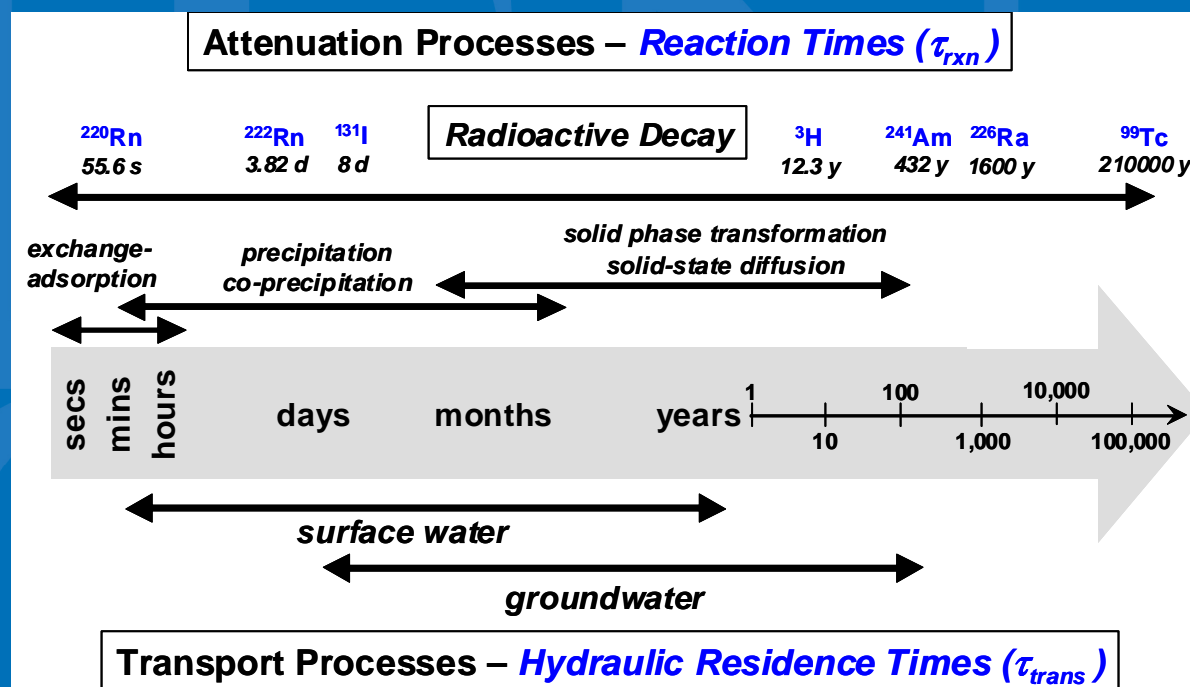


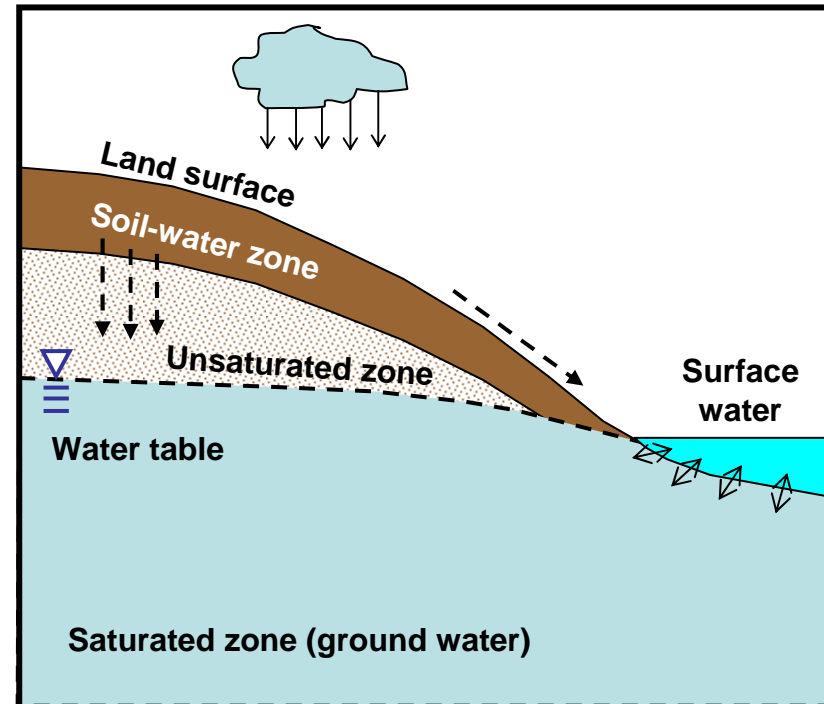
# Subsurface Characterization to Support Evaluation of Radionuclide Transport and Attenuation

