

EPA
United States
Environmental Protection
Agency

Subsurface Characterization to Support Evaluation of Radionuclide Transport and Attenuation

Robert G. Ford

Attenuation Processes - Reaction Times ($t_{1/2}$)

Radionuclide	Half-life ($t_{1/2}$)
^{238}Pu	87.7 y
^{239}Pu	24,100 y
^{241}Pu	14.3 y
^{241}Am	432 y
^{242}Pu	373 y
^{244}Pu	80,000 y
^{244}Cm	18.1 y
^{244}Pu	243,000 y

Attenuation Processes: exchange-adsorption, precipitation-co-precipitation, solid phase transformation, solid-state diffusion

Transport Processes - Hydraulic Residence Times (t_{HYD})

Time Scale: secs, mins, hours, days, months, years, 10, 100, 1,000, 10,000, 100,000

Surface water, groundwater

Office of Research and Development, National Risk Management Research Laboratory
Land Remediation and Pollution Control Division, Cincinnati, OH

11 March 2009
RIC - North Bethesda, MD

EPA
United States
Environmental Protection
Agency

Presentation Outline

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

Land surface
Soil-water zone
Unsaturated zone
Water table
Saturated zone (ground water)
Surface water

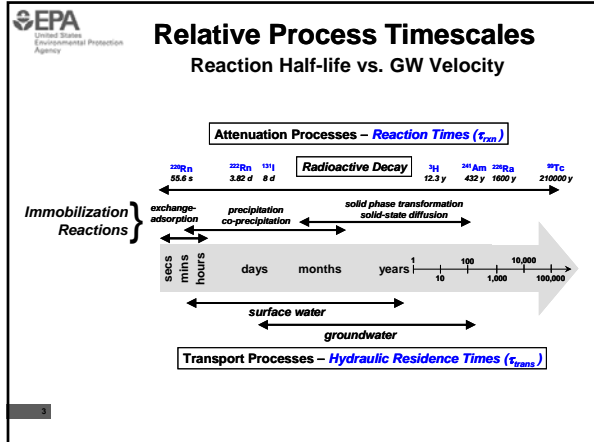
Nothing in this presentation changes Agency policy regarding remedial selection criteria, remedial expectations, or the selection and implementation of MNA. The information presented does not supersede any guidance. Its intended purpose is to provide a technical perspective for evaluation of MNA as a 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*

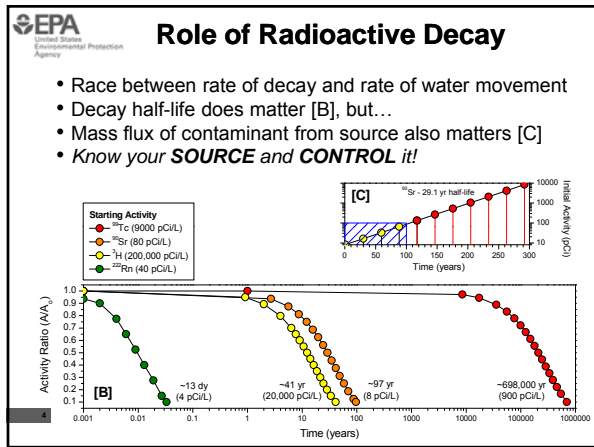
EPA
United States
Environmental Protection
Agency

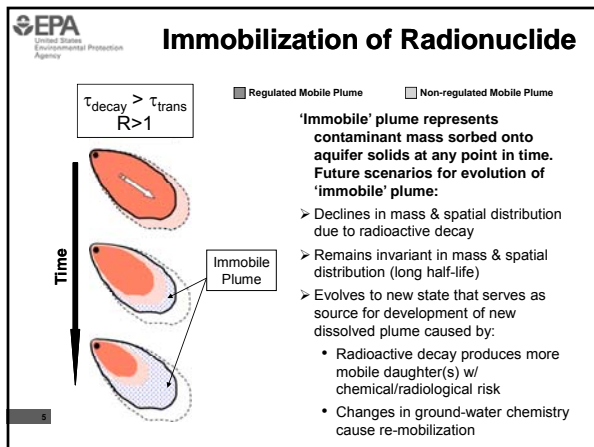
Controls on Plume Size & Transport

- **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.









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)

EPA
United States Environmental Protection Agency

Acquisition of Subsurface Samples

Preservation of In-situ Chemistry (Aqueous)

1 Reduced
High Fe^{2+}
 $HS^- \gg SO_4^{2-}$
No DO

2 Mildly Reduced
Low Fe^{2+}
 $HS^- \sim SO_4^{2-}$
Low DO

3 Oxidized
No Fe^{2+}
 SO_4^{2-} , No HS^-
High DO

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

9

EPA
United States Environmental Protection Agency

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

10

EPA
United States Environmental Protection Agency

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

11

EPA
United States
Environmental Protection
Agency

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)

12

EPA
United States
Environmental Protection
Agency

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

13

EPA
United States
Environmental Protection
Agency

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

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>

14



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

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

15



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>

16
