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PNNL Deep Vadose Zone Research and Development

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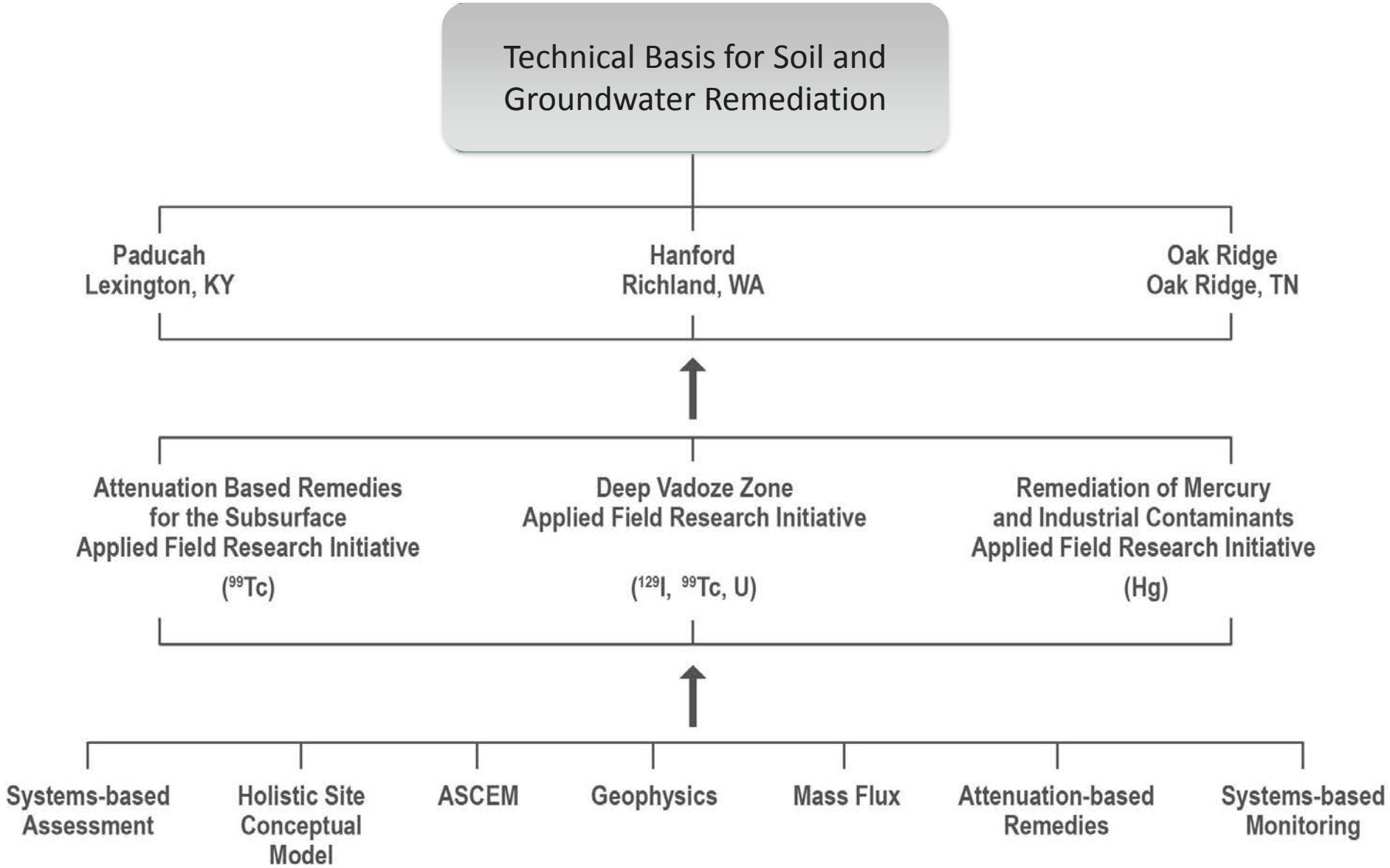
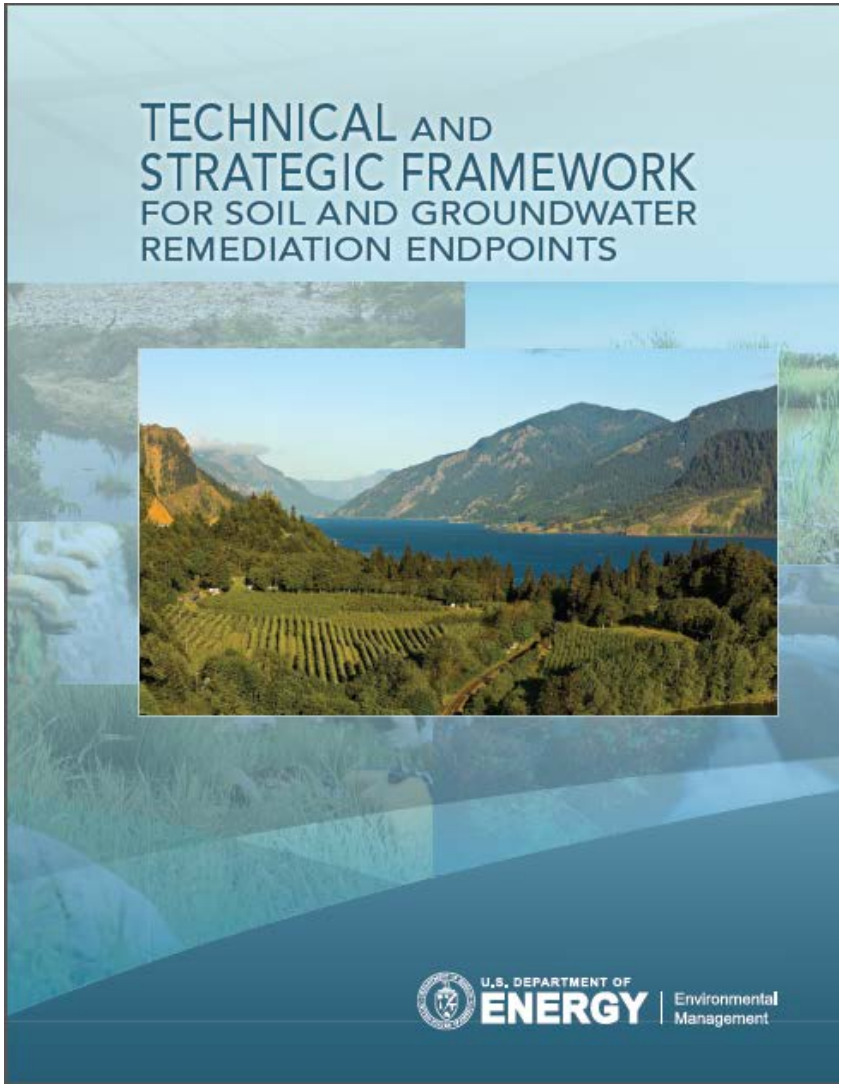
Soil and Groundwater Remediation
Strategic DOE EM Program