*Robert G. Ford*



# Presentation Outline

- Attenuation Concepts for Radionuclides
- Site Characterization Goals
- Potential Pitfalls
- Case Study
- Final Remarks



Nothing in this presentation changes Agency policy regarding remedial selection criteria, remedial expectations, or the selection and implementation of MNA. The information presented does not supersede any guidance. Its intended purpose is to provide a technical perspective for evaluation of MNA as a potential ground-water cleanup remedy as described in OSWER Directive 9200.4-17P, "Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites"

# Controls on Plume Size & Transport

## ➤ Physical constraints:

- Contaminant source mass, spatial distribution, & release rate to saturated zone
- Spatial distribution of flow paths
- Spatial distribution of flow velocities
- Temporal variability of flow velocity & direction

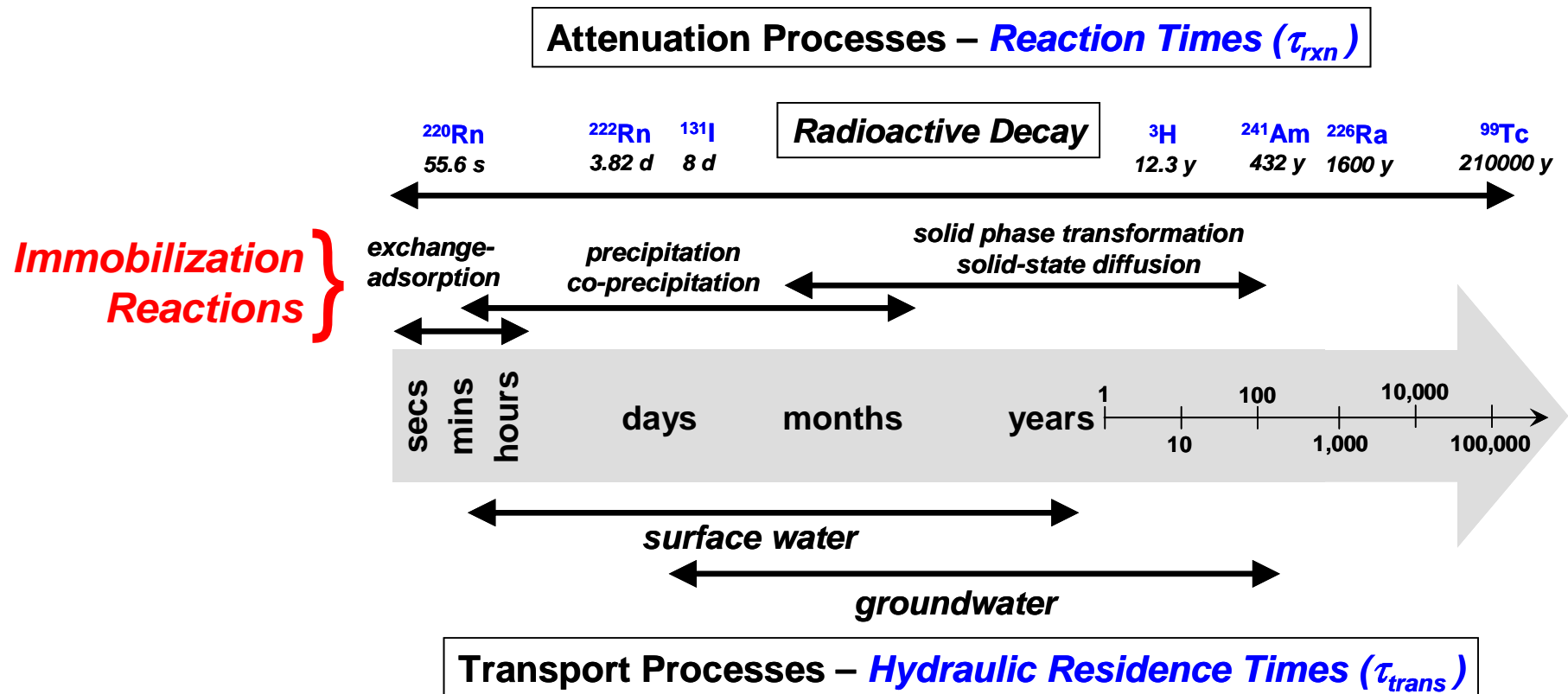
## ➤ Chemical constraints:

- Contaminant properties (decay rate, *sorption affinity = potential for adsorption, co-precipitation, precipitation*)
- Subsurface solids properties (mass distribution, *sorption affinity, chemical stability*)
- Ground-water chemistry – as it affects 1) *contaminant chemical speciation* and 2) *subsurface solids stability & sorption characteristics*

***This information determines accuracy of conceptual or predictive site model, which is the basis for projecting contaminant transport.***

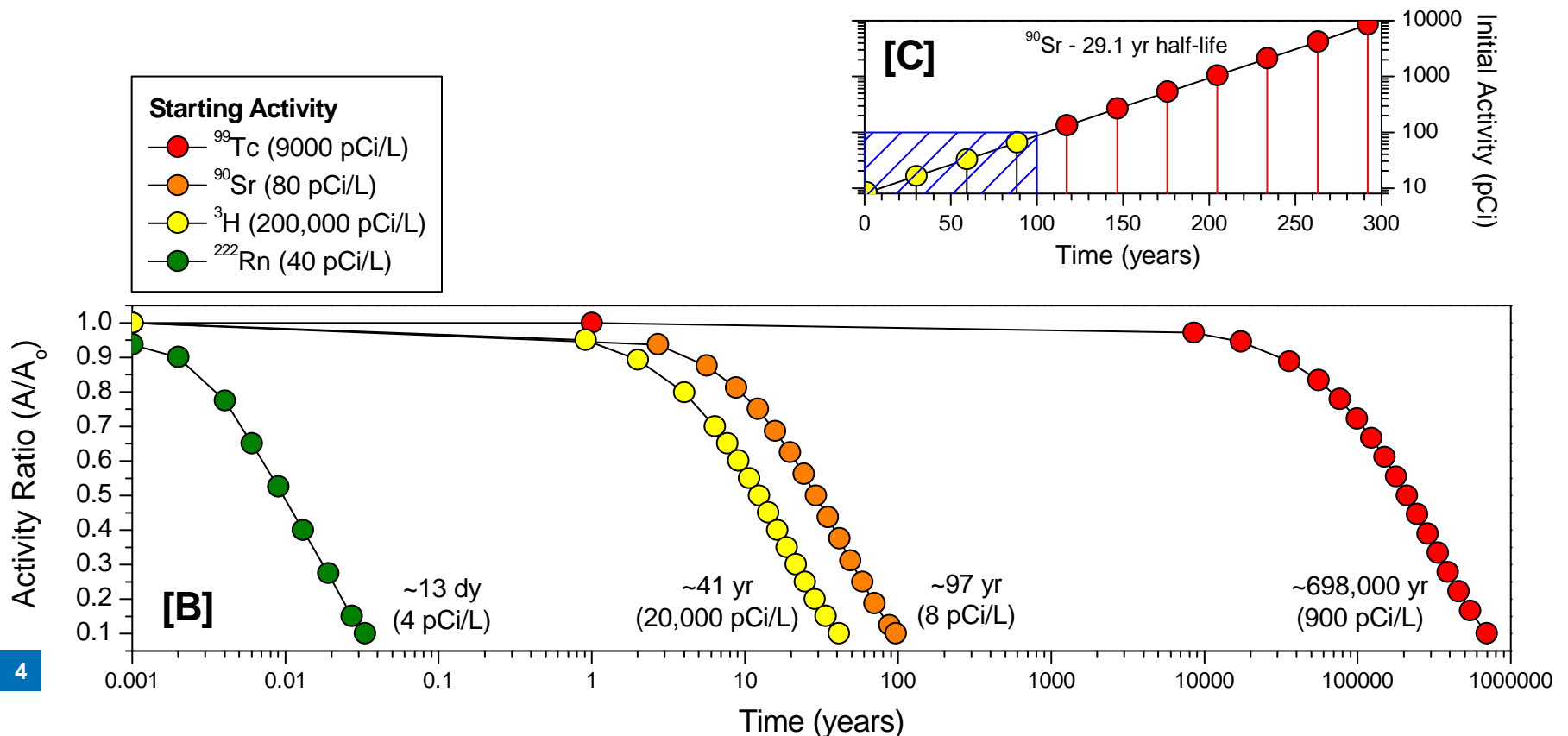
# Relative Process Timescales

## Reaction Half-life vs. GW Velocity

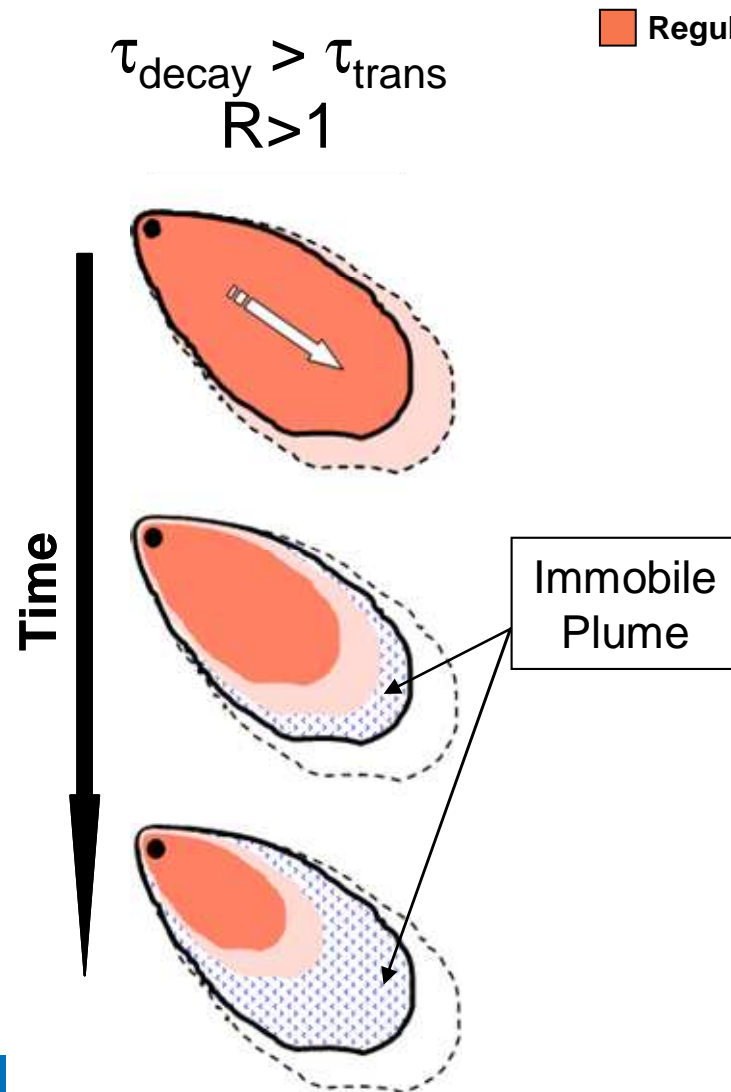


# Role of Radioactive Decay

- Race between rate of decay and rate of water movement
- Decay half-life does matter [B], but...
- Mass flux of contaminant from source also matters [C]
- *Know your **SOURCE** and **CONTROL** it!*



# Immobilization of Radionuclide



Regulated Mobile Plume

Non-regulated Mobile Plume

**‘Immobile’ plume represents contaminant mass sorbed onto aquifer solids at any point in time. Future scenarios for evolution of ‘immobile’ plume:**

- Declines in mass & spatial distribution due to radioactive decay
- Remains invariant in mass & spatial distribution (long half-life)
- Evolves to new state that serves as source for development of new dissolved plume caused by:
  - Radioactive decay produces more mobile daughter(s) w/ chemical/radiological risk
  - Changes in ground-water chemistry cause re-mobilization

## Questions to be Addressed through Site Characterization & Analysis

- What are the transport pathways within the aquifer?
- What is the rate of fluid flow along critical transport pathways?
- What processes control attenuation of the contaminant along transport pathways?
  - Transport faster than decay?
  - What reactants control immobilization (sorption)?
- What are the rates of attenuation & capacity of aquifer to sustain contaminant attenuation?
  - Magnitude of source loading to saturated zone?
  - Is the stability of the immobilized contaminant sufficient to resist re-mobilization?

