Geochemical Fate and Transport of Radionuclides in Groundwater

“One thing, however, caused us great uneasiness—our water reserve was already half exhausted.”

—Henry Lawson in “Journey to the Center of the Earth” by Jules Verne.
Environmental Impacts

The environmental movement of radionuclides in air, water, soil, and plants animals and depends on:

The chemical properties of the specific radionuclide.

The geological characteristics of the area impacted.
Environmental Fate and Pathways

The hydrogeology and climate that determines water availability and movement.

Atmospheric dispersion depends on meteorological conditions, topography, plume depletion caused by precipitation, decay, and interaction with the ground.

The type of organism, and habitat.
Ideally, wastes should remain immobile and unreactive, but if groundwater reaches the waste package, some radionuclides may dissolve or leach and move from the disposal area (more about leaching later).

Radionuclides may be transported by water in the vadose zone (water unsaturated material).
Radionuclides may be transported by water to the saturated zone ("water table") and migrate with groundwater flow. Depending on the type of radionuclide, the composition of the subsurface materials, the rate of groundwater movement, and time, a plume of contaminated groundwater may spread, and contaminate wells and surface water.
Environmental Pathways

Depending on the type of radionuclide, the gas permeability and water content of the subsurface materials, volatile radionuclides can diffuse from the disposal area into the atmosphere such as radon (Rn).

As radionuclides move away from the disposal area, their concentrations may be attenuated (lessened in severity) by a number physical and chemical processes.
Attenuation Mechanisms

Diffusion: the spontaneous movement of radionuclides (or any chemical or molecule) from an area of greater concentration to that of a lesser concentration.

Diffusion will occur if there is a concentration gradient (the Second Law of Thermodynamics: entropy increases).
Transport by Diffusion

At some (molecular) level nothing is completely impermeable.

Diffusion from waste packages:
- Steel barrels and canisters
- Ceramic and vitrified waste forms.

Diffusion from disposal sites:
- Movement through compacted clays and soils, and rock formations.
- Movement in groundwater even if the water is not moving.
Diffusion through a solid mass

Thickness $d$, and area $A$, and donor reservoir volume $V_d$
Diffusion through a solid mass

\[ D = \frac{(V_d \times d)}{(A_c d)} \times \frac{(c_i'' - c_i')}{t'' - t'} \]

where

- \( D \) = the diffusion coefficient
- \( c_d \) = radionuclide concentration in donor tank
- \( c_i \) = concentration in receptor side at time \( t \)
Diffusion coefficients (cm$^2$/sec)

Soil (based on 50-year field data)
- $^{137}$Cs: 0.6 to 3 x $10^{-4}$
- $^{90}$Sr: 1.6 to 2.6 x $10^{-9}$

Cement and concrete (lab meas.)
- $^3$H: 1.5 x $10^{-7}$
- $^{36}$Cl: 3.0 x $10^{-7}$
- $^{137}$Cs: 2.71 x $10^{-15}$
Diffusion coefficients (cm$^2$/sec)

Granite (lab measurements)

$^3$H: $1.5 \times 10^{-7}$

$^{99}$Tc: $4.6 \times 10^{-8}$

$^{85}$Sr: $1 \times 10^{-9}$

Stainless Steel (lab measurement at 700° C)

$^{134}$Cs: $3 \times 10^{-17}$

How can the coefficients be used?
Porosity: volume of void spaces divided by the volume of mass.

Tortuosity: the ratio of the diffusion path in air to the diffusion path in a solid. Radionuclides would have longer paths in solids to move through as they diffuse around particles or along fractures.

Go to:
Diffusion of $^{90}\text{Sr}$ in soil. 1% concentration.
Porosity = 0.2. tortuosity = 0.8
Attenuation Mechanisms

In unsaturated/saturated groundwater flow:

Water-air partitioning (Henry’s Law)

Vapor-phase concentration = $K_H \times S$

where $K_H = \text{chemical-specific constant}$

$S = \text{solubility in water}$
Chemical reactions

Precipitation-dissolution reactions

Example strontium-90: $^{90}\text{Sr}^{2+} + \text{SO}_4^{2-} = ^{90}\text{SrSO}_4$

(celestite)

$(^{90}\text{Sr}^{2+})(\text{SO}_4^{2-}) = \text{Ion activity product (IAP)}$

At equilibrium, IAP = reaction constant ($K_T$)

When IAP > $K_T$ celestite precipitates

When IAP < $K_T$ celestite dissolves
Attenuation Mechanisms

Ion exchange

Exchange between ions in solution with those on a stationary solid phase.

Process used to purify chemicals and decontaminate liquid samples.
Ion Exchange Resin

\[
\text{O}--\text{H}^+ + \text{Cs}^+ \rightarrow \text{O}--\text{Cs} + \text{H}^+ 
\]
Ion Exchange by Geologic Materials

Soils, clay minerals and soil organic matter can also remove ions from solution by ion exchange.

Ion exchange is a type of (ad)sorption reaction.

\[ \equiv\text{Ca} + \text{Sr}^{2+} \Leftrightarrow \equiv\text{Sr} + \text{Ca}^{2+} \]

Surfaces of clay minerals often have a negative charge resulting from isomorphous substitution within the clay structure.
STRUCTURE OF ILLITE/MICA

MODIFIED FROM GRIM (1962)
Sorption

Cations are concentrated on the surfaces to balance the negative charge. Hence, the cation is removed from solution and it immobilized.

Natural organic matter in soil also has positive and negative functional groups (sites) that can sorb ions.
Sorption of radionuclides cannot be predicted \textit{a priori}, but must be measured experimentally.

The experimental results are usually generalized as an sorption isotherm, a plot of the amount sorbed versus the equilibrium concentration.
Attenuation Mechanisms

If the sorption isotherm is linear, the data can be generalized as

$$\frac{x}{m} = K_d \ C$$

where

- $x = \text{mass sorbed}$
- $m = \text{mass of sorbent}$
- $K_d = \text{partition coefficient (volume/mass)}$
- $C = \text{concentration (mass/volume)}$
Partition or sorption coefficients give an idea about the mobility of a radionuclide subsurface environments.

If $K_d = 0$, no retention. The radionuclide moves at the same rate as groundwater.

In general, anionic radionuclides are more mobile than cationic radionuclides in saturated soil-water systems.
Sorption Coefficients

Default $K_d$ values used in modeling studies (cm$^3$/g) from Argonne National Laboratory’s “User’s Manual for RESRAD Version 6”

<table>
<thead>
<tr>
<th>Element</th>
<th>$K_d$ (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3$H</td>
<td>0</td>
</tr>
<tr>
<td>Sr</td>
<td>30</td>
</tr>
<tr>
<td>Tc</td>
<td>0</td>
</tr>
<tr>
<td>Cs</td>
<td>500</td>
</tr>
<tr>
<td>I</td>
<td>0.1</td>
</tr>
<tr>
<td>Ra</td>
<td>70</td>
</tr>
<tr>
<td>Th</td>
<td>60,000</td>
</tr>
<tr>
<td>Np</td>
<td>0</td>
</tr>
<tr>
<td>Pu</td>
<td>2,000</td>
</tr>
<tr>
<td>Am</td>
<td>20</td>
</tr>
</tbody>
</table>
Sorption isotherms for Pu, Cs, and Tc
How does $K_d$ relate to transport by advection?

Retardation = velocity of groundwater/velocity of radionuclide

$$R = 1 + \left[ \rho_b \frac{(K_d)}{\theta} \right]$$

where

$\rho_b =$ dry bulk density

$\Theta =$ volumetric water content
How does $K_d$ relate to transport by advection?

Distance traveled = $t(K_{sat})i/Rn_e$

where

$t = \text{time}$

$K_{sat} = \text{saturated hydraulic conductivity}$

$i = \text{hydraulic gradient}$

$n_e = \text{water-conducting porosity}$
Movement in sand away from a leaking tank

If we let

Dry bulk density = 1.7 g/cm$^3$

Volumetric water content = 0.30 cm$^3$/cm$^3$

$K_{sat} = 10^{-3}$ cm/sec (sand)

Gradient = 0.1 cm/cm

Water-conducting porosity = 0.3
## Distance traveled in 30 days

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>R (unitless)</th>
<th>Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3$H</td>
<td>1</td>
<td>28 feet, 8.53 m</td>
</tr>
<tr>
<td>TcO$_4^-$</td>
<td>1</td>
<td>28 feet, 8.53 m</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>2,830</td>
<td>0.8 inch, 2.0 cm</td>
</tr>
<tr>
<td>Pu$^{3+}$</td>
<td>11,330</td>
<td>0.2 inch, 0.5 cm</td>
</tr>
</tbody>
</table>
Attenuation Mechanisms

Reduction-Oxidation reactions

These are chemical reactions in which the valence or oxidation state of a radionuclide is changed by adding or removing electrons.

Chemically reduced systems are typically oxygen-poor systems such as deep groundwater.
Reduction-Oxidation reactions

Example:

Oxidizing (aerated) conditions

$\text{TcO}_4^- (\text{Tc VII})$, a mobile anion ($K_d = 0$).

Under reducing conditions

$\text{TcO}_2 (\text{Tc IV})$ which precipitates as a solid phase.
In surface water

Contamination groundwater discharges into a river or lake:

Dilution

Bioconcentration by aquatic organisms; the increase in concentration of a radionuclide in an organism resulting from tissue absorption levels exceeding the rate of metabolism and excretion.
Bioconcentration Factor (BCF) =

Concentration of a radionuclide in an organism / concentration of same radionuclide in water.

At equilibrium and often for aquatic organisms.
## Examples of BCFs

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>BCF</th>
<th>Organism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Americium</td>
<td>2,500</td>
<td>Bass</td>
</tr>
<tr>
<td></td>
<td>4,200</td>
<td>Catfish</td>
</tr>
<tr>
<td>Strontium</td>
<td>2,400 to 63,00</td>
<td>Fish bones</td>
</tr>
<tr>
<td>Plutonium</td>
<td>10 to 40</td>
<td>Fish</td>
</tr>
<tr>
<td></td>
<td>1,000</td>
<td>Algae</td>
</tr>
<tr>
<td>Mercury</td>
<td>10,000 to 40,00</td>
<td>Oysters</td>
</tr>
</tbody>
</table>
Atmospheric Dispersion

All gases and particulates released to atmosphere are progressively diluted in the course of travel downwind as result of diffusion and deposition processes (dry and wet).

Radionuclides are subject additionally to radioactive decay.
Fate of fission and activation gases

Recall releases of $^{133}\text{Xe}$ for example.

Xe is a relatively inert gas.

Once released into the atmosphere:

Soluble in water (6 g/L); can be removed from the atmosphere by rainout.
Atmospheric fate of $^{133}$Xe

Radioactive half-life of 5.27 days.

If only radioactive decay is considered the atmospheric residence time ($\tau$) of $t_{1/2} = 0.693\tau = 7.6$ days.

$^{133}$Xe decays to stable $^{133}$Cs by $\beta^-$ decay.
Decay while traveling

Short-lived radionuclides, with half-lives of a few hours or less are not radiologically important at large distances.

With typical wind speeds of about 10 m/s, noble gas $^{135}$Xe, which has a half-life of 9.2 h, decays to about 12.5% of its original activity in the time taken to travel 1,000 km (621 miles).
Persistent Radionuclides

Some radionuclides found in airborne effluents from nuclear facilities have extremely long radioactive half-lives.

Some long-term radionuclides are not efficiently removed from the plume by other processes such as wet and dry deposition, which are effective in depleting the plume of particulate nuclides. Such radionuclides are radiologically important on regional and global scales.
Persistent Radionuclides

Most well-known and important radionuclides in this category are:

$^3\text{H} \ (t_{1/2} = 12.3 \text{ yr})$

$^{14}\text{C} \ (t_{1/2} = 5,730 \text{ yr})$

$^{85}\text{Kr} \ (t_{1/2} = 10.7 \text{ yr})$

$^{129}\text{I} \ (t_{1/2} = 1.57 \times 10^7 \text{ yr})$
Fate Chemistry of Plutonium

Under natural environmental conditions, plutonium solubility is limited by the formation of amorphous plutonium hydroxide \([\text{Pu(OH)}_4]\) or polycrystalline plutonium oxide \((\text{PuO}_2)\). Pu solubility in water (Torretto et al., 1995):

\[
\text{pH 7, 25° C, Eh}_Z = 175 \text{ mV in 0.18 M NaClO}_4 \; \text{is} \; 12.93 \pm 2.54 \; \mu\text{g/L}
\]

All things considered, if Pu escapes from the disposal area, it will not move far (relatively immobile) because of sorption and precipitation (default \(K_d = 2,000\)).
Fate Chemistry of Uranium

Uranium has sixteen isotopes, all of which are radioactive. Naturally occurring uranium nominally contains 99.28305% by weight $^{238}\text{U}$, 0.7110% $^{235}\text{U}$, and 0.0054% $^{234}\text{U}$.

Uranium can exist in five oxidation states: +2, +3, +4, +5, and +6; however, only the +4 and +6 states are stable enough to be of practical importance.
Default $K_d = 50$
Fate Chemistry of Uranium

Tetravalent uranium is reasonably stable and forms hydroxides, hydrated fluorides, and phosphates of limited solubility.

Hexavalent uranium is the most stable state, and the most commonly occurring state is $\text{U}_3\text{O}_8$. Major compounds of uranium include oxides, fluorides, nitrates, chlorides, acetates, and others.
Uraninite (UO$_2$)
Fate Chemistry of Neptunium

Np solubility in water (Torretto et al., 1995)
pH 7, 25° C, Eh$_Z$ = 431 mV in 0.18 M NaClO$_4$
45.5 ± 4.98 μg/L

In soil, Np is generally mobile (default $K_d = 0$), but dependent both on pH and the oxidation state.

At pH 8, $K_d = 215$ L/kg on limestone.
At pH 9, $K_d = 0$ on limestone. Also less mobile under reducing conditions.
Fate Chemistry of Neptunium

Np can exist in five oxidation states: +3, +4, +5, +6, and +7. The +5 state is the most stable ion in aqueous solution.
Fate Chemistry of Neptumium

Np can be taken up by plants, but at plant concentrations similar to soil concentrations. Np compounds are ionic and would not volatilize from moist or dry soil surfaces.

BCF for fish = 10

BCF = 300 for green algae.
Fate Chemistry of Americium

The four principal americium isotopes are $^{241}\text{Am}$ (half-life 432.2 y), $^{242\text{m}}\text{Am}$ (141 y), $^{242}\text{Am}$ (16.1 h), and $^{243}\text{Am}$ (7,370 y).

The known oxidation states of americium are +2, +3, +4, +5, and +6. However, the stable oxidation states are +3 and +4; the common oxidation state is +3.
Fate Chemistry of Americium

The bioconcentration of $^{241}$Am in fish is insignificant, especially to the edible parts of the fish. In a study performed in a nuclear waste pond, the levels of $^{241}$Am were about 3 orders of magnitude greater than background levels (ATSDR, 2004).
Hydrogeology of groundwater

Groundwater flows through porous geological media at a rate that depends on the driving force (gravity), the gradient (change in elevation), and the ability of the material to transmit water (saturated hydraulic conductivity). Henri Darcy generalized that, for a volume of homogeneous, isotropic material . . .
Darci’s law

\[
\frac{(K_{\text{sat}} \ A \Delta h)}{L} = Q \quad (4.3)
\]

where \( K_{\text{sat}} \) = hydraulic conductivity

\( A \) = cross-sectional area of the volume of porous material

\( \Delta h \) = change in elevation or hydraulic gradient (i)

\( L \) = distance of the flow path

\( Q \) = flow rate
Transport by dispersion

Dispersion is a process in which radionuclides spontaneously spread out in porous media in flowing groundwater. At the microscopic level, dispersion results from the flow through different pore sizes and flow paths around particles of different sizes and shapes. At larger scales, dispersion results from geological heterogeneities and anisotropic materials.
Transport by diffusion

\[ D = \alpha_1 V + D^* \]

where \( D \) = dispersion coefficient

\( \alpha_1 \) = longitudinal dispersivity of the media

\( V \) = average linear groundwater velocity

\( D^* \) = effective diffusion coefficient from eq. 4.5

The longitudinal dispersivity component is best estimated from laboratory measurements of flow in soil columns using a non-reactive tracer.
Transport by Advection-Dispersion-Reaction

\[
\frac{\partial C}{\partial t} = D_x \left( \frac{\partial C^2}{\partial x^2} \right) - V_x \left( \frac{\partial C}{\partial x} \right) - \left( \frac{\rho_b}{\theta} \right) \left( \frac{\partial S}{\partial t} \right)
\]

where \( C \) = concentration of the radionuclide in solution

\( D_x \) = the effective dispersion coefficient along flow path \( x \)

\( V_x \) = mean convective flow along flow path \( x \)

\( \rho_b \) = bulk density of the geomedia

\( \theta \) = volumetric water content

\( S \) = amount of sorbate per mass of sorbent

\( t \) = time
Transport by Advection-Dispersion-Reaction

The analytical solution of this second-order differential equation is

\[
\frac{C}{C_0} = 0.5 \left\{ \text{erfc} \left( \frac{x - Vt^*}{2(D_x t^*)^{0.5}} \right) + \exp \left( \frac{V_x}{D_x} \right) \text{erfc} \left( \frac{x + Vt^*}{2(D_x t^*)^{0.5}} \right) \right\}
\]

where \( \frac{C}{C_0} \) = ratio of the radionuclide concentration in groundwater at time \( t \) and distance \( x \) to the initial concentration \( C_0 \),

\[\text{erfc} \] = complimentary error function

\( V \) = average linear pore-water velocity

\( D_x \) = dispersion coefficient

\( T^* \) = retarded time (actual time divided by the retardation factor \( R \))
Groundwater monitoring for radionuclides

Gross alpha and gross beta measurements indicate the combined amount of radioactive substances in air, soil, and water.

Used for many years because of their ease, speed, and low analytical cost. However, these measurements do not identify the specific source(s) of the activity.
Gross counting

Gross counting is commonly applied as a screening tool to identify situations in which there may be a need to determine the specific radionuclides using other analytical methods. Gross measurements of water samples for a groundwater monitoring program are commonly made by first evaporating the water, then counting the alpha and beta particles emitted from the solid residue using a gas-flow proportional counting system.
## Likely natural sources of alpha and beta activity in groundwater

<table>
<thead>
<tr>
<th>Element</th>
<th>Isotope</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium</td>
<td>U-234</td>
<td>alpha</td>
</tr>
<tr>
<td></td>
<td>U-235</td>
<td>alpha</td>
</tr>
<tr>
<td></td>
<td>U-238</td>
<td>alpha</td>
</tr>
<tr>
<td>Thorium</td>
<td>Th-228</td>
<td>alpha</td>
</tr>
<tr>
<td></td>
<td>Th-230</td>
<td>alpha</td>
</tr>
<tr>
<td></td>
<td>Th-232</td>
<td>alpha</td>
</tr>
<tr>
<td>Potassium</td>
<td>K-40</td>
<td>beta</td>
</tr>
<tr>
<td>Radium</td>
<td>Ra-226</td>
<td>alpha</td>
</tr>
<tr>
<td></td>
<td>Ra-228</td>
<td>beta</td>
</tr>
<tr>
<td>Radon</td>
<td>Rn-222</td>
<td>alpha</td>
</tr>
</tbody>
</table>
Example of interpreting gross count data

Leachate B water sample

Gross \( \alpha = 13.3 \text{ pCi/L} \)

but \( ^{226}\text{Ra} = 0.49 \text{ pCi/L} \) and \( ^{238}\text{U} = 0.88 \text{ pCi/L} \).

What is missing?

Radium decays into short-lived radon, polonium, and lead radionuclides,

\[ ^{226}\text{Ra} \rightarrow ^{222}\text{Rn} + \alpha \quad (^{226}\text{Ra} \text{ half-life of 1,620 years}) \]

\[ ^{222}\text{Rn} \rightarrow ^{218}\text{Po} + \alpha \quad (^{222}\text{Rn} \text{ half-life of 3.8 days}) \]

\[ ^{218}\text{Po} \rightarrow ^{214}\text{Pb} + \alpha \quad (^{218}\text{Po} \text{ half-life of 3 minutes}) \]
Interpretation of gross data

The additional sources of alpha particles were from the decay of $^{226}$Ra that formed before the sample was analyzed before gross counting (holding time was exceeded).

Gross $\beta = 561$ pCi/L

The sample contained 637 mg/L K

$\text{mg/L K} \times 0.852 = \text{pCi/L } ^{40}\text{K}$

The sample contained $\sim 534$ pCi/L $^{40}\text{K}$

Conclusion: uncontaminated background sample.