Endpoint Framework

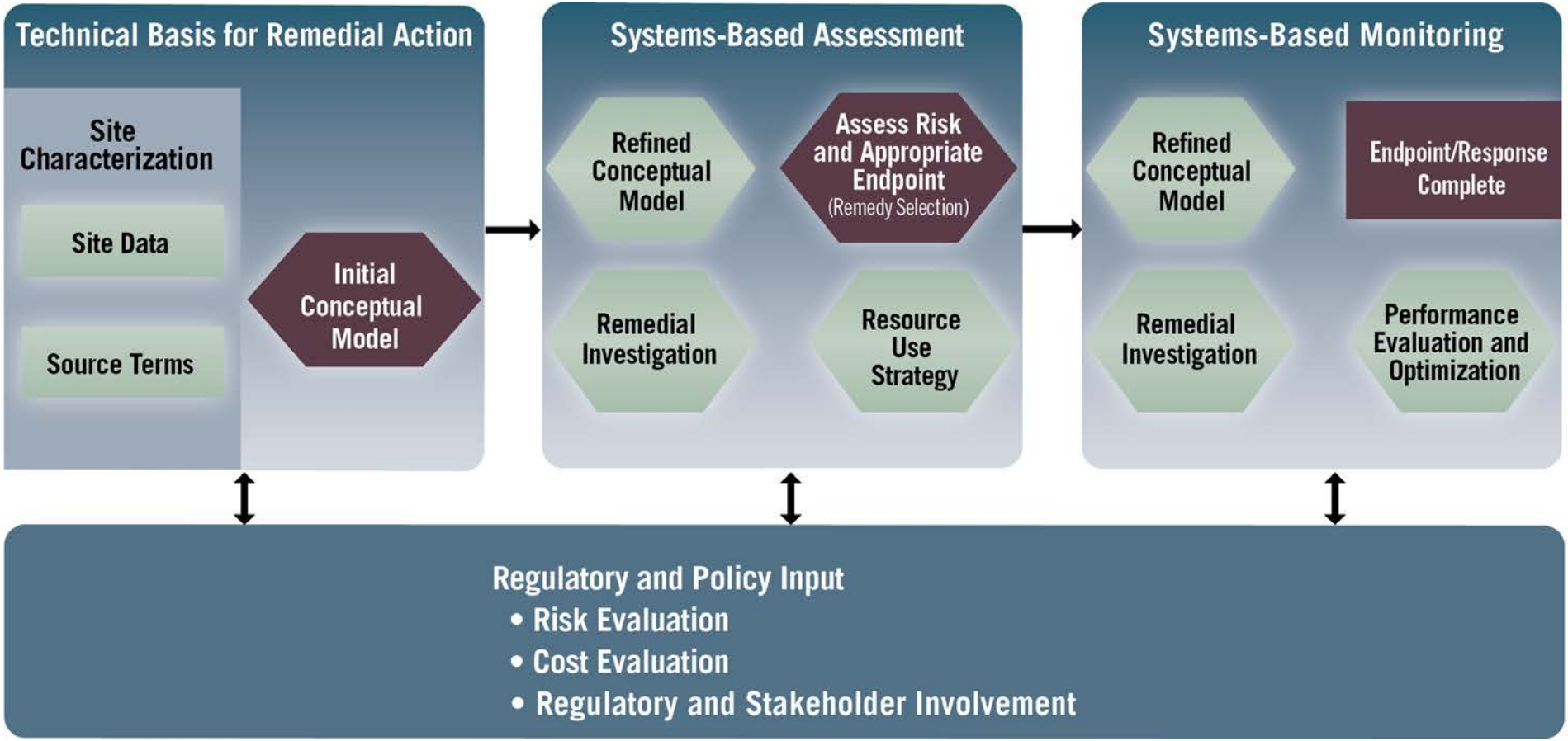


What is an endpoint framework?

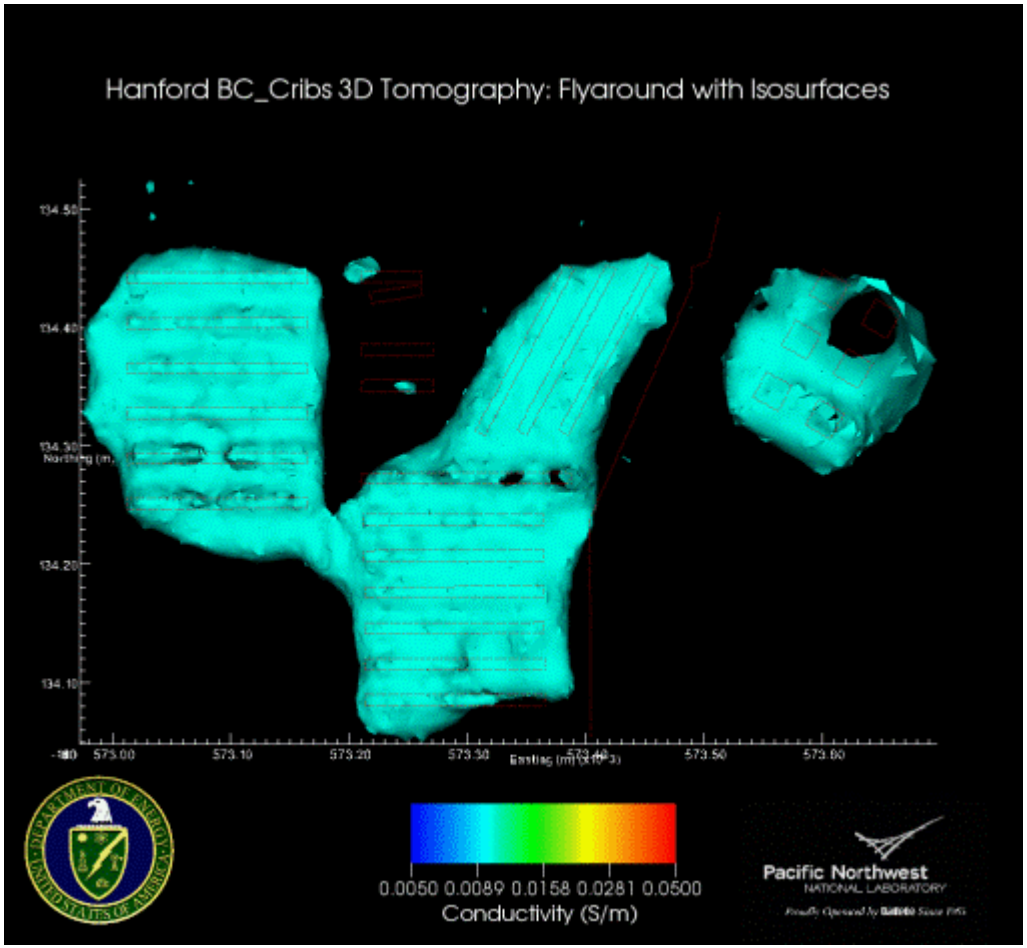
- Systematic understanding of a problem to provide understanding and justification for decision making
  - *Risk informed remediation goals*
  - *Permitted by regulations*
  - *Protective of human health and the environment*

