Monitored Natural Attenuation for Radionuclides in Ground Water – Technical Issues

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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

Generalized Site Scenario

Contaminant Release

Seepage into Surface Water

Municipal or Private Water Supply Well

Contaminant Plume

Contaminant Concentration (above MCL or ARAR)

High

Low

Human Exposure

Ecosystem Exposure

Reduce contaminant flux in subsurface...

Use of MNA to remediate dilute portion of plume...

GW

MNA
OSWER Directive 9200.4-17P
Monitored Natural Attenuation
http://www.epa.gov/swerust1/directive/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

CERCLA defines plume dimensions based on concentration/activity criterion; expectation that contaminant migration is arrested. Source control measures are 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.


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., 3H, 137Cs, 90Sr)

Note: Retardation may benefit this process.

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, ClO4−, Cr, Cu, Ni, NO3−, 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, 3H, I, Ra, Rn, Sr, Tc, Th, U)


Attenuation Process Timescales

<table>
<thead>
<tr>
<th>Attenuation Processes – Reaction Half-Life (τrxn)</th>
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<tbody>
<tr>
<td>222Rn 55.6 s</td>
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<tr>
<td>226Ra 1600 y</td>
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<tr>
<td>239Pu 432 y</td>
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<tr>
<td>238Pu 1000 y</td>
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<tr>
<td>232Th 210000 y</td>
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Transport Processes – Hydraulic Residence Times (τtrans)

- surface water
- groundwater

<table>
<thead>
<tr>
<th>Radioactive Decay</th>
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<tbody>
<tr>
<td>12.5 y</td>
</tr>
<tr>
<td>33.07 y</td>
</tr>
<tr>
<td>210000 y</td>
</tr>
<tr>
<td>1000 y</td>
</tr>
<tr>
<td>10000 y</td>
</tr>
<tr>
<td>100000 y</td>
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</tbody>
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<table>
<thead>
<tr>
<th>Immobilization Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>exchange-adsorption</td>
</tr>
<tr>
<td>precipitation co-precipitation</td>
</tr>
<tr>
<td>solid phase transformation</td>
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<tr>
<td>solid-state diffusion</td>
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</tbody>
</table>
**Hydrologic Timescales**

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

**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**

- '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
Radiometric and mass-based techniques (each have pros & cons)

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

**Contaminant Flux from Source Area**

- For rad decay alone, contaminant flux to subsurface impacts performance (3H 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)

**Types of Characterization Data**

- Important for field evaluation
- Immobilization & retardation
- Production and migration
- Distribution and chemical speciation
- Chemistry and transport

**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)

**Dal, 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).**
**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.

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**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


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**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 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)

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

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)