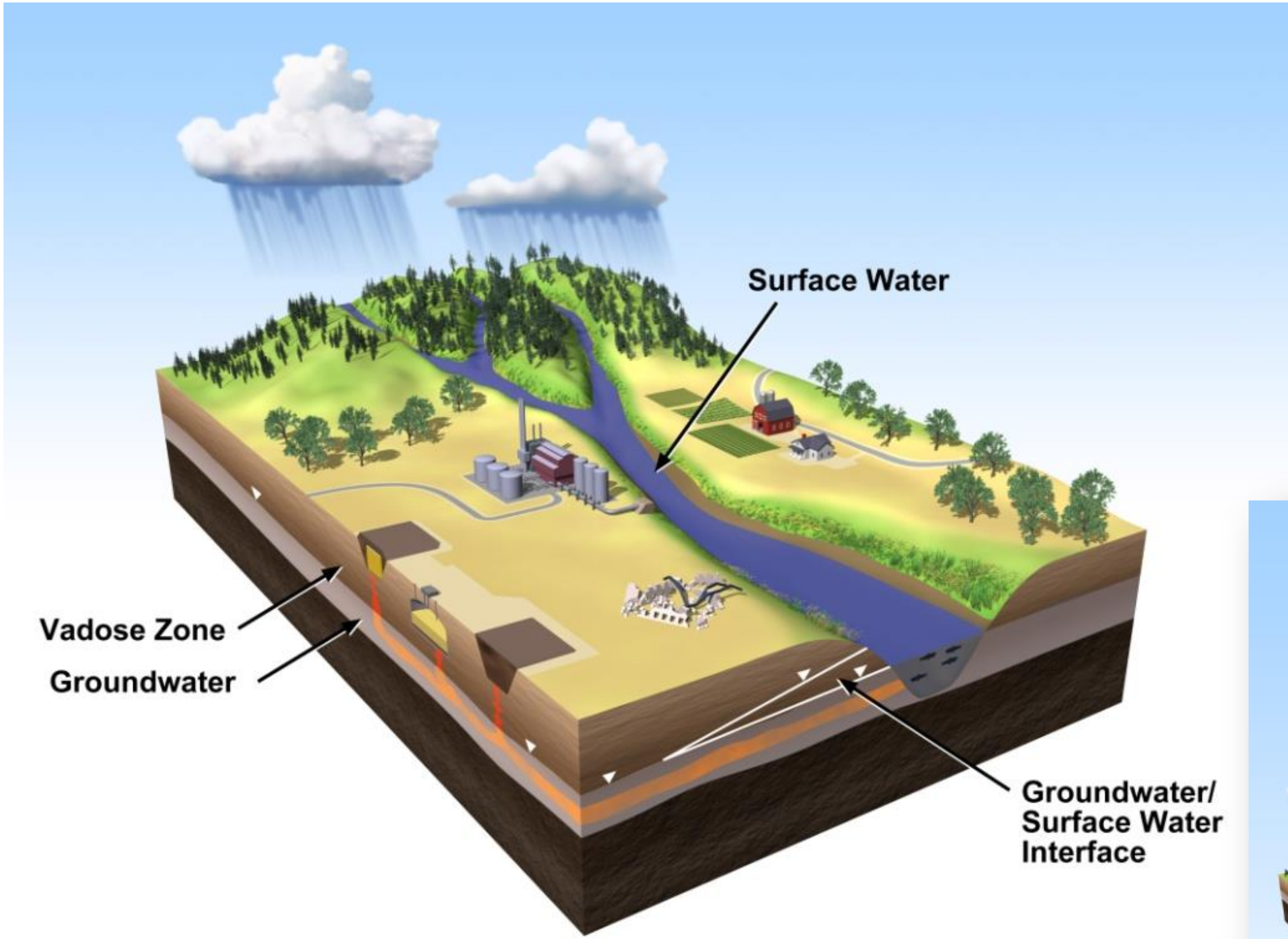
http://ascemdoe.org/

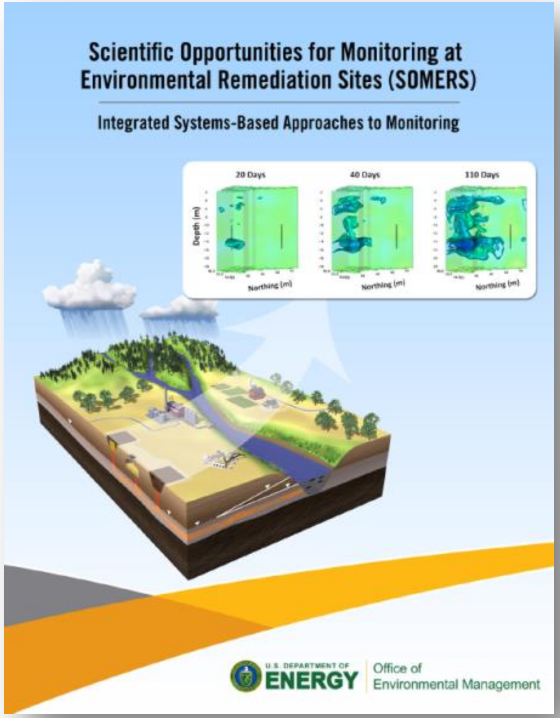


Remediation Monitoring

- How does monitoring data support key remediation decisions?
- What are the drivers for water flow and contaminant transport?
- What is the timescale of plume behavior and how does this inform monitoring frequency?
- Are there locations (e.g., transects) where monitoring of concentration changes or mass flux are diagnostic of plume behavior?
- Are there surrogate measures or leading indicators of plume behavior?

Systems-Based Monitoring



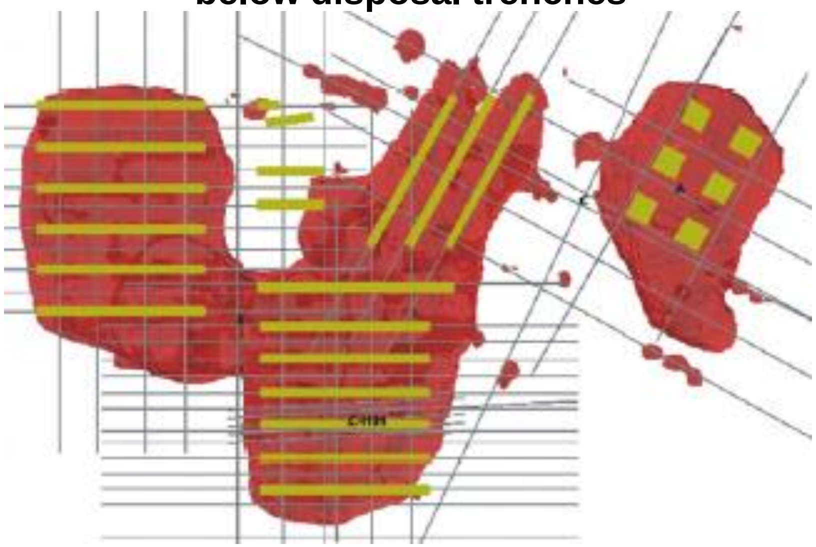


