Monitored Natural Attenuation for Radionuclides in Ground Water – Technical Issues

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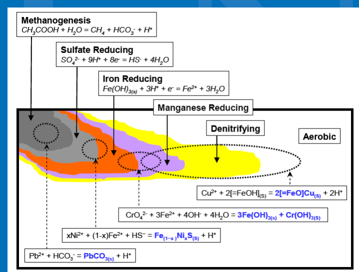

NRC Briefing
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Office of Research and Development
Land Remediation and Pollution Control Division, Cincinnati, OH

Outline of Topics

- Technical Basis for Selecting Remedial Technology
- Technical Basis for MNA under CERCLA
- Technical Information that needs to be Evaluated during Site Characterization
- Performance Confirmation Monitoring to Determine Its Effectiveness

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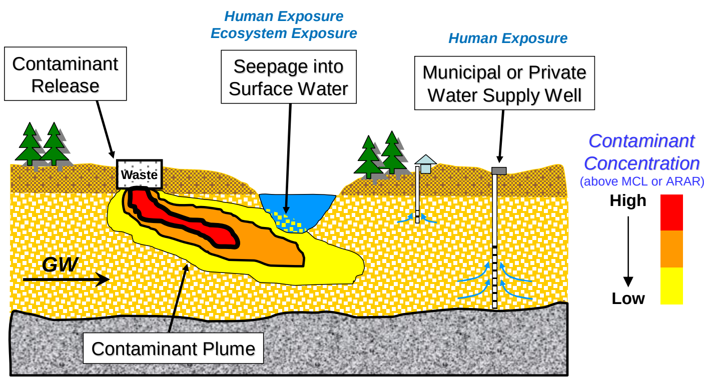
Generalized Site Scenario



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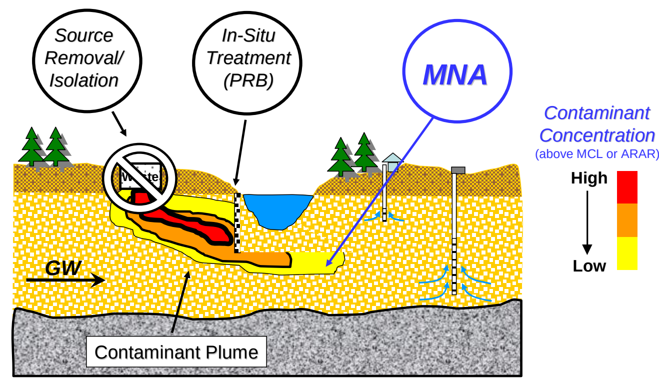
Generalized Site Scenario

1 Reduce contaminant flux in subsurface…

2 Use of MNA to remediate dilute portion of plume…



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OSWER Directive 9200.4-17P

Monitored Natural Attenuation

http://www.epa.gov/swerust1/directiv/d9200417.pdf

- **Stable or shrinking plume** – *CERCLA defines plume dimensions based on concentration/activity criterion; expectation that contaminant migration is arrested.*
- **Source control measures** (*important to limit flux of contaminant being "fed" into the plume*)
- **Identify mechanism(s) of attenuation** (*performance characteristics*)
- **Demonstrate irreversibility of attenuation process** ("sorption") – *recognizes that many inorganic contaminants will persist in subsurface*

USEPA. Common Radionuclides Found at Superfund Sites. EPA 540/R-00-004, Office of Radiation and Indoor Air, Office of Solid Waste and Emergency Response, Washington, DC (2002). http://www.epa.gov/superfund/health/contaminants/radiation/pdfs/nuclides.pdf

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Attenuation Processes

- **Dispersion/dilution?** (May factor into dimensions of "regulated" plume, but not likely sufficient to arrest migration)
- **Transformation** – conversion to something that has different regulatory constraints (e.g., nitrate or perchlorate)
- **Immobilization** – adsorption, coprecipitation, precipitation (majority of the contaminants in the three-volume set, including long-lived radionuclides) ***Note: Immobilization ≠ Retardation***
- **Radioactive Decay** – may be applicable for short-lived radionuclides (e.g., ^{3}H, ^{137}Cs, ^{90}Sr) ***Note: Retardation may benefit this process.***

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Development of EPA Technical Resource Documents for MNA