# Data Quality Objectives

[ See also NUREG/CR-6948, Volumes 1 & 2 ]

## Characterization Goals

- Identify reaction mechanisms/processes that control contaminant transport
- Collect data that:
  - Support evaluation of Conceptual Site Model (*verify assumptions!*), and
  - Verify performance of identified attenuation process(es)
- Employ sample collection and analysis procedures that:
  - Maintain sample integrity (*chemical speciation*)
  - Characterize the factors that control contaminant speciation or partitioning between aqueous and solid matrices



# Potential Pitfalls in Site Characterization

## ➤ Acquisition of subsurface samples

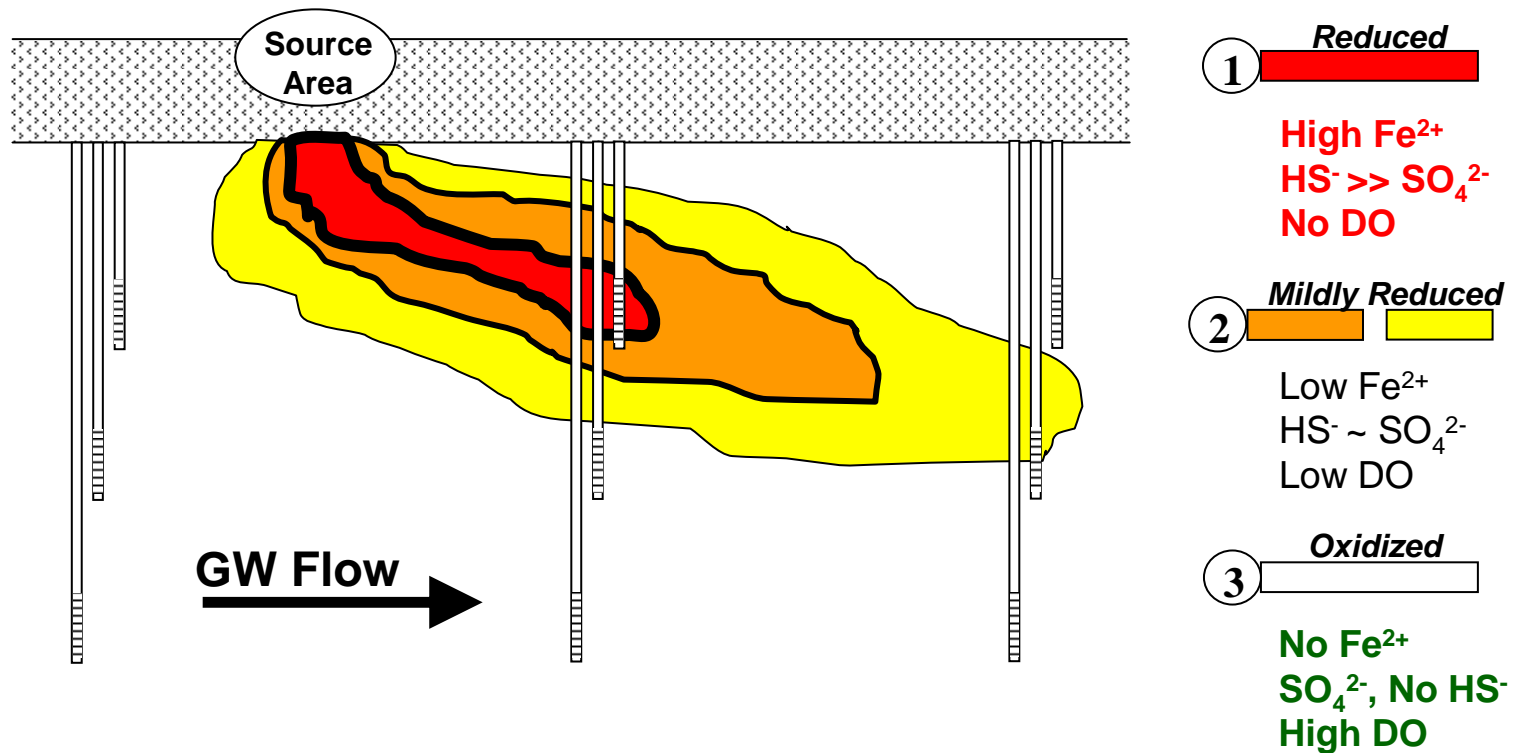
- Representative samples (e.g., drilling methods, well development, purging & sampling)
- Preservation of in-situ chemistry
  - Sample handling (liquids & solids)
- Collection procedures for *mobile* colloids