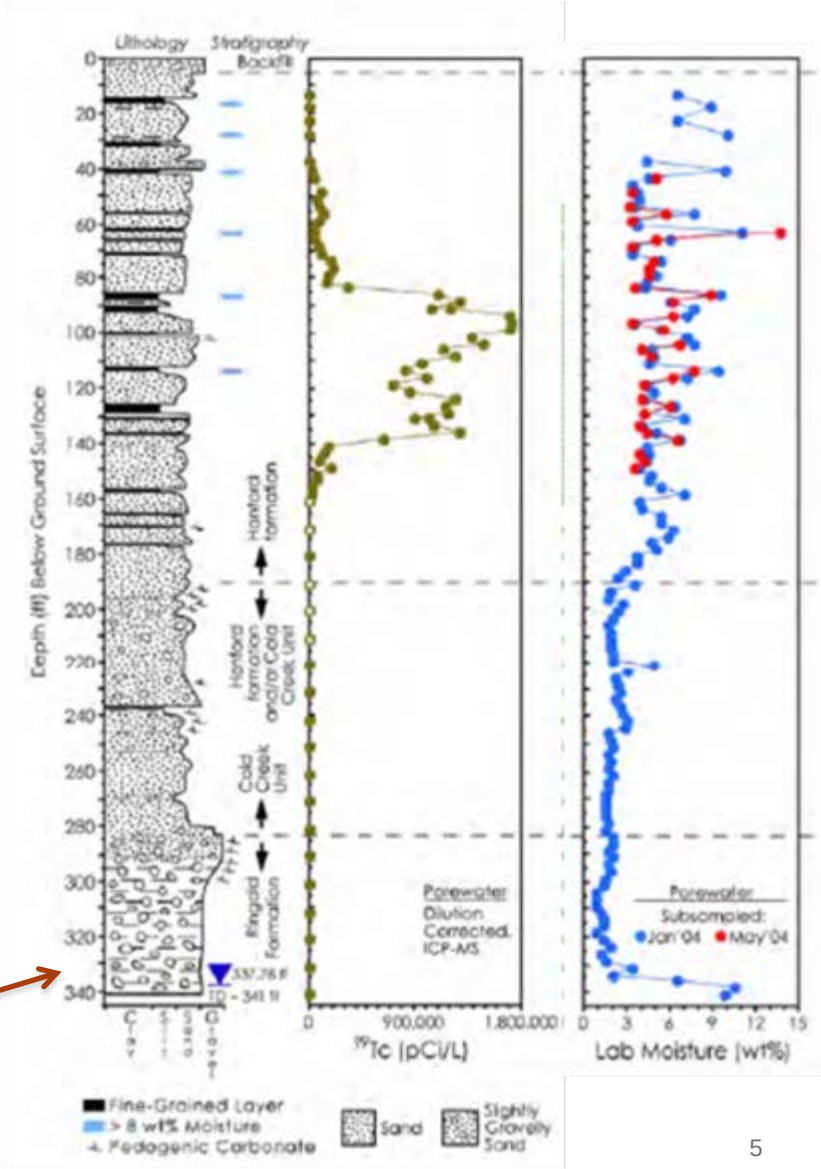
Framework

Establish Technical Basis for Remediation



Vadose Zone Characterization



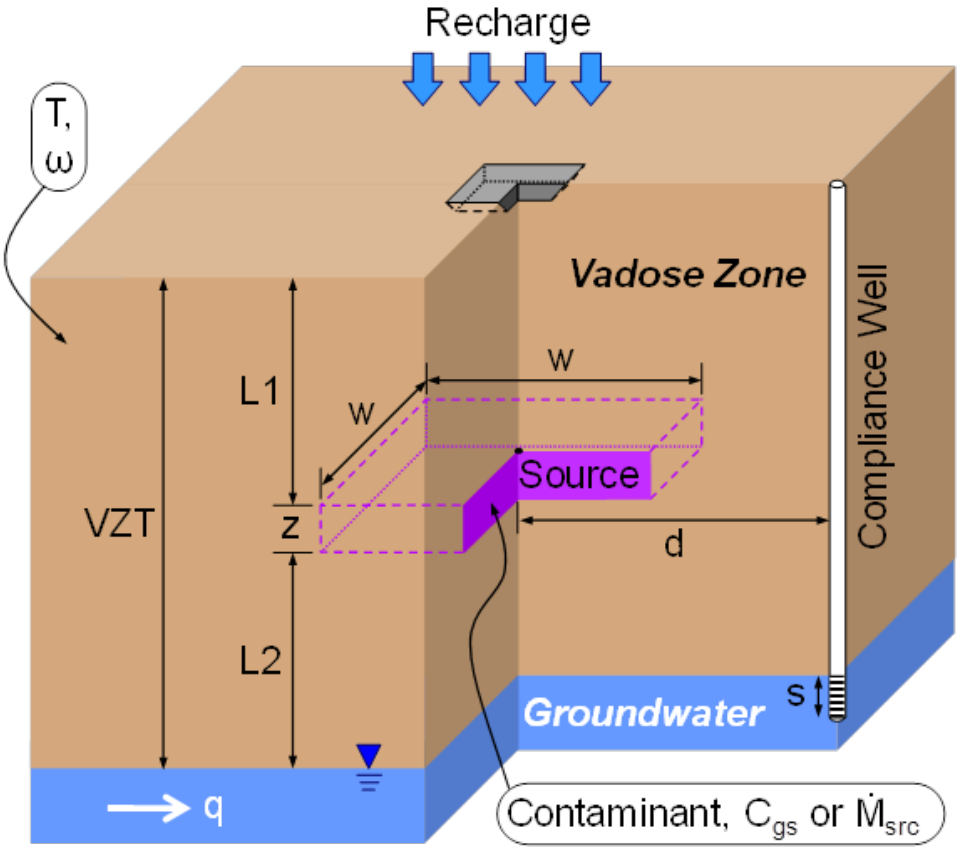


Borehole data shows relative contaminant and water movement

Johnson et al. 2012
Jansik et al. 2012. *Vadose Zone J.* (submitted)