Bunn AL, DM Wellman, RA Deeb, EL Hawley, MJ Truex, M Peterson, MD Freshley, EM Pierce, J McCord, MH Young, TJ Gilmore, R Miller, AL Miracle, D Kaback, C Eddy-Dilek, J Rossabi, MH Lee, RP Bush, P Beam, GM Chamberlain, J Marble, L Whitehurst, KD Gerdes, and Y Collazo. 2012. Scientific Opportunities for Monitoring at Environmental Remediation Sites (SOMERS): Integrated Systems-Based Approaches to Monitoring . PNNL-21379, Pacific Northwest National Laboratory, Richland, WA.

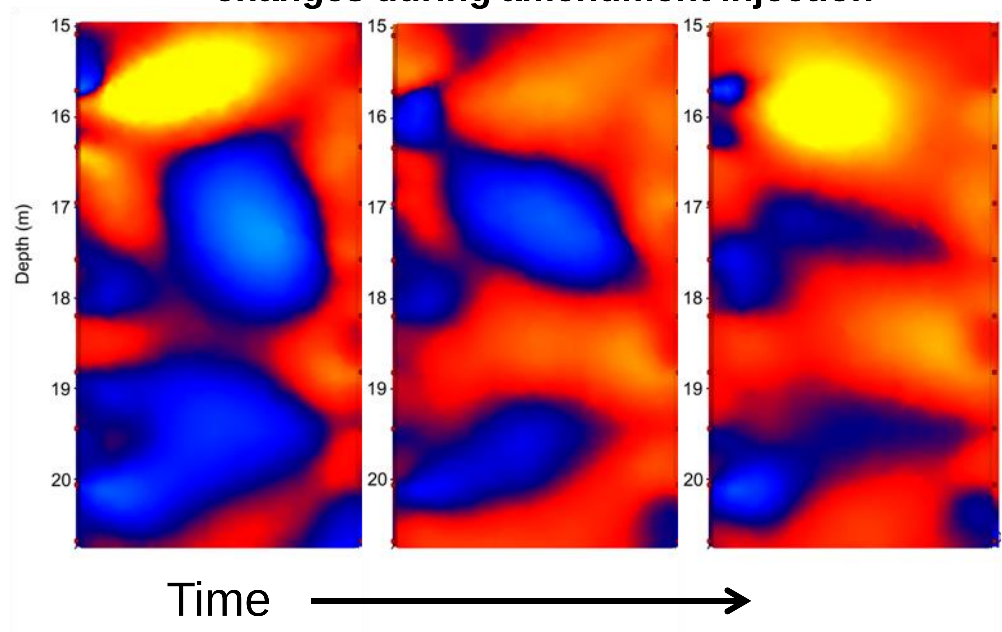
Monitoring Approaches and Tools

- Surrogates and indicators
  - Sensor arrays for lines of evidence (water level, pH, SpC)
- Geophysical assessment tools
  - Electrical Resistance Tomography (ERT)
    - Characterization line of evidence
    - Autonomous temporal monitoring