## ➤ Characterization of subsurface samples

- Field vs. laboratory procedures
- Scaling models vs. subsurface heterogeneity
- Methods for solid phase characterization
  - Mineralogy of subsurface solids
  - Contaminant speciation (e.g., oxidize/reduced)

# Acquisition of Subsurface Samples

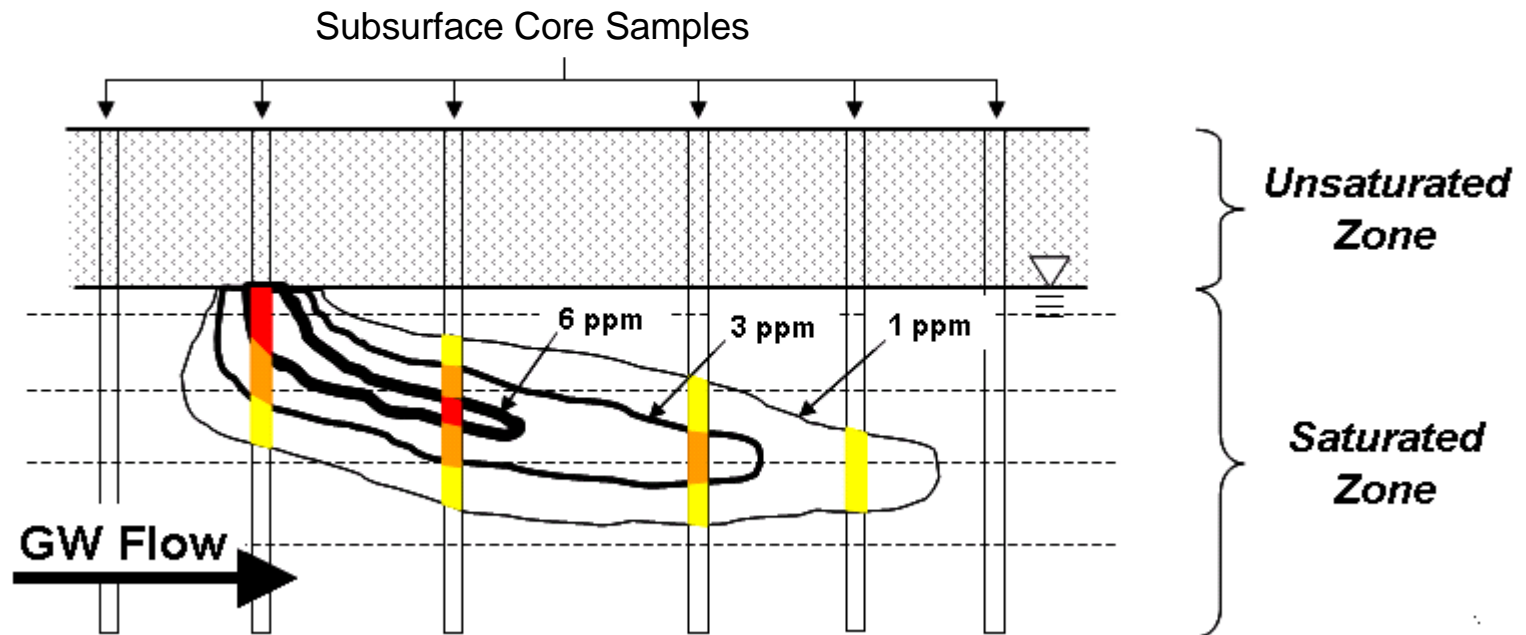
## Preservation of In-situ Chemistry (Aqueous)



- *GW wells* – map spatial and temporal variability (permanent and temporary installations)
- *Redox chemistry* – controlled by subsurface microbiology & natural/anthropogenic sources of degradable compounds