Mass Flux Assessment for Metals and Rads

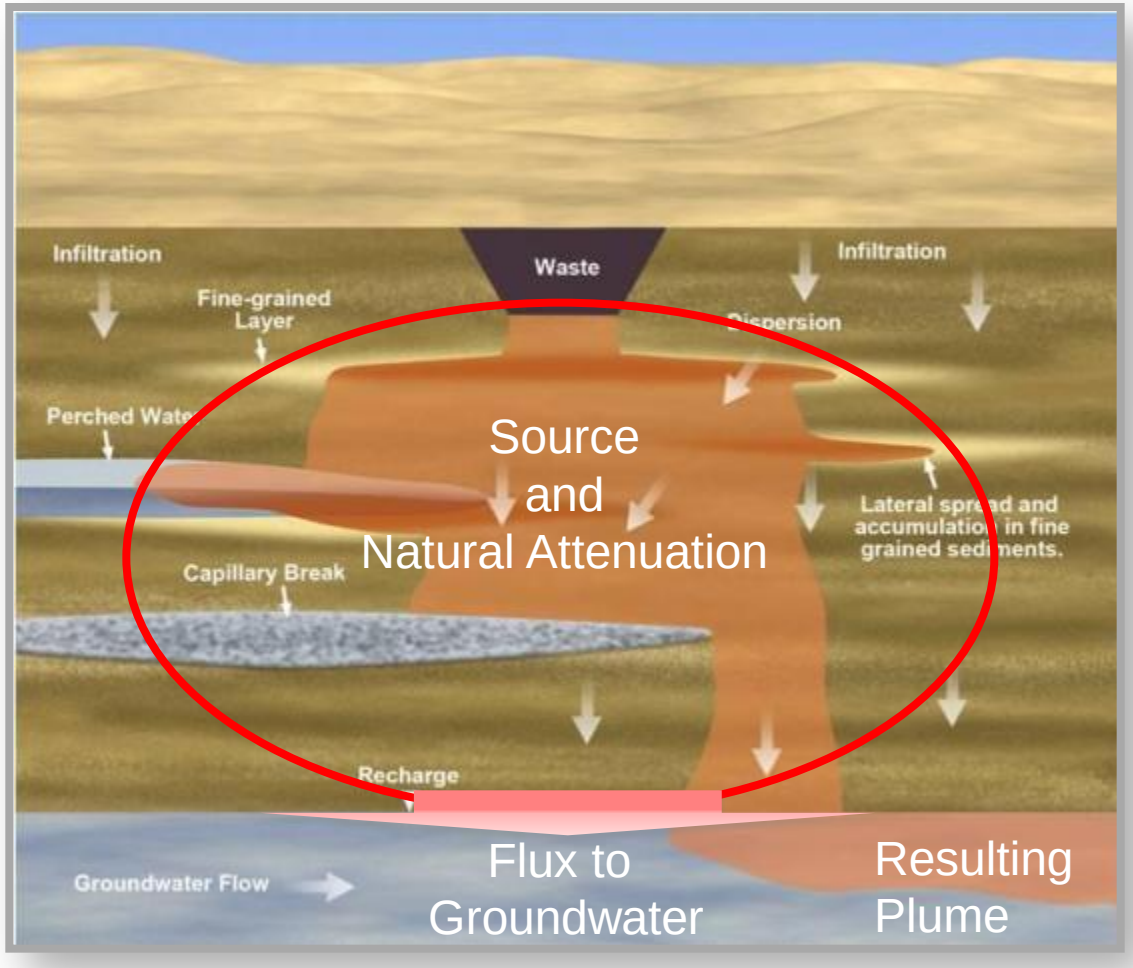
- Quantify source
  - Where is the persistent source?
  - How strong is the source (contaminant discharge rate)?
- Quantify contaminant movement and flux to groundwater
- Risk evaluated at multiple levels
  - Human Health
  - Ecological



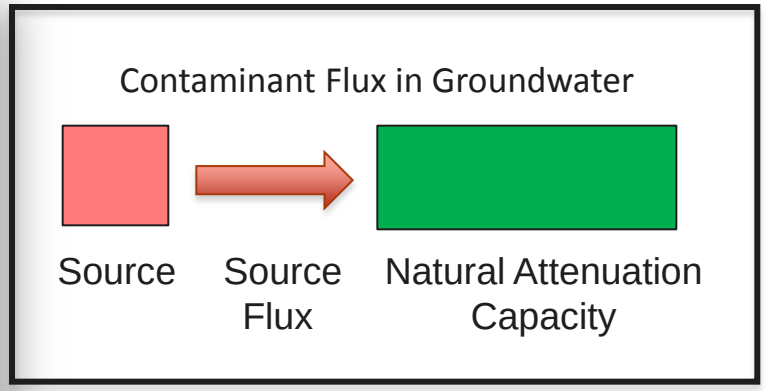
Truex et al. 2012. PNNL-21843
Carroll et al. 2012. *J Contam. Hydrol*.
Oostrom et al. 2012. *GWMR* (submitted)
Oostrom et al. 2010 *GWMR*
Brusseau et al. 2010 *GWMR*
Truex et al. 2009. *GWMR*