Plan view of conductive zones below disposal trenches



Cross section view of temporal changes during amendment injection



Monitoring Approaches and Tools

- Monitoring Design and Integration
  - Integration of conceptual model, predictive analysis, monitoring, and assessment
  - Streamlined monitoring for long term
- Mass flux/mass discharge measurements
  - Remediation metric
  - Integration of plume elements

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National Efforts for Complex Sites

- DOE Endpoint Approach
  - System-based approach
  - Adaptive management approach
- National Academy of Science reports
  - *Alternatives for Managing the Nation's Complex Contaminated Groundwater Sites*
  - Workshop: *Best Practices for Risk-Informed Decision Making Regarding Contaminated Sites*
- ITRC team: Remediation Management of Complex Sites

Resources

- www.itrcweb.org: new project team "Remediation Management of Complex Sites"
- National Academy of Science Report: *Best Practices for Risk-Informed Decision Making Regarding Contaminated Sites* http://www.nap.edu/catalog.php?record_id=18747
- National Academy of Science Report: *Alternatives for Managing the Nation's Complex Contaminated Groundwater Sites* http://www.nap.edu/catalog.php?record_id=14668
- Bunn AL, DM Wellman, RA Deeb, EL Hawley, MJ Truex, M Peterson, MD Freshley, et al. 2012. *Scientific Opportunities for Monitoring at Environmental Remediation Sites (SOMERS): Integrated Systems-Based Approaches to Monitoring*. PNNL-21379, Pacific Northwest National Laboratory, Richland, WA.
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- Szecsody, J.E., M.J. Truex, L. Zhong, T.C. Johnson, N.P. Qafoku, M.D. Williams, J.W. Greenwood, E.L. Wallin, J.D. Bargar, and D.K. Faurie. 2012. Geochemical and Geophysical Changes During NH3 Gas Treatment of Vadose Zone Sediments for Uranium Remediation. *Vadose Zone J.* 11(4) doi: 10.2136/vzj2011.0158.

Resources

- Truex, MJ, PV Brady, CJ Newell, M Rysz, M Denham, and K Vangelas. 2011. *The Scenarios Approach to Attenuation Based Remedies for Inorganic and Radionuclide Contaminants*. SRNL-STI-2011-00459, Savannah River National Laboratory, Aiken, SC. Available at www.osti.gov, OSTI ID 1023615, doi: 10.2172/1023615.
- Yabusaki, S. B., et al. 2008. Building conceptual models of field-scale uranium reactive transport in a dynamic vadose zone-aquifer-river system. Water Resources Research 44(12): 24.
- Zachara JM, MD Freshley, GV Last, RE Peterson, and BN Bjornstad. 2012. Updated Conceptual Model for the 300 Area Uranium Groundwater Plume. PNNL-22048, Pacific Northwest National Laboratory, Richland, WA.

Resources

- DOE Rifle IFRC
  - Variably Saturated Flow and Biogeochemical Reactive Transport Modeling
    - Yabusaki, S. B., Fang, Y., Long, P. E., Resch, C. T., Peacock, A. D., Komlos, J., Jaffe, P. R., Morrison, S. J., Dayvault, R. D., White, D. C., and Anderson, R. T., 2007. Uranium Removal from Groundwater via In situ Biostimulation: Field-Scale Modeling of Transport and Biological Processes. *Journal of Contaminant Hydrology* **93**, 216-235
    - Fang, Y., Yabusaki, S., Morrison, S., Amonette, J. P., and Long, P., 2009. Multicomponent reactive transport modeling of uranium bioremediation field experiments. *Geochim Cosmochim Acta* **73**, 6029-6051.
    - Yabusaki, S. B., et al. (2011). "Variably saturated flow and multicomponent biogeochemical reactive transport modeling of a uranium bioremediation field experiment." Journal of Contaminant Hydrology 126(3-4): 271-290.
  - Publications: http://www.rifleifrc.org/publications
- NRC Uranium Bioremediation
  - Shallow Uranium Plumes:
    - Technical Basis for Assessing Uranium Bioremediation Performance (NUREG/CR-6973) http://pbadupws.nrc.gov/docs/ML0825/ML082540171.pdf
  - In Situ Recovery Site Biorestoration
    - Assessing the Potential for Biorestoration of Uranium In Situ Recovery Sites (NUREG/CR-7167) http://pbadupws.nrc.gov/docs/ML1418/ML14184B139.pdf