# Acquisition of Subsurface Samples

## Preservation of In-situ Chemistry (Solid)



① **Reduced**

**Reduced Fe Minerals; Sulfides; Anaerobic Microorganisms**

② **Mildly Reduced**

Mixed Fe(II)-Fe(III) Minerals; Carbonates-Sulfides(?); Mixed Microbial Populations

③ **Oxidized**

**Fe Oxides; No sulfides (unless native); Aerobic Microorganisms**

# Case Study - Immobilization

## Hanford 300 Area - Uranium

### ➤ Types of characterization data

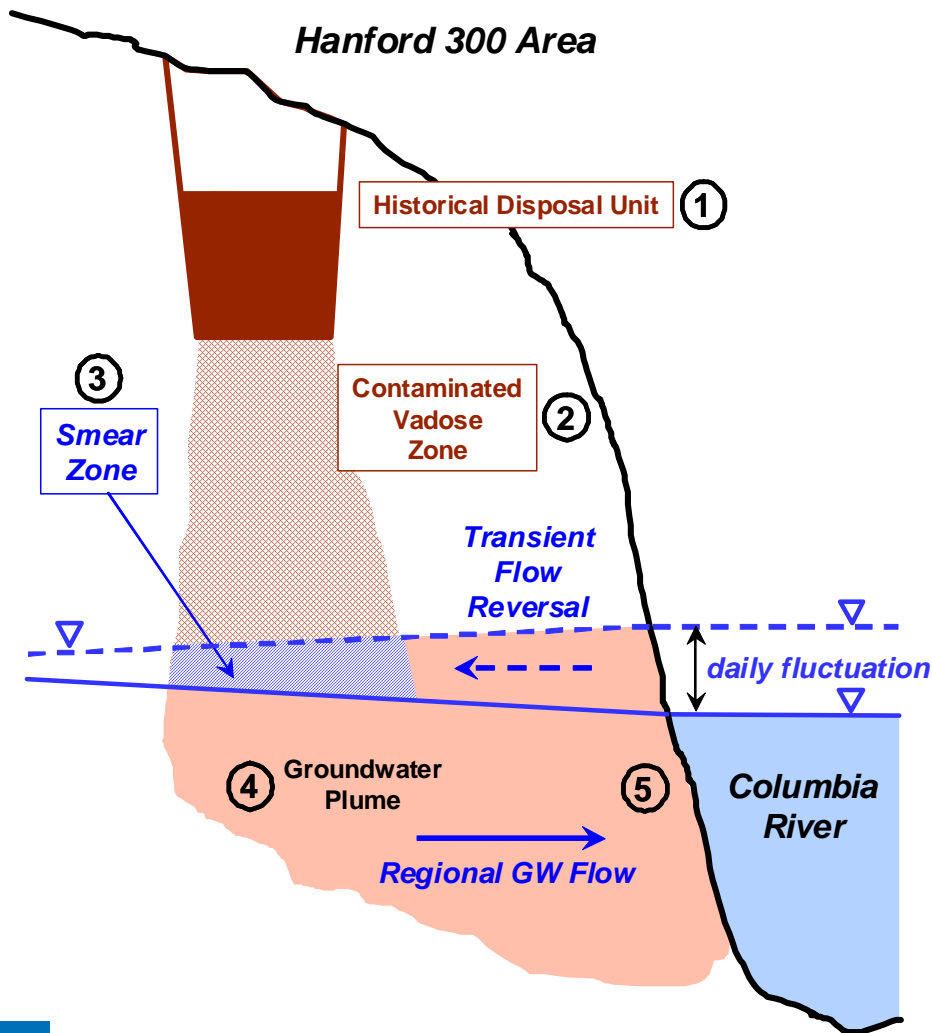
- Elemental association of U in solids from source zone, vadose zone & shallow saturated zone
- Chemical speciation of U in solids (oxidation state and solid-phase association)
- Spatial & temporal variations in U solid-phase partitioning

### ➤ Pitfalls in original characterization effort

- Reliance on contaminant transport model that assumed no continuing source to saturated aquifer (surface soils removal action)
- Development of U partition coefficient ( $K_d$ ) that did not account for influence of variable GW chemistry
- Transport modeled using annual, mean gradients vs. transient states influenced by Columbia River stage

# Case Study - Immobilization

## Hanford 300 Area - Uranium



- ① Contaminated surface soils (source removal)
- ② Dispersed residual contamination in vadose solids
- ③ Zone impacted by water table fluctuations (GW-SW interactions)
- ④ Plume in continuously saturated zone
- ⑤ Transition zone between GW & SW (includes sediments)

## ***The Burden of Proof***

- Mass of contaminant that is currently moving and anticipated to move through saturated zone
- Identification of process causing attenuation
  - Radioactive decay or immobilization
- Determination of capacity within subsurface to attenuate contaminant (*natural or engineered*)
- Determination of stability of immobilized contaminant to resist re-mobilization
- Identification of monitoring parameters that can be used to track continued performance
  - Hydrology & water chemistry

# Subsurface Hydrology & Monitoring

## **Subsurface Hydrology & GW-SW Interactions**

*USGS Circular 1139* “Ground Water and Surface Water: A Single Resource”  
<http://pubs.usgs.gov/circ/circ1139/pdf/circ1139.pdf>

*TM 4-D2* “Field Techniques for Estimating Water Fluxes Between Surface Water and Ground Water”  
<http://pubs.usgs.gov/tm/04d02/>

## **Influence of GW-SW Interactions on Contaminant Transport**

*EPA/600/S-05/002* “The Impact of Ground-Water/Surface-Water Interactions on Contaminant Transport with Application to an Arsenic Contaminated Site”  
[http://www.epa.gov/ada/download/briefs/epa\\_600\\_s05\\_002.pdf](http://www.epa.gov/ada/download/briefs/epa_600_s05_002.pdf)

## **GW Performance Monitoring Considerations (MNA for VOCs)**

*EPA/600/R-04/027* “Performance Monitoring of MNA Remedies for VOCs in Ground Water”  
<http://www.epa.gov/ada/download/reports/600R04027/600R04027.pdf>

## **Evaluating Performance of Hydraulic Capture (P&T systems)**

*EPA/600/R-08/003* “A Systematic Approach for Evaluation of Capture Zones at Pump and Treat Systems”  
<http://www.epa.gov/ada/download/reports/600R08003/600R08003.pdf>

# Subsurface Sampling & Analysis

## **Sampling Considerations for Variable Redox Systems**

*EPA/600/R-02/002* “Workshop on Monitoring Oxidation-Reduction Processes for Ground-water Restoration”

[http://www.epa.gov/ada/download/reports/epa\\_600\\_r02\\_002.pdf](http://www.epa.gov/ada/download/reports/epa_600_r02_002.pdf)

## **Preservation of Subsurface Solids from Reduced Zones**

*EPA/600/R-06/112* “Mineralogical Preservation of Solid Samples Collected from Anoxic Subsurface Environments”

<http://www.epa.gov/ada/download/issue/600R06112.pdf>

## **Analysis of Subsurface Samples for Radionuclides**

*NUREG-1576 (EPA 402-B-04-001B)* “Multi-Agency Radiological Laboratory Analytical Protocols Manual, Volume II: Chapters 10-17 and Appendix F”

<http://www.nrc.gov/reading-rm/doc-collections/nuregs/staff/sr1576/>

<http://www.epa.gov/radiation/marlap/manual.html>

*EPA 402-R-06-007* “Inventory of Radiological Methodologies For Sites Contaminated With Radioactive Materials”

[http://www.epa.gov/narel/IRM\\_Final.pdf](http://www.epa.gov/narel/IRM_Final.pdf)



# Characterizing Immobilization

## **Technical Context for Characterizing Immobilization**

[EPA/600/R-07/139](#) “Monitored Natural Attenuation of Inorganic Contaminants in Ground Water, Volume 1 – Technical Basis for Assessment”

<http://www.epa.gov/ada/download/reports/600R07139/600R07139.pdf>

## **Overview for Some Inorganic Contaminants**

[EPA/600/R-07/140](#) “Monitored Natural Attenuation of Inorganic Contaminants in Ground Water, Volume 2 – Assessment for Non-Radionuclides Including Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, Nitrate, Perchlorate, and Selenium”

<http://www.epa.gov/ada/download/reports/600R07140/600R07140.pdf>

## **Site Case Studies for Arsenic and Uranium**

[EPA/600/R-08/114](#) “Site Characterization to Support Use of Monitored Natural Attenuation for Remediation of Inorganic Contaminants in Ground Water”

<http://www.epa.gov/nrmrl/pubs/600r08114/600r08114.pdf>