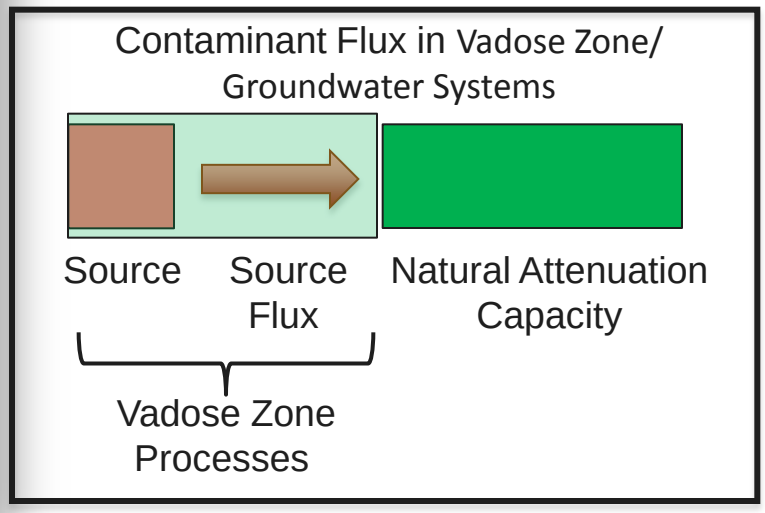
Systems-based Assessment

Coupled Vadose Zone/Groundwater System



Adapted from Dresel et al. 2011. *Environ. Sci. Technol.*

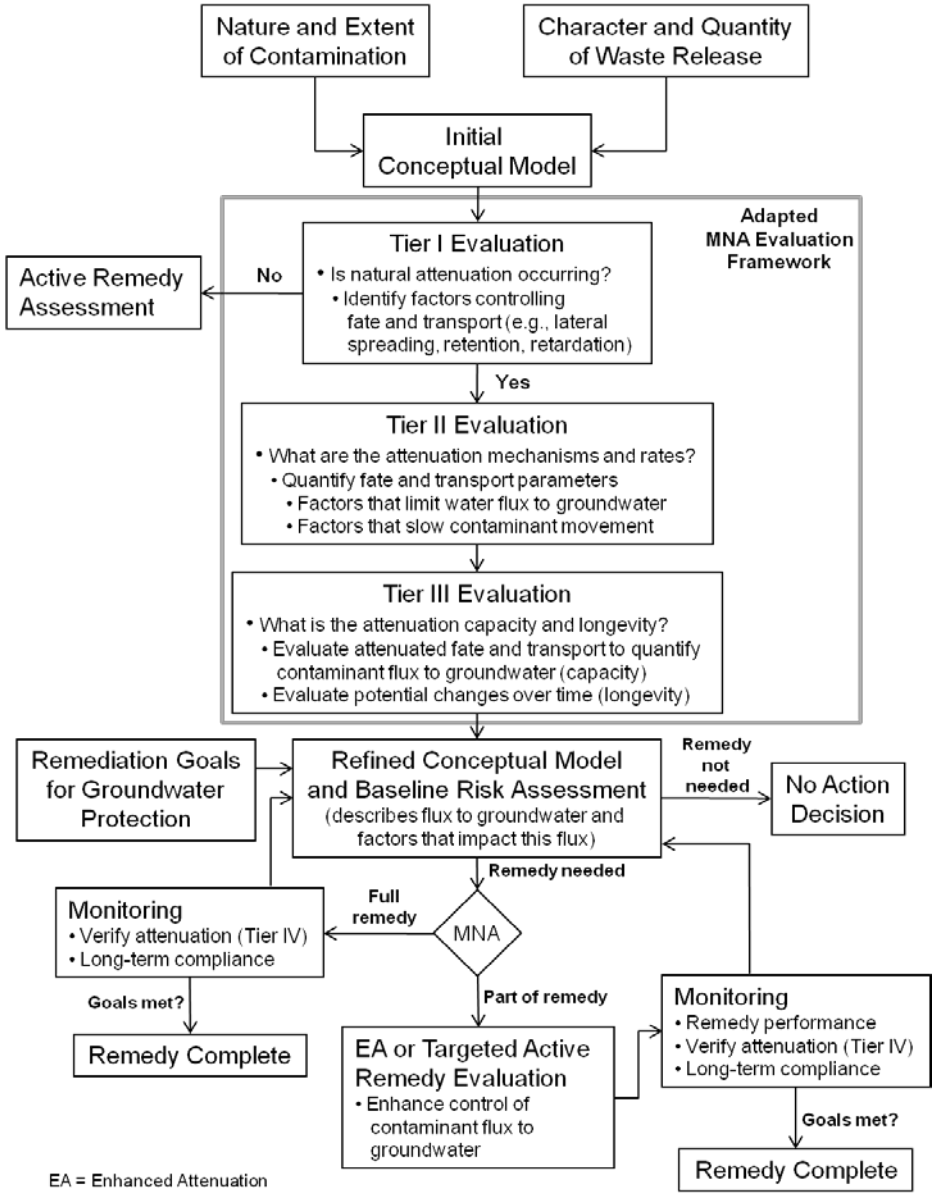




Truex and Carroll. 2012. PNNL-21815

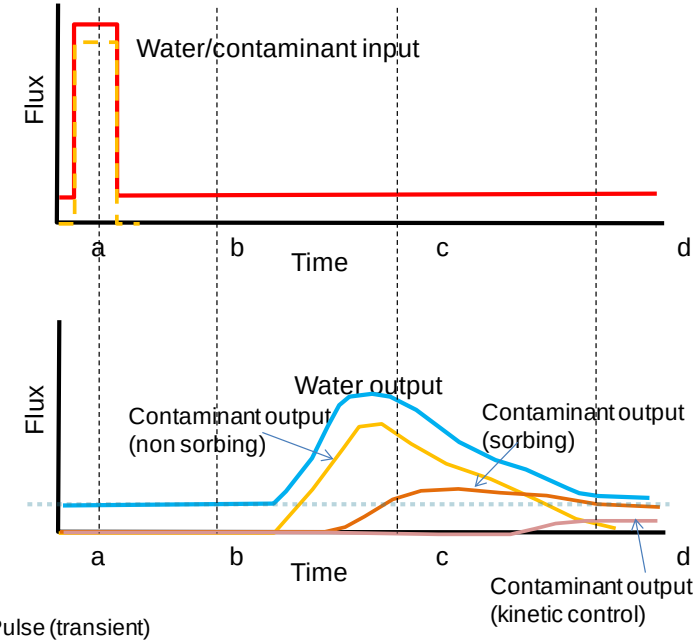
Vadose Zone Remedy Framework

- Enables determining baseline risk and appropriate remedies for deep vadose zone waste sites
  - Fits within the RI/FS (or CMS) process
  - Integrates understanding of natural system attenuation capacity for contaminants, mass flux and assessment of risk
  - Provides a framework for remedy evaluation

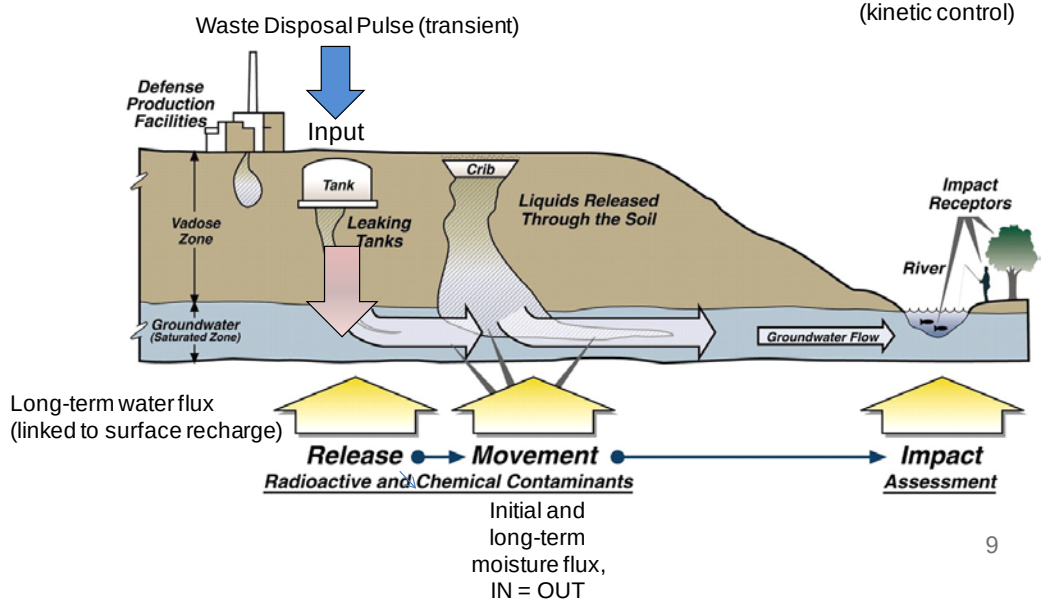


Vadose Zone Remedy Framework (cont' d.)

- Flux Reduction Approaches
  - Transport of contaminants in the vadose zone is significantly attenuated by hydraulic processes and dispersion in addition to potential geochemical attenuation
  - Design remediation approaches for
    - contaminant mass reduction
    - contaminant stabilization
    - hydraulic control



- Enhance Natural Processes
  - Identify enhancements to attenuation processes that reduce flux to groundwater



Systems-based Monitoring

Scientific Opportunities for Monitoring at Environmental Remediation Sites (SOMERS)

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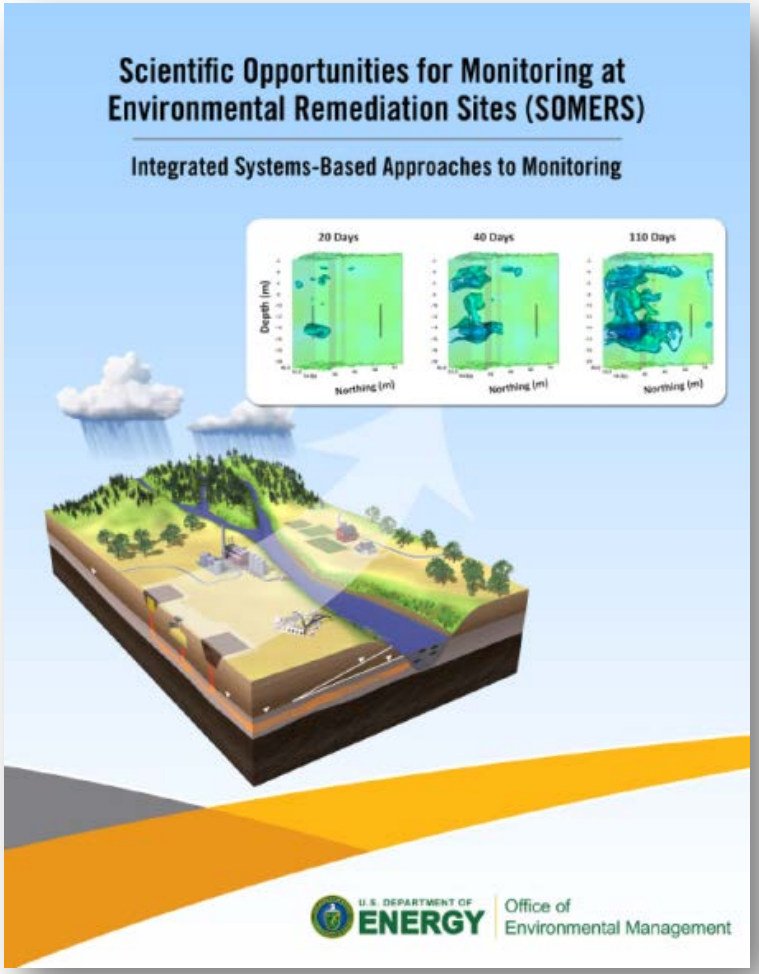
- Integrated systems-based approaches to monitoring
  - Compliant, defensible, cost-effective monitoring approach
  - Whole system approaches versus point-based monitoring
  - Uses multiple “lines of evidence”
  - Aligns key objectives at each phase of remediation
  - Guides transition of remediation phases with goal of meeting end state
  - Iterative feedback to conceptual site model



Gas-phase Tracers and Electrical Resistivity Tomography
Quantifying Moisture Content

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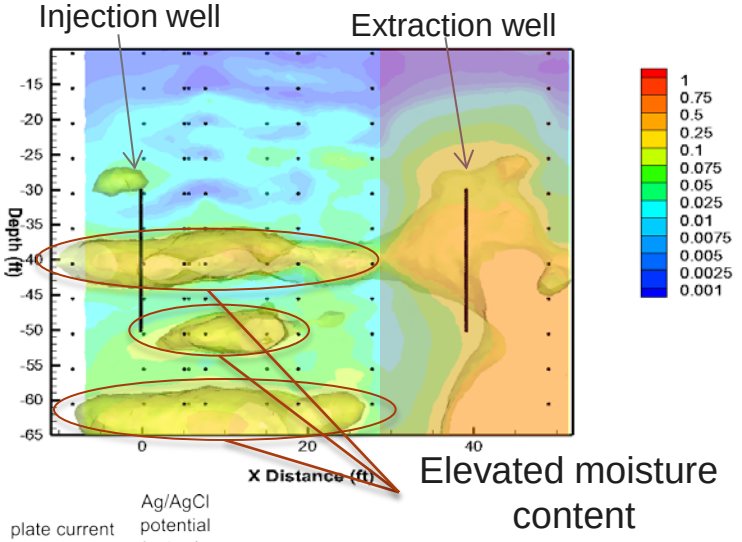
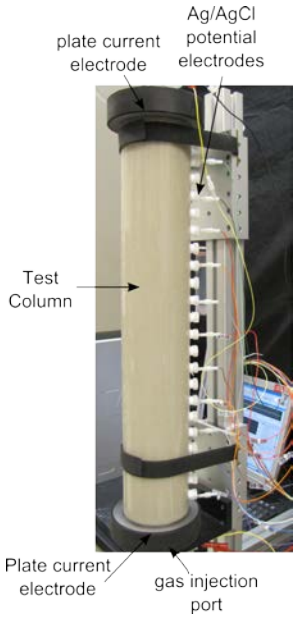
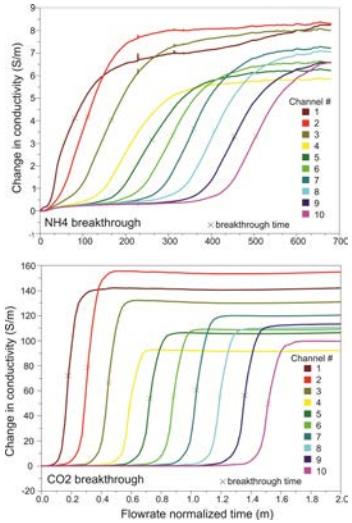
- Locate contaminated zones and quantify 3D moisture content, a primary driver for contaminant migration toward the water table.
- Image gas tracer migration through the vadose zone
  - Tracer velocity is controlled by moisture content
  - Moisture content is calculated from tracer velocity
  - Locate zones of elevated moisture content = elevated contamination = elevated conductivity

ERT Image of Desiccation Treatability Test Site







Waste Chemistry Impacts and Immobilization

- Waste chemistry impact on uranium
  - Waste chemistry of disposal alters subsurface conditions and results in uranium precipitation with minerals
  - Gradual mineral dissolution can increase ionic strength and impact (decrease) sorption
- Waste chemistry impact on ^{99}Tc
  - Field-contaminated sediments show ^{99}Tc in unidentified surface phases at low pH (<4)
  - Surface precipitates likely coated by aluminosilicate precipitates
  - ^{99}Tc remains immobilized even when oxidized
- Gas-phase remediation of ^{99}Tc
  - Eliminates risk of mobilization during treatment
  - Hydrogen sulfide and ammonia precipitates as stable compound

Potential Future Development Activities

- Technical basis for remediation
  - Contaminant mass reduction
    - Refine pore water contaminant extraction
  - Contaminant stabilization
    - Develop uranium sequestration
  - Hydraulic control
- Mass flux framework
- Systems-based closure monitoring
  - Enhance geophysical characterization and monitoring (ERT)

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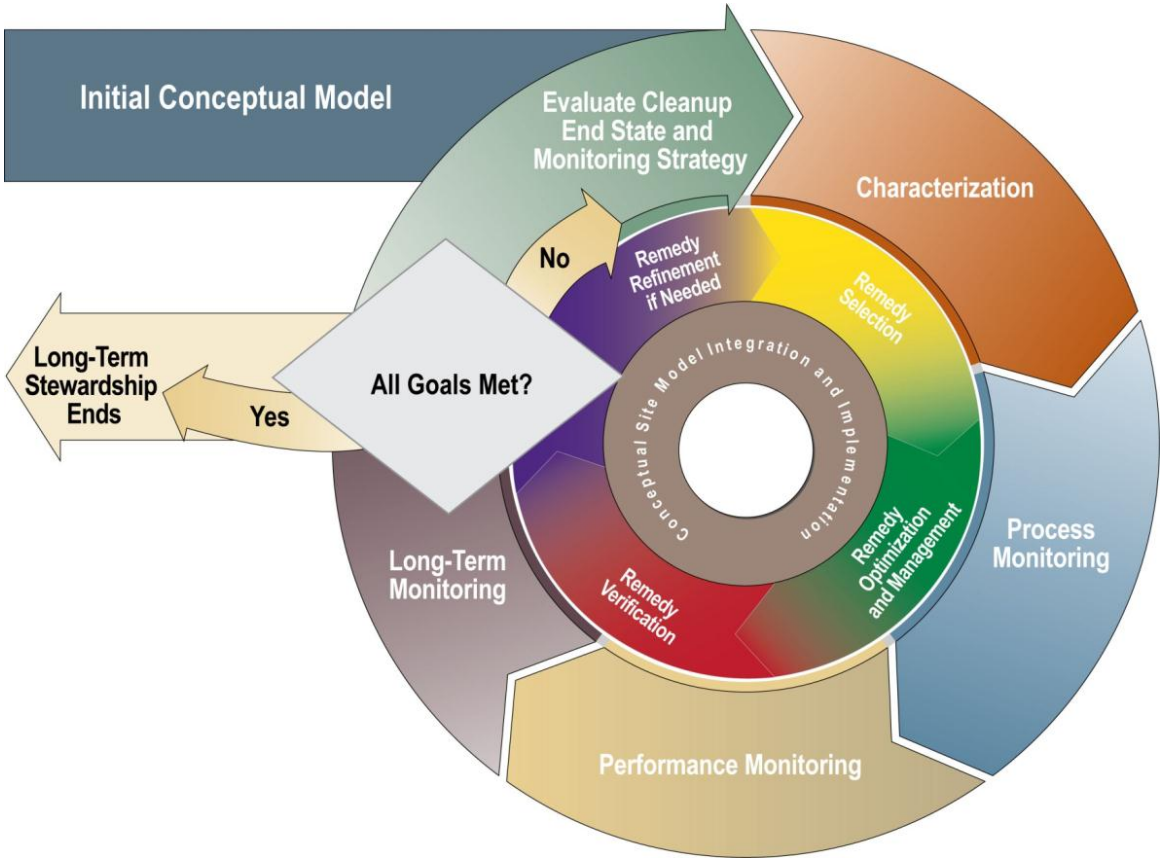
Questions?

Systems-based Monitoring

Integrated Approach to Environmental Monitoring

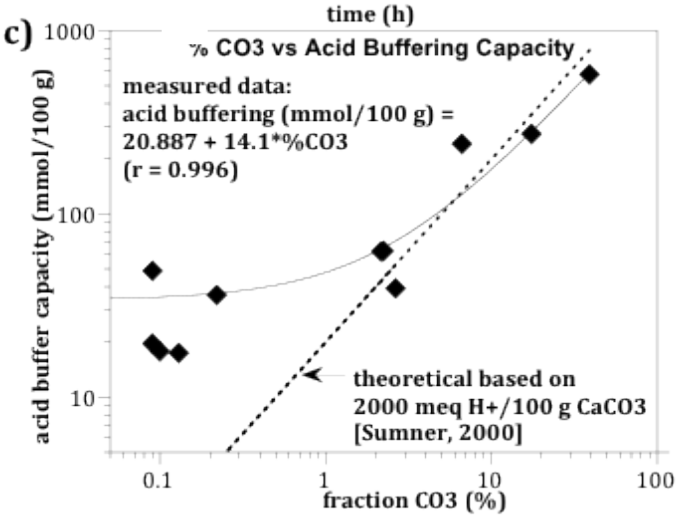
- Relative to conventional compliance monitoring approaches, a monitoring framework that
  - Uses multiple lines of evidence
  - Provides insight to the important remedial/transport processes
  - Integrates with conceptual site models and predictive analyses
  - Encompasses the remediation phases of design, implementation, and performance assessment
  - Informs endpoints

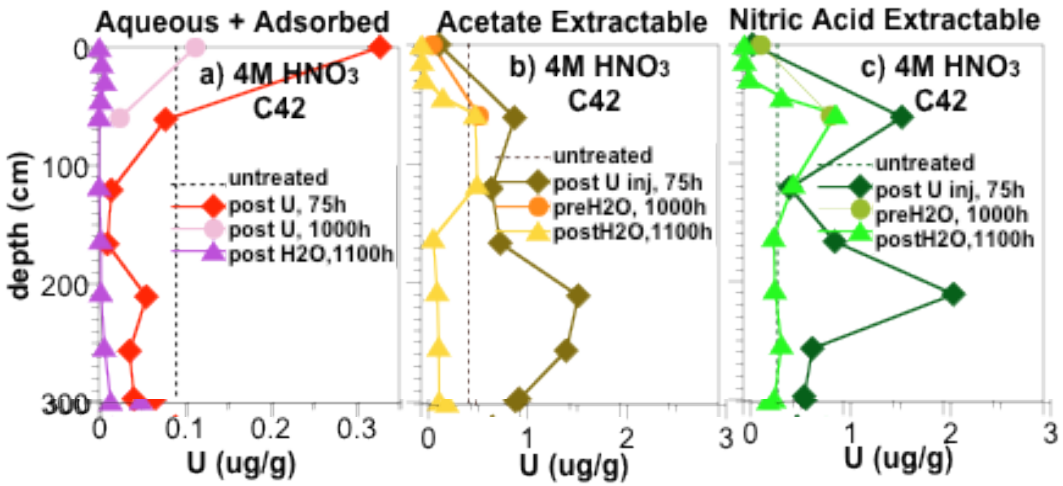


Impacts of Waste Chemistry

- How does disposed waste chemistry impact the fate and transport of uranium in the vadose zone?
  - Acid releases carbonate and phosphate from sediments that precipitate some of the uranium after the pH increases.
  - Base releases silica from sediments that precipitates some of the uranium at high pH above about 9.5.
  - Mineral Dissolution
    - Neutralizes added acid or base
    - Can release background uranium
    - Can increase ionic strength and decrease sorption

(Szecsody et al., 2013a, JCH)

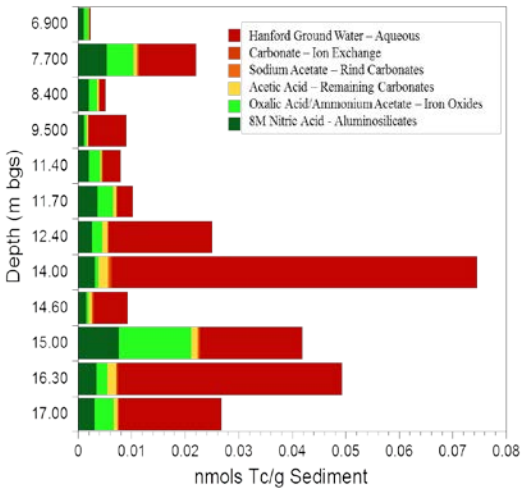




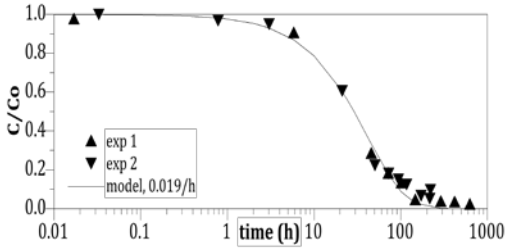
Impacts of Waste Chemistry on Tc-99

- Field-contaminated sediments show Tc-99 in unidentified surface phases
- TcO_4^- shows nearly no sorption except at pH < 4
- Under highly alkaline conditions
  - Biotite dissolution produces sufficient Fe^{2+} (aq) to reduce TcO_4^-
  - Surface Tc-99 precipitates likely coated by aluminosilicate precipitates - also associated with specific surface phases (Fe oxides?)
  - Surface Tc-99 remains immobilized even when oxidized as Tc(IV)

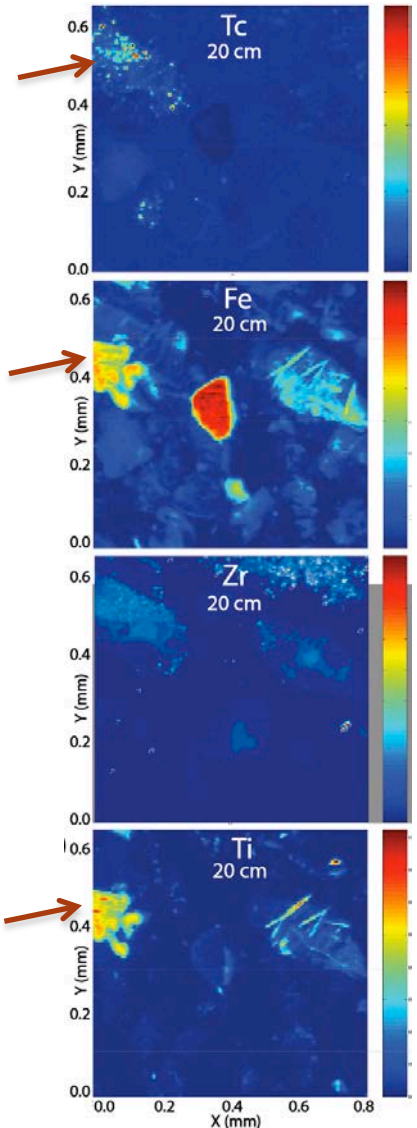
Tc-99 in Hanford Sediments: Physical and Chemical Retention



TcO4- Reduction in NaOH-treated Hanford Sediment



Microprobe Elemental Map: Tc associated with Fe, Ti oxides

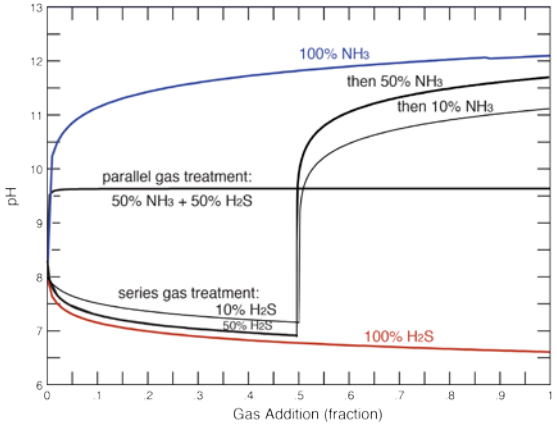


(Jansik et al, 2013, in preparation
Szecsody et al., 2013b, Chemosphere, in preparation)

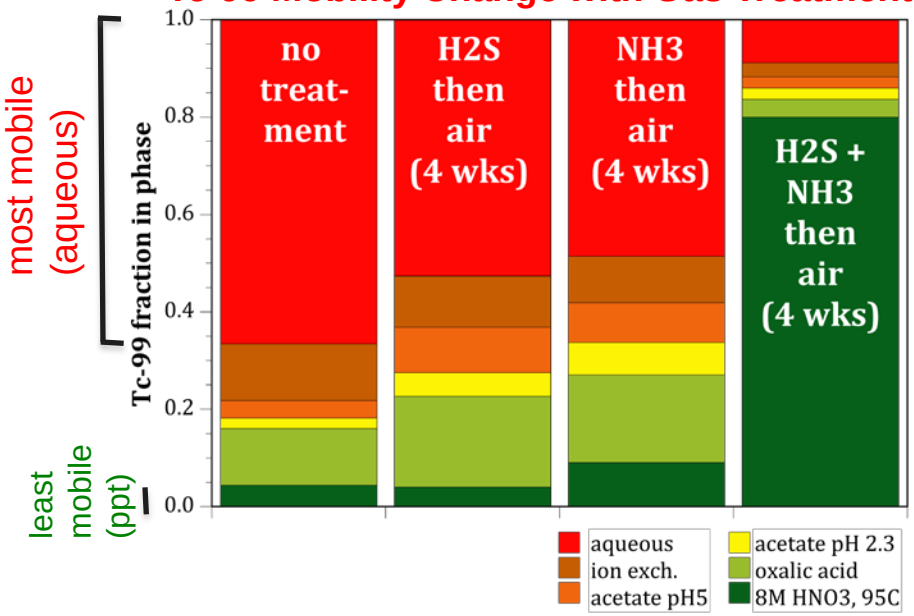
Tc Immobilization

- Gas phase remediation approaches eliminate risk of mobilization during treatment
- $H_2S + NH_3$
  - Alkaline conditions from injection of NH_3 dissolve aluminosilicates
  - As sediment pH equilibrates to natural conditions minerals precipitate
  - TcO_4^- precipitates as stable compound with no possibility to re-oxidize and release

pH in sequential H_2S then NH_3 gas treatment



Tc-99 Mobility Change with Gas Treatment



(Szecsody et al., 2013c in preparation)