- What is covered in the EPA three-volume set on MNA for inorganic contaminants in ground water?
  - Volume 1 – Immobilization and transformation processes along with methodological approach for site characterization
  - Volume 2 – Contaminant-specific discussions of attenuation processes and characterization approaches for "metals" (As, Cd, ClO_4, Cr, Cu, Ni, NO_3, Pb, Se)
  - Volume 3 – Discussion of radioactive decay as a factor in plume development and characterization requirements; contaminant-specific discussions of attenuation processes and characterization approaches for radionuclides (Am-Pu, Cs, ^{3}H, I, Ra, Rn, Sr, Tc, Th, U)

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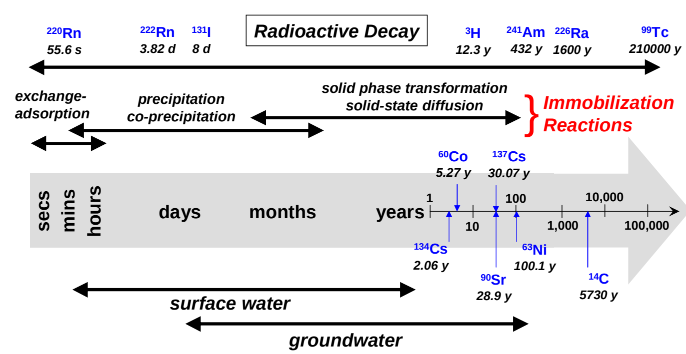
Attenuation Process Timescales

Attenuation Processes – *Reaction Half-Life (τ_{rxn})*



Transport Processes – *Hydraulic Residence Times (τ_{trans})*

See EPRI Report No. 1011730 "Groundwater Monitoring Guidance for Nuclear Power Plants", September 2005

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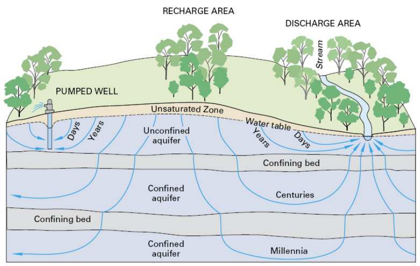
Hydrologic Timescales

Saturated Zone

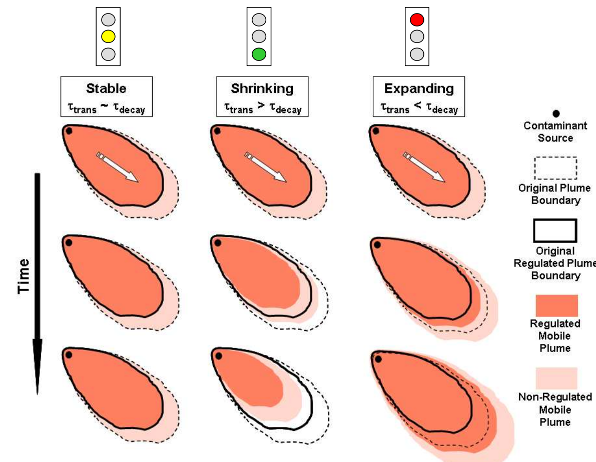


- Location of NPP within watershed (surface & subsurface) relative to receptors
- "Confining" layer may actually be "semi-confining"; hydraulic short-circuits

- Focazio, M. J., Reilly, T. E, Rupert, M. G., Helsel, D. R. "Assessing Ground-Water Vulnerability to Contamination: Providing Scientifically Defensible Information for Decision Makers" USGS Circular 1224, U.S. Geological Survey, Denver, CO (2002).
- Winter, T. C., Harvey, J. W., Franke, O. L., Alley, W. M. "Ground Water and Surface Water: A Single Resource" USGS Circular 1139 , Denver, CO (1998).

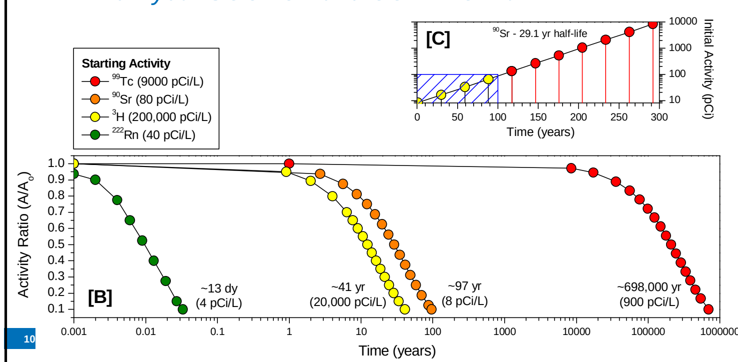
Role of Radioactive Decay

Conservative Chemical Transport



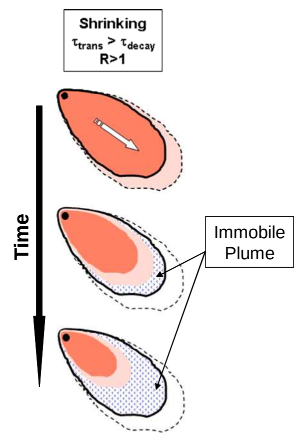
Role of Radioactive Decay

- 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

Non-Conservative Chemical Transport

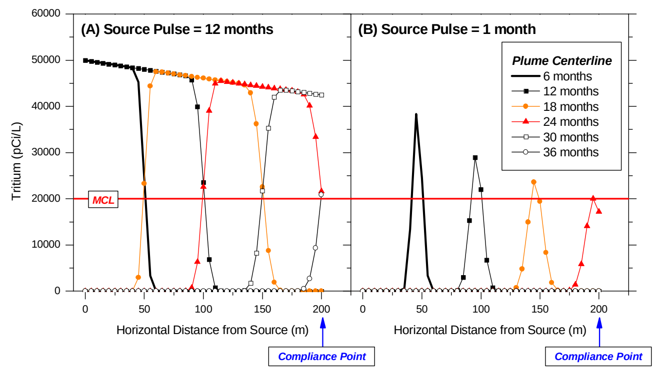


'Immobile' plume represents contaminant mass sorbed onto aquifer solids at any point in time. Future scenarios for evolution of 'immobile' plume:

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

Contaminant Flux from Source Area

- For rad decay alone, contaminant flux to subsurface impacts performance (*^{3}H plume below*)
- Source control may make MNA use feasible



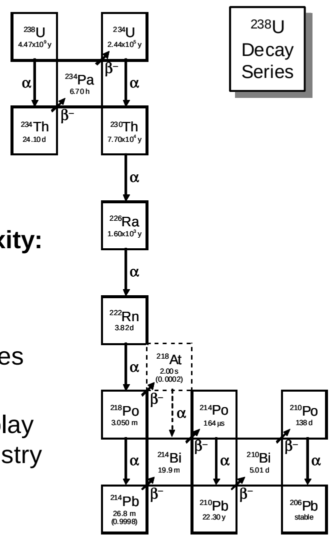
Importance of Understanding Contaminant Source

- Radionuclide may be a current component in waste or "grown in" from other waste constituents
- "In-growth" may occur in source area and/or plume
- Example – plutonium radioisotopes derived from decay of several radionuclides that are likely to exist in contamination from production/processing of nuclear fuels (americium, curium, neptunium)

Dai, M., Kelley, J. M., and Buesseler, K. O. Sources and migration of plutonium in groundwater at the Savannah River Site. *Environmental Science and Technology* 36:3690-3699 (2002).

Contaminant Radionuclide	Decay Progenitor	Decay Mode	Progenitor Decay Half-life
^{239}Pu	^{239}Am	EC	11.9 h
	^{239}Np	β^-	2.355 d
	^{243}Cm	α	28.5 d
	^{243}Am (via ^{239}Np)	α (β^-)	7380 y
^{240}Pu	^{240}Am	EC	50.8 h
	^{240}Np	β^-	65 m
	^{244}Cm	α	18.11 y
	^{244}Am (via ^{244}Cm)	β^- (α)	10.1 h

Immobilization of Radionuclide



Uranium illustrates complexity:

- Multiple radioisotopes
- Complex redox chemistry
- Known contamination sources and natural sources
- Daughter radioisotopes display unique radioactivity & chemistry

Types of Characterization Data

Immobilization & Retardation

- Aqueous measurements
  - Chemical setting, including redox
  - Oxidation state of radionuclide
  - Chemical speciation of radionuclide
  - Distribution of radioisotopes (including possible progenitors)
- Solid phase measurements
  - Mineralogy
  - Major and trace element distribution
  - Oxidation state of radionuclide
  - Chemical association of radionuclide with solid components
  - Distribution of radioisotopes
- Radiometric and mass-based techniques (each have pros & cons)

Types of Characterization Data

Immobilization & Retardation

Why radioisotope distribution and oxidation state?

- Distribution of radioisotopes can be used for source determination (contamination vs. natural) - ***Capacity***
- Distribution of radioisotopes in water and solids can be used to understand immobilization mechanism – ***Capacity & Stability***
- Oxidation state in water and solids can be used to understand immobilization mechanism – ***Capacity & Stability***

A range of laboratory-based methods exists to differentiate matrix distribution and oxidation states for radionuclides in subsurface samples.

Role of Models in Site Characterization

A model is not a substitute for adequate site characterization!

- First step is development of a technically sound CSM (***SOURCE*** to receptor) – revised based on site data
- Next step is developing water transport model that adequately captures spatial heterogeneity and time-dependent variability
- Next step is to incorporate chemical reactions that capture all important factors for radionuclide speciation (aqueous & solid)
- Need to confirm that chemical reaction database is current and accurate for contaminant and important major element chemistry

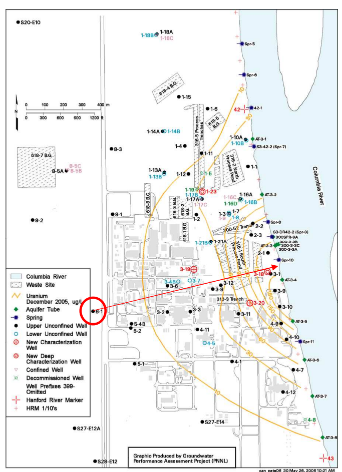
USEPA. Documenting Ground-Water Modeling at Sites Contaminated with Radioactive Substances, EPA/540/R-96/003, Office of Radiation and Indoor Air, Office of Solid Waste and Emergency Response, Washington DC (1996). (http://www.epa.gov/rpdweb00/docs/cleanup/540-r-96-003.pdf)

Role of Models in Site Characterization

Hanford 300 Area

Pitfalls in original characterization effort supporting model development:

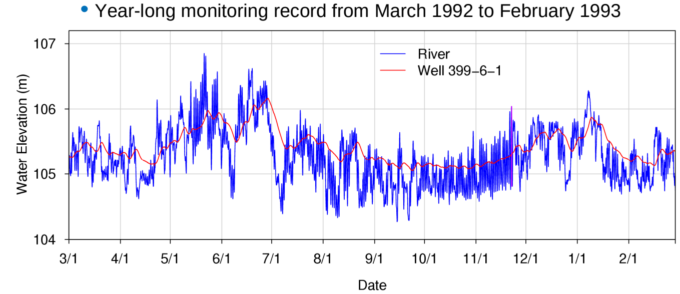
- Assumed no continuing source to saturated aquifer (surface soils removal action)
- Development of U partition coefficient (Kd) that did not account for influence of SW on variable GW chemistry (alkalinity)
- Transport modeled using annual, mean hydraulic gradients vs. transient states influenced by Columbia River stage



Role of Models in Site Characterization

Hanford 300 Area

- Well 399-6-1 is ~900 meters inland from Columbia River
- Year-long monitoring record from March 1992 to February 1993

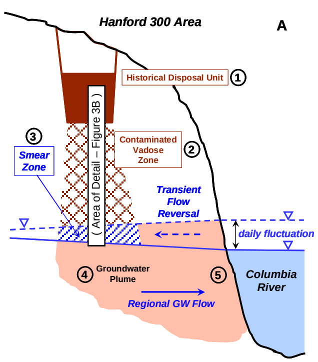


Waichler, S. R. and S. B. Yabusaki. Flow and Transport in the Hanford 300 Area Vadose Zone-Aquifer-River System. PNNL-15125, Pacific Northwest National Laboratory, Richland, WA (2005). http://www.hanford.gov/docs/gpp/library/programdocs-300/PNNL-15125.pdf

Yabusaki, S. B., Y. Fang, and S. R. Waichler (2008), Building conceptual models of field-scale uranium reactive transport in a dynamic vadose zone-aquifer-river system, Water Resour. Res., 44, W12403, doi:10.1029/2007WR006617.

Role of Models in Site Characterization

Hanford 300 Area uranium plume provides a clear example of the potential pitfalls of contaminant transport modeling (EPA/600/R-08/114)



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)

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Reminder…

Q: How does MNA differ from an engineered remedy?

1) Engineered remedy is designed from the “ground up” to achieve a specific removal process, e.g., reactive media in a permeable reactive barrier (PRB)
2) Natural Attenuation is due to some process *to be evaluated* to understand performance characteristics
   – Need to identify reactive media and system hydraulic characteristics
   – Need to understand factors under which reactive media are functioning
   – Need to determine performance criteria relative to site-specific GW conditions

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The Burden of Proof

- Mass of contaminant that is currently moving and anticipated to move through the subsurface
- Identification of process causing attenuation – radioactive decay and/or immobilization
- Determination of capacity within aquifer to attenuate contaminant
- Determination of stability of immobilized contaminant to resist re-mobilization
- Identification of monitoring parameters that can be used to track continued performance (*hydrology & chemistry*)

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