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Environmental Chemistry of Plutonium

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Plutonium Handbook

24. ENVIRONMENTAL CHEMISTRY OF PLUTONIUM

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Table of Contents (auto-generated and paginated at layout stage)

1. INTRODUCTION

This chapter discusses key aspects related to the assessment of the environmental impact of plutonium, such as sources, speciation, and underlying processes important for ecosystem transfer, mobility, and bioavailability. Plutonium released into the environment can be present in different physico-chemical forms, varying from simple ions to complexed species to colloids, particles, and even fragments. Master variables, such as pH, redox conditions, and the presence of inorganic and organic ligands and surfaces, can change the speciation over time and thereby influence the eco- and geosystem behavior of plutonium.

Individual sections provide an overview of present knowledge on nuclear sources and historical events that have contributed to the release of plutonium into the environment and deal with plutonium behavior in the eco- and geosphere. For contaminated sites, remediation approaches are also discussed. Plutonium behavior in subsoil (geosphere) is of great interest in the context of nuclear waste disposal, and potential releases from nuclear waste forms are described. Investigating natural analogue sites, such as the natural reactor at Oklo, can also provide valuable insight into the long-term geochemical behavior of plutonium.

Since the first explosion of a nuclear weapon device in 1945, plutonium has been distributed into the environment on a global scale and can be identified in water, vegetation, soils, sediments, rock, and glacial ice. With the advent of the nuclear age, the global inventory of plutonium on earth has increased by a factor of approximately 10^6. Geoscientists have therefore proposed using the characteristic pattern of plutonium isotopes as a radiogenic indicator, among others, for the clearly visible human technological impact on nature defining a new geological epoch: the "Anthropocene."[1, 2]

The environmental behavior of plutonium is characterized by a broad complexity in chemical species occurring in different environmental compartments (air, water, soil, subsoil, geosphere); these species vary as a function of chemical and geochemical boundary conditions. Notably, transition within different redox states, sorption processes, colloid formation, interaction with inorganic and organic particles, and establishment of a multiplicity of complex species impairs the prediction of plutonium mobility and bioavailability in environmental systems. Because plutonium is a refractory element, a large fraction released into the environment from nuclear events, such as nuclear weapons tests and reactor accidents, is associated with particles ranging in size from submicron particles to fragments. Thus, information on plutonium particle characteristics, including weathering rates, is essential for evaluating the environmental behavior of plutonium in particle-affected areas.

Existing literature on issues related to the environmental chemistry of plutonium is extensive and could not be considered in an all-encompassing manner here. The present overview is based on available literature that is considered up to date and reliable (e.g., UNSCEAR reports). Due to extensive research ongoing at many contaminated sites, however, new information is expected to become available in the years to come.

2. GENERAL ASPECTS OF ENVIRONMENTAL PLUTONIUM CHEMISTRY

In the past few decades, there has been increased interest in plutonium environmental chemistry (e.g., see various chapters in Ref. 3). Several important reviews have recently been published summarizing the environmental chemistry aspects of plutonium.[4, 5] Actinide (including plutonium) aquatic chemistry,[6] mineral–water interface reactions,[7, 8] interaction with microbes,[9-11] and plutonium association with particles[12] are summarized in reviews or other chapters in this handbook (e.g. Chapter 21, "Aqueous Solution and Coordination Chemistry", and Chapter 25, "Plutonium Microbial Interactions in the Environment").

According to the International Union of Pure and Applied Chemistry (IUPAC),[13] chemical species of an element are "defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure". Plutonium released from a source can be present in different physico-chemical forms, ranging in nominal molecular mass from simple ions and molecules to colloids or nanoparticles, pseudocolloids, particles, and even fragments (Figure 1). The systems are dynamic, the transitions between categories are gradual, and over time a series of transformation processes can change plutonium species originally deposited in the environment. Growth mechanisms, such as hydrolysis, complexation, and aggregation, increase the nominal molecular mass of low-molecular-mass (LMM) species, reducing the mobility, whereas desorption, dissolution, and dispersion processes (e.g., weathering of radioactive particles) mobilize LMM species from high-molecular-mass (HMM) species or particles.[14, 15] LMM species are believed to be mobile and potentially bioavailable, whereas HMM species are more inert.[5, 13]

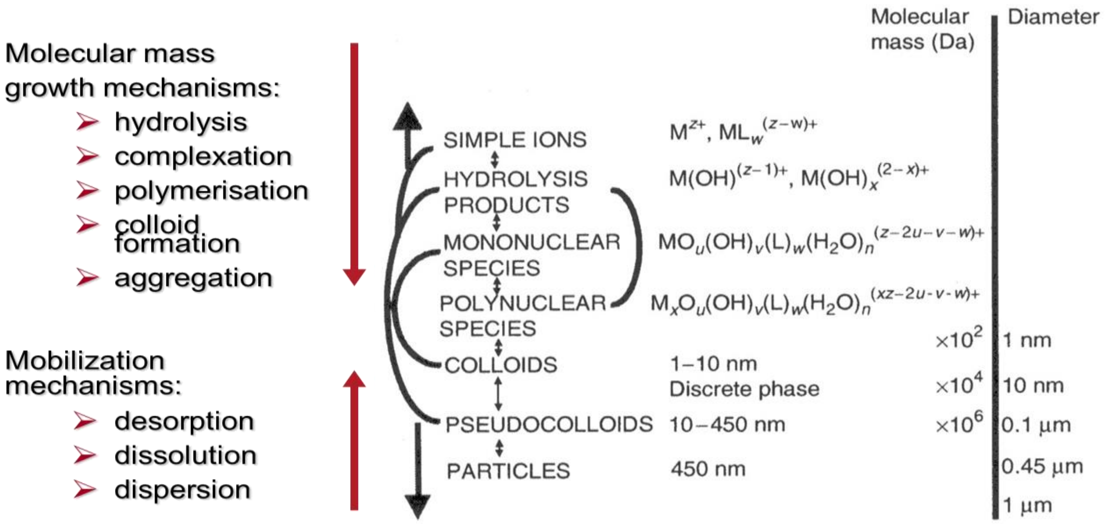


Figure 1. Radionuclides, such as plutonium, can be present in different physicochemical forms and sizes, ranging from simple ions to particles and fragments.[16]

Natural systems, such as soils and sediments, are characterized by complex composition, heterogeneity, and chemical gradients. Because of interactions and transformation processes, the speciation of plutonium originally deposited in an ecosystem can vary in time and space.

2.1 The K_d Value as an Empirical Indicator for Plutonium Mobility in Environmental Compartments

Often, empirical parameters, such as the solid–liquid distribution coefficient, K_d, are utilized to assess plutonium mobility. However, as already mentioned, the environmental behavior strongly depends on certain key parameters that may change within a heterogeneous environmental compartment: redox conditions, pH, presence of complexing ligands such as CO_3^{2-} and organic complexants, colloidal and particulate matter, the nature of solid surfaces, and the action of biota. Thus, more mechanistic approaches that explicitly address the plutonium speciation, solubility, complexation, and ion-exchange processes in environmentally relevant conditions are needed.[12, 15-17] Transfer coefficient K_d (L/kg or mL/g) values refer to reversible processes and assume that equilibrium conditions have been established in the ecosystem under consideration. As the actual plutonium speciation is not taken into account, the K_d coefficient based on bulk samples (Bq/kg per Bq/L) represents an indicator providing only a rough estimate of plutonium environmental behaviour at a given observation time. For most radionuclides, including plutonium, published K_d values, therefore, vary by orders of magnitude (e.g., Ref. 18), as seen in Tables 1 and 2, and uncertainties associated with K_d-based environmental assessments are also large.

Table 1. K_d values (in mL/g) for Plutonium in Soils Grouped According to Texture/Organic Matter.[18]

Soil group	Geometric mean	Minimum	Maximum
All soils	7.4×10^2	3.2×10^1	9.6×10^3
Sand	4.0×10^2	3.3×10^1	6.9×10^3
Loam + clay	1.1×10^3	1.0×10^2	9.6×10^3
Organic	7.6×10^2	9.0×10^1	3.0×10^3

Table 2. K_d values (in mL/g) for Plutonium in Freshwater Ecosystems.[18]

Data origin	Geometric mean	Minimum	Maximum
Labs[a]	7.9×10^4	2.1×10^4	2.9×10^5
Labs[b]	3.0×10^5	2.9×10^4	3.2×10^6
Field	2.4×10^5	1.1×10^4	5.2×10^6

[a] Laboratory adsorption experiments; [b] Laboratory desorption experiments.

Field-derived K_d values are usually based on total activity concentrations in soils/sediments and unfiltered water. If particle-bound plutonium is retained in soils, the apparent K_d can be extremely high. However, the assumption of equilibrium conditions is not always valid, and the apparent K_d can decrease over time as e.g. particle weathering occurs. Time-dependent solid–liquid partitioning is also observed in laboratory experiments in which well-defined plutonium tracer solutions have been used. [19] This became apparent when Pu(III,IV) aquo ions, Pu(III,IV) citrate, Pu(III,IV) ethylenediamine tetraacetic acid (EDTA), and Pu(V,VI) aquo ions added to Mayak soil–water mixtures.[15] As seen in Figure 2, Pu(III,IV) is especially surface-reactive with a low mobility (high K_d), whereas Pu(V,VI) and plutonium associated with organics are rather mobile (low K_d). In this case, the K_d clearly depends on radionuclide speciation. Additionally, it is well known that the K_d depends on the soil type, in particular the organic material content and pH.[18] These examples clearly demonstrate that empirical K_d values are useful for screening purposes, but that they capture neither the role of contaminant speciation variations nor the dynamics of processes controlling transfer. Thus, K_d values should be considered as variable with time and geochemical conditions rather than as constant.[20]

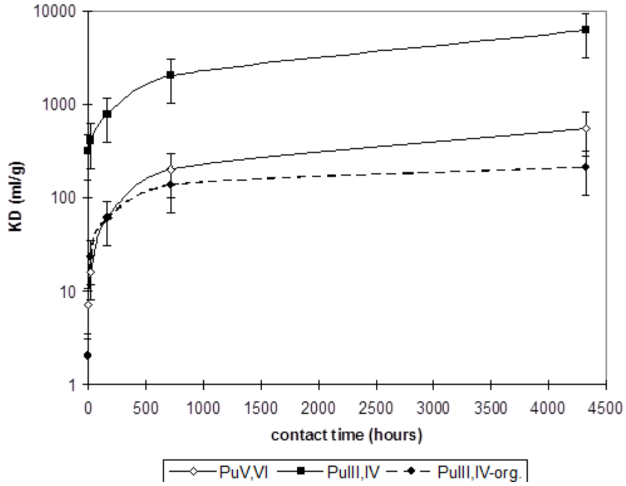


Figure 2. K_d (ml/g) as a function of contact time for Pu(V,VI), Pu(III,IV) ionic/colloidal, and Pu(III,IV) organic complexes in a Mayak PA Resservoir 10 sediment–seawater system (Reprinted from Ref. 15 with permission).

2.2 Redox Reactions

Geochemical parameters, notably Eh and pH, have a tremendous impact on aquatic plutonium chemistry and thus on environmental behavior. Figure 3 shows an Eh/pH diagram containing predominant aqueous plutonium species in solution. Solubility, strength of complexation with inorganic and organic ligands, and therefore mobility as well as bioavailability strongly depend on redox state. Although Pu(III) and Pu(IV) can exist as complexes of the respective Pu^{3+} and Pu^{4+} aquo ions under natural conditions, Pu(V) and Pu(VI) occur as linear trans-dioxo plutonyl cations

PuO_2^+ and PuO_2^{2+} in all of their complexes.[21] Constants for redox equilibria are given in Table 3, and the corresponding redox potentials are provided in Table 4.[22]

Table 3. Plutonium Redox Equilibria.[22]

Redox reaction	Log K ($I = 0$)
$PuO_2^{2+} + e^- \rightleftarrows PuO_2^+$	15.82
$PuO_2^{2+} + 4\,H^+ + 2e^- \rightleftarrows Pu^{4+} + 2H_2O$	33.27
$PuO_2^+ + 4\,H^+ + e^- \rightleftarrows Pu^{4+} + 2H_2O$	17.45
$Pu^{4+} + e^- \rightleftarrows Pu^{3+}$	17.69

Table 4. Electrochemical Potentials (Eh, V) for Plutonium Redox Couples[5,23] versus the Standard Hydrogen Electrode

Redox couple	Acidic	Neutral	Alkaline
Pu(IV)/Pu(III)	+0.982	−0.39	−0.96
Pu(V)/Pu(IV)	+1.170	+0.70	−0.67 + 0.52[a]
Pu(VI)/Pu(V)	+0.913	+0.6	+0.12
Pu(VI)/Pu(IV)	+1.043	+0.65	+0.34
Pu(V)/Pu(III)	—	+1.076	—
Pu(VII)/Pu(VI)	—	—	+0.85
Pu(V)/Pu(IV)	+1.17	—	—

[a] Oxidation potential.

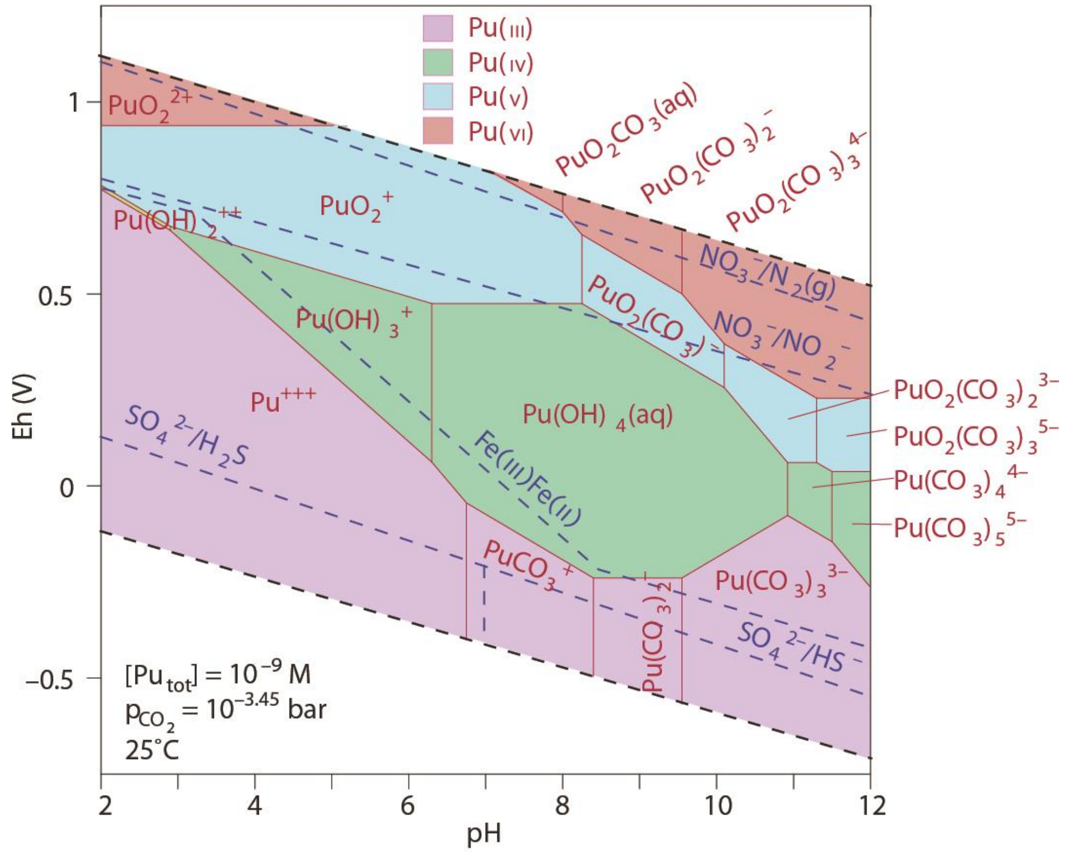


Figure 3. Predominance domains of the major plutonium aqueous species are shown as a function of Eh and pH. Colors represent the different oxidation states. Dashed lines indicate redox borderlines for most relevant environmental redox buffers (Reprinted by permission from Macmillan Publishers Ltd: Nature Materials, (Ref. 24), copyright (2015))

The oxidation state of plutonium species controls the solubility of solid phases, aqueous complexation, sorption to mineral surfaces, and colloid formation. Figure 3 clearly shows that Pu(IV) species predominate under a wide range of relevant Eh/pH conditions. These species are generally considered less mobile and less bioavailable than other oxidation states because of their low solubility and strong sorption property. Reduction to Pu(III) under reducing conditions typical of deep groundwater or oxidation to PuO_2^+ in oxygenated surface waters in the intermediate pH region and to PuO_2^{2+} at high pH generally leads to increased solubility and weaker sorption of plutonium to available surfaces.

Redox transformations play an important role in the fate of plutonium in soils and sediments. For instance, particulate plutonium species are observed in the mud patch in the Irish Sea outside the Windscale/Sellafield site in the United Kingdom. It is assumed that plutonium was deposited in the mud patch since the early 1950s as Pu(III,IV) and plutonium associated with particles. During the last decades, plutonium has been remobilized from the contaminated sediments, probably because of oxidation of plutonium to more mobile Pu(V,VI) species (access to O_2-rich water during storm events) or interactions with organics. Thus, the presently observed transport of plutonium into the North Sea is attributed to remobilization from the contaminated mud patch acting as a diffuse source and not to reprocessing activities at Sellafield.[25-27]

2.3 Complexation Reactions

The strength of complexation with ligands in homogeneous solution, and of surface complexation at mineral surfaces, usually increases with the effective charge of the plutonium cation (i.e., in the order $\mathrm{Pu(V)O_2^+} < \mathrm{Pu(VI)O_2^{2+}} \sim \mathrm{Pu(III)^{3+}} < \mathrm{Pu(IV)^{4+}}$). The most relevant inorganic ligands in aqueous solutions are hydroxide and carbonate. Pu(III/IV) forms cationic hydroxo complexes $[\mathrm{Pu(OH)}_x]^{3-x}/[\mathrm{Pu(OH)}_y]^{4-y}$ and at elevated pH non-charged $\mathrm{Pu(OH)_3/Pu(OH)_4}$ species with very limited solubility. Penta- and hexavalent plutonium can form anionic hydroxo species, leading to increased solubilities at high pH. Formation of anionic carbonates or mixed hydroxo carbonate complexes (e.g., $\mathrm{Pu(OH)_2(CO_3)_2^{2-}}$)[28] in carbonate-rich water increases Pu(IV) solubility and mobility. Recