DR. WARD WHICKER, (CSU)

Plutonium Mobility in the Environment

Overview

Chemical, physical and biological processes control the movement of any contaminant within the environment. Chemical processes include the movement of soluble forms of plutonium from the soil through plant roots or into biological tissues (such as the lungs or gut). Physical processes can include wind and water erosion, as well mechanical movement, such as might occur when a vehicle drives across a contaminated roadway and resuspends soil particles. Finally, biological transport encompasses activity such as burrowing or grazing which can result in the redistribution of contaminated materials.

This paper briefly examines the factors that contribute to the movement of plutonium through the environment. It represents a brief overview of material that has been covered in depth in many other publications. Plutonium has been extensively studied for half a century. This paper attempts to present only those aspects of plutonium which are considered relevant to its environmental and biological behavior.

Plutonium the Element

Plutonium is element number 94 in the periodic table of the elements. It is considered part of the actinium series. Plutonium is not routinely found in nature, except under extremely rare circumstances. Instead, essentially all of the plutonium present on earth today can be attributed to human activities. It has several isotopes; all are radioactive. The most common ones are ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, and, ^{242}Pu. The chemistry of plutonium is complex, in that it has several valence states (Pu (III - VII); these can simultaneously exist in the same system.

Sources and Forms of Plutonium

Plutonium is produced in reactors through neutron capture reactions. When it is initially created it is surrounded by uranium fuel. Only after dissolution of the fuel and chemical extraction can the plutonium be purified and separated from other constituents. During the separation processes the plutonium may assume several chemical forms, including organic complexes, nitrates, oxides, or even pure metal. Once plutonium is separated and purified it may be used in several ways - as fuel for nuclear reactors, as thermo-electric generators for space craft, for research, or for nuclear weapons.

Plutonium that is found in the environment has come from several sources. The major source is from the detonation of atmospheric nuclear weapons - a practice that has largely been discontinued since the late 60s. Most of this plutonium released from nuclear weapons was presumed to have been as a high-fired oxide, due to the extreme temperatures present at the time of weapons detonation. There have also been localized

discharges to soil, water, and air from routine and accidental discharges at fuel processing and weapons manufacturing plants. Non-nuclear accidents resulting in the destruction of nuclear weapons, such as those which occurred in Palomares, Spain and Johnston Atoll, have also contributed to the presence of environmental plutonium. A small amount of plutonium (principally ^{238}Pu) has also been introduced into the atmosphere by the re-entry of satellites powered by plutonium-based electric generators. Table 1 lists the major sources and forms of plutonium in the environment.

Table 1. Plutonium compounds of potential interest (from IAEA, 1986 and Watters et. al., 1980)

Source	Form
Nuclear weapons testing	Oxide
Pu production, fuel fabrication, processing and extraction	Oxides, metal, nitrates, organic complexes
Non-nuclear destruction of weapons and satellites	Oxides, metal

Environmental Plutonium

The chemical form, or species, of plutonium found in the environment varies according to the source and the time since release (see Table 1). Its potential movement through the ecosystem depends on its initial solubility in surface waters, interstitial waters of soils and sediments, and in the biological fluids of the exposed organisms. The solubility is a function of the chemical and physical properties of the compound as well as the system into which it is deposited.

For example, fallout plutonium consists, in part, of oxides formed at high temperatures in the process of weapons detonation. A substantial portion of the fallout Pu (approximately 66%), however, was created through the activation of ^{238}U to produce ^{239}U with its subsequent chain decay through ^{239}Np to ^{239}Pu. Although this form of plutonium is also in oxide form, it appears to be more soluble than that created through high temperature effects on the original weapons material.

Once dissolved, plutonium is subject to the chemical reactions governing dissolved salts. Acidic forms entering the environment, on dilution, can be rapidly hydrolyzed and subsequently precipitated onto particle surfaces. Regardless of the form of plutonium initially deposited to soils, sediments, or water, it is largely converted to Pu(IV). This oxidation state is generally insoluble, and sorption of plutonium to soils and sediments results in its relative immobility in these media (Watters et. al, 1980).

Observations on the environmental behavior of plutonium show that the concentration in soils and sediments are typically greater than in water or other environmental media by orders of magnitude. Its tendency to form insoluble compounds typically results in

removal from aqueous systems (Katz et. al, 1986). More than 99% of the inventory in most terrestrial ecosystems is found in the soil, particularly in the soil surface.

Because it exists in a strongly-adsorbed state on surface soils, the primary route of transport in the environment is through the processes governing the distribution and movement of soil (Whicker and Schultz, 1982; Watters et al., 1980). The principal transport mechanisms for movement of soil are wind and water erosion. Wind has been identified as a major source of movement in agricultural ecosystems as well (Little et al, 1980; Little and Whicker, 1977; Pinder et al; 1990). As the surface soil mixes with deeper layers, wind erosion becomes less important as a distributive mechanism. However, other processes, such as uptake by plant roots, earth-worm activity, and even frost heaving, may increase in significance as the contamination moves into the root zone (Higley, 1999, Loch, 1982).

Plutonium Chemistry in Soils and Aqueous Systems

Plutonium exhibits multiple oxidation states, ranging from +3 to +7, four which can coexist in acidic aqueous systems. Plutonium has a high ionic charge, which means that it tends to undergo hydrolysis, leading to the formation of polymers in systems with pH>2. The chemistry of Pu in the soil system is dictated by pH, organic matter content, and mineralogy. For example, Nishita and Hamilton (1980) demonstrated that the solubility of Pu(IV) was dictated by the carbonated concentration in solution. In systems that contain no carbonate, the pH had to be raised to 8-10 to cause a corresponding increase in extractable plutonium. This was attributed to dissolution of alkali-soluble portions of organic matter. In general under acidic (pH<3) or alkaline (pH>7) conditions and with a high percentage of organic matter, plutonium becomes more mobile in a kaolinitic soils. With little organic content, raising the pH above 6 resulted in only the extraction of small amounts of material. In general, the association of plutonium in the soil is largely with the Fe-Mn oxides (~70-80%), a lesser amount (<10%) with the organic fraction of soil. The remainder (~20%) is in mineral lattice (Muller, 1978).

Plutonium in the Soil/Plant System

The downward movement in soil of plutonium is a relatively slow process (Bunzel et al., 1992; Muller, 1978). Several mechanisms have been proposed to account for this movement, including the chelation by naturally occurring soil organic constituents (Bondietti et al., 1976; Francis 1973), and by earthworms (Litaor, 19xx), and by extreme events (Higley, 1999). In long term field studies plutonium concentrations in soils remained relatively constant with depth over periods of several years. It is also known that plutonium is more mobile in coarser textured soils and less so in peats and mucks (Federov et al., 1986).

Plutonium Uptake by Plants

Several studies have been conducted on measuring the degree of Plutonium uptake by plants. Most of the work has focused on agriculturally significant crops. These studies examined uptake through surface deposition as well as root uptake. Pimpl and Schuttlelkopf (1981) conducted a literature review that detailed the magnitude of reported values of the concentration ratio (also called a transfer factor). This factor measures the ratio of activity in the plant to that in the surrounding soils. Values ranged from 10^{-9} to 10^{-3}, and depended on the soil type, the cation exchange capacity, and the soil pH.

Another factor that was found to determine the magnitude of the concentration ratio was whether the original source was from atmospheric deposition onto plant surfaces or from root uptake. In one study of winter wheat (*Triticum aestivum*), it was reported that 70 percent of the contamination of grain was due directly to redeposition of contaminated dust during harvesting (McLeod et al., 1980). In a later study the same author determined that varying cropping rotations and liming the same contaminated soil resulted in decreased assimilation of plutonium by all crops.

Plutonium Uptake by Animals

Plutonium is not a biologically essential element, nor does it serve as an analogue for any other essential element. Consequently, its uptake into animals (and plants as well) is considered largely opportunistic. Analyses of animals exposed to plutonium contaminated soils and vegetation have shown that the bulk of the plutonium resides in those tissues or organs directly exposed; e.g., pelts or skin, lungs, and gastrointestinal tracts (Bradley et al, 1977; Little, 1976). The absorption of plutonium into the gut of an animal requires that it be present in a soluble form.

Pu in soils at the Rocky Flats Environmental Technology Site

Comparisons have been made as to the mobility and bioavailability of plutonium at RFETS relative to other locales. For example, the plutonium at RFETS was found to be more insoluble than that from sites at the Oak Ridge Plant, located near Oak Ridge, Tennessee, or Mound Laboratories, located near Miamisburg, Ohio, but similar to that from the Nevada Test Site (NTS) near Las Vegas Nevada (Bondietti and Taumra, 1980). The solubility differences were attributed to the original source of material - metallic plutonium at the NTS and RFETS sites, and a soluble form at the Oak Ridge and Mound locations. Their study highlighted the inherent problem of trying to compare the environmental behavior of plutonium across locations without knowing the chemical form of the source material.

Previous work on the distribution of Pu in the ecosystems of RFETS indicated >99% of the contaminants were associated with soil particles (Little, 1976, Tamura, 1977; Langer,

1986). This behavior is consistent with the soil type of the RFETS which, although variable across the site, largely consists of Denver Kutch clay loams with montmorillonitic clays.

Conclusion

The nature of the source of release of plutonium is important in dictating its initial deposition and distribution. However, over time, environmental processes which include physical, chemical and biologic activity can alter the composition and distribution. Regardless of the origin, soils and sediments become the ultimate repository for the majority of plutonium. Even though the soils and sediments represent a reservoir of plutonium, chemical and biological processes cause only a small fraction of it to be released as soluble species into the environment. While plutonium is incorporated into plant and animal tissues, the concentrations are typically orders of magnitude less than found in the soils and sediments. Biomagnification of plutonium (concentration from one trophic level to the next) does not occur, with very minor exceptions.

References

Bradley, W.G., Moor, K.S.; and Naegle, S.R.; Plutonium and other transuranics in small vertebrates: A review, in Transuranics in Natural Environments, Symposium proceedings, Gatlingurg, Tenn, Oct 5-7, 1976, ERDA Report NVO-178, pp. 385-406, Nevada Operations Office, NTIS.

Bondietti, E.A., S.A. Reynolds and M.H. Shanks. 1976. Interaction of plutonium with complexing substances in soils and natural waters. IAEA-SM-199/51. p. 273-287.

Bondietti, E.A.; Tamura, T. Physicochemical associations of plutonium and other actinides in soils. In: Transuranic elements in the environment. U.S. Department of Energy, National Technical Information Service; DOE/TIC-22800; 145-164; 1980.

Bunzl, K., W. Kracke and W. Schimmack. 1992. Vertical migration of plutonium-239 + -240, americium-241 and cesium-137 fallout in a forest soil under spruce. Analyst. 117:469-474.

Federov, Ye. A., A.S. Bakurov, M.N. Fedorova and F. Rasulev. 1986. Behavior of plutonium in the soil and its entry into plants. Agrokhimiya. 12:83-88.

Francis, C.W. 1973. Plutonium mobility in soils and uptake by plants: a review. J. Environ. Qual. 2(1):67-70.

Higley, K.A., "*Modeling Intermittent Processes in Radionuclide Migration in Soil Systems*" I. Linkov and W.R. Schell (ed's), Contaminated Forests, Kluwer Academic Publishers. 1999. Printed in the Netherlands. Pps 231-238.

International Commission on Radiological Protection. The metabolism of plutonium and related elements. Oxford, Pergamon Press. ICRP Publication 48, 1986.

Katz, J.J; Morss, L.R.; Seaborg, G.T. Summary and comparative aspects of the actinide elements. In: Katz, J.J.; Seaborg, G.T.; Morss, L.R.; The chemistry of the actinide elements. Second edition. Chapman and Hall, London. 1986: Ch. 14:1121-1195.

Langer,G. Dust transport - wind blown and mechanical resuspension, July 1983 to December 1984. Rockwell International; RFP-3914; 1986.

Little, C.A. and F.W. Whicker. 1977. Plutonium distribution in Rocky Flats soil. Health Physics. 34:451-457.

Little, C.A., F.W. Whicker and T.F. Winson. 1980. Plutonium in a grassland ecosystem at Rocky Flats. J. Environ. Qual. 9(3):350-354.

(Litaor, 19xx), Health Physics

Loch, J.P.G. State of the art report - frost heaving actions in soils. In: Developments in geotechnical engineering vol 28: ground freezing, 1980. Selected papers of the Second International Symposium on Ground Freezing; held in Trondheim, June 24; 226, 1980. Elsevier Scientific Publishing Company, Amsterdam, 1982:213-224.

McLeod, K.W., D.C. Adriano, A.L. Boni, J.C. Corey, J. H. Horton, D. Paine and J.E. Pinder III. 1980. Influence of a nuclear fuel chemical separations facility on the plutonium contents of a wheat crop. J. Environ. Qual. 9(2):306-615.

Muller, R.N. 1978. Chemical characterization of local and stratospheric plutonium in Ohio soils. Soil Sci. 125(3)131-136.

Nishita, H. and M. Hamilton. 1980. The influence of several soil components and their interaction on plutonium extractability from a calcareous soil. Soil Sci. 13(1):56-59.

Pimpl, M. and H. Schüttelkopf. 1981. Transport of plutonium, americium, and curium from soils into plants by root uptake. Nuclear Safety. 22: 214-225.

Pinder, J. E. III, K.W. McLeod, D.C. Adriano, J.C. Corey and A.L. Boni. 1990. Atmospheric deposition, resuspension and root uptake of Pu in corn and other grain producing agroecosystems near a nuclear fuel facility. Health Physics. 59(6):853-867.

Tamura, T. Effect of pretreatment on the size distribution of plutonium in surface soil from Rocky Flats. In: Transuranics in Desert Ecosystems; Nevada Applied Ecology Group. NVO-1871 UC-11; 173-186-1977.

Watters, R.L.; Edgington, D.N.; Hakonson, T.E.' Hanson, W.C.; Smith, M.H.; Whicker, F.W.; Wildung, R.E., Synthesis of the research literature. In: Hanson, W.C., ed., Transuranic elements in the environment. U.S. Department of Energy/ National Technical Information Service; DOE/TIC-22800; 1980:1-44.

Whicker, F.W.; Schultz, V. Radioecology: nuclear energy and the environment. Boca Raton, Fl: CRC Press, INC.; 1982 (2 vol).