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Geochemistry and biogeochemistry of radioactive substances

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Anthropogenic radioactive substances can enter the environment from nuclear weapons testing, routine discharges from nuclear power plants and reprocessing facilities, mining and mineral processing, medical facilities and from nuclear accidents. Their environmental behaviour is controlled by whether they sorb to mineral surfaces, form complexes or colloids, or are subject to redox transformations – in the same way as their equivalent non-radioactive isotopes and metals in general. Crucially, all of these factors can be influenced by microbial processes and so understanding the biogeochemistry of radioactive substances is essential in order to predict their fate and environmental impact.

The most important radionuclides, in terms of their environmental abundance and radioactivity, are the actinides ^{235,238}Uranium, ^{237}Neptunium, ^{238,239,240,241}Plutonium, ^{241}Amercium, fission products ^{137}Caesium, ^{90}Strontium, ^{129}Iodine, ^{99}Technetium, and tritium (^{3}H).

Factors that Affect the Environmental Behaviour of Radionuclides

Sorption to Mineral Surfaces: Radionuclides can sorb to mineral surfaces through ion exchange, or the formation of inner sphere or outer sphere complexes. Ion exchange is the strongest form of sorption; Cs^+ readily exchanges for other positively charged cations in the interlayer sites of illite, a common clay mineral, and over time this process becomes irreversible. The amount of sorption (or desorption) is pH dependent. Under acidic conditions, mineral surfaces become protonated which reduces their affinity for positively charged cations such as Sr^{2+}. Fungi are known to generate acidity by secreting organic acids, including oxalic acid, which can enhance

the dissolution of depleted uranium. Bacteria can also lower the pH of the environment by producing organic acids fr om the breakdown of complex organic matter. Some microbial processes can also cause the pH to increase, for example via denitrification (the reduction of nitrate to nitrogen) and ureolysis (degradation of urea to ammonium and carbonate), which allows the precipitation of Sr^{2+} in calcite ($CaCO_3$). Although many radionuclides have been shown to sorb to microbial biomass, this is a temporary situation because the biomass eventually dies and decomposes, causing the radionuclides to desorb and become remobilised.

Complexation: In general, the complexation of radionuclides by ligands increases their environmental mobility. Complexing agents, including ethylenediaminetetraacetic acid (EDTA) and citric acid, are often used in the nuclear industry to decontaminate facilities. However, both Np and Pu ions are known to be more bioavailable when complexed to organic ligands such as EDTA. In the environment, uranyl carbonate complexes are highly soluble and have a lower electrostatic affinity to mineral surfaces compared to uranyl hydroxides. Natural organic matter in the form of humic or fulvic acids and fungal-secreted organic acids will complex radionuclides and increase their mobility. Microorganisms are also able to produce ligands that cause radionuclides to precipitate from solution as insoluble biominerals. For example, many bacteria use phosphatase enzymes to generate inorganic phosphate, and this can precipitate U from solution as autunite (UO_2PO_4), whilst the sulfide produced by sulfate-reducing bacteria can precipitate Tc as TcS_2.

Colloid formation: Colloids are defined by IUPAC as molecules or poly-molecular particles dispersed in a medium that have, at least in one direction, a dimension roughly between 1 nm and 1 μm. In environmental systems colloids behave as aqueous complexes and remain suspended in water where they are highly mobile and can be transported long distances. Colloids can be removed from the water column by sorption onto surfaces or by aggregation to form particles that precipitate. Radionuclides can form colloids, or sorb onto colloids of other materials such as clays, iron oxides and organic matter. Plutonium has been shown to be transported distances of more than a kilometre from nuclear sites when associated with colloidal particles.
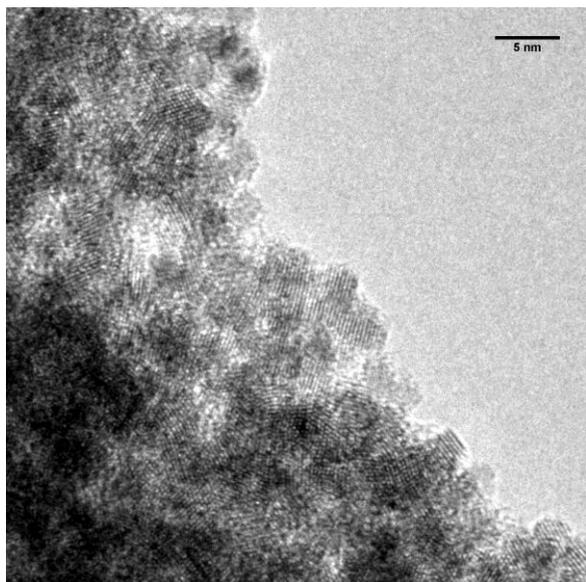
Figure 1. *Uranium(IV) biominerals produced by bacteria. Image credit: Laura Newsome.*

Redox transformation: In general, redox-sensitive radionuclides are more soluble in their oxidised forms. U(VI), Tc(VII), Np(V), Pu(V) form stable oxycations (e.g. UO_2^{2+}) or oxyanions (e.g. TcO_4^-) that are mobile under the oxidising conditions typically encountered in surface waters and groundwater. However, under reducing conditions, they are sparingly soluble and tend to become associated with the solid mineral phase through sorption, or, if present at high enough concentrations, can precipitate as reduced phases such as UO_2. Microbial activity can affect the behaviour of redox-sensitive radionuclides by direct enzymatic reduction, that is microorganisms can gain energy from the reductive respiration of $U(VI)O_2^{2+}$ to $U(IV)O_{2(s)}$ coupled to the oxidation of organic electron donors. Alternatively, microorganisms can generate reducing conditions which cause the reductive precipitation of radionuclides. For example, microbial Fe(III) reduction is ubiquitous in the natural environment and the biogenic Fe(II) so formed can react with aqueous Tc(VII) to produce $Tc(IV)_{(s)}$, which can become incorporated into Fe(II) mineral crystal structures.

Summary of Environmental Behaviour of Key Radioactive Substances

Tritium: tritiated water (^3H_2O) is common and behaves identically to water. It can be incorporated into organic matter as organically bound tritium, which is more bioavailable than tritiated water.

^{137}Cs: exists in the environment as Cs^+ and does not form aqueous complexes in soil or water environments. It has a strong affinity with clay minerals, and substitutes for Na^+ or K^+, becoming trapped in the interlayer sites.

^{90}Sr: is mobile in groundwater as Sr^{2+} but can sorb to mineral surfaces through weakly bound outer sphere complexes. Sr^{2+} behaves similarly to Ca^{2+} and can become incorporated into the calcite mineral structure.

^{99}Tc: is a common groundwater contaminant at nuclear sites and highly mobile as pertechnetate ion ($Tc(VII)O_4^-$). It can be removed from solution by reduction to Tc(IV), mediated by Fe(II) generated by microorganisms, or by reaction with, for example, zero-valent iron.

^{129}I: can be present in the environment as iodide (I^-), iodine (I_2) and iodate (IO_3^-), all of which are stable and mobile. Soil microorganisms can volatilise iodide through methylation to CH_3I. Iodate can sorb to soils, but the development of reducing conditions can mobilise sorbed iodate as iodide.

^{235,238}U: is commonly found in oxidising environments as highly mobile uranyl ($U(VI)O_2^{2+}$) and uranyl carbonate complexes. U(VI) can be removed from solution by direct enzymatic reduction by microorganisms, by complexation with microbially-produced phosphate, and it can sorb to iron oxide minerals and natural organic matter such as peat. Fungi can transform depleted uranium to insoluble U(VI) phosphate minerals.

^{237}Np: neptunyl ($Np(V)O_2^+$) is highly soluble and exhibits limited sorption to surfaces. It can be reduced to insoluble Np(IV) by soil microorganisms and by Fe(II).

^{238,239,240,241}Pu: plutonium has complex redox chemistry; Pu(V) and (VI) are considered to be oxidised forms, while Pu(III) and Pu(IV) are the reduced forms. All of these can be stable under natural environmental conditions. Pu predominantly associates with soils, sediments and particulate matter as Pu(IV). It is not readily desorbed from soils, and transport in the environment is primarily in colloidal form.

^{241}Am: is present as Am(III) in the environment. It is stable over a wide range of environmental conditions and sorbs readily to sediments.

Further Reading

1. Choppin G, Liljenzin J-O, Rydberg J. (2002). Chapter 22. Behavior of radionuclides in the environment. In: Radiochemistry and Nuclear Chemistry Third Edition. Butterworth-Heinemann: London, pp 653–685.
2. Hester, R. E. and Harrison, R. M. (Eds) (2011). Issues in Environmental Science and Technology, 32. Nuclear Power and the Environment. Royal Society of Chemistry, 2011.
3. Newsome L, Morris K, Lloyd JR. (2014). The biogeochemistry and bioremediation of uranium and other priority radionuclides. Chemical Geology 363: 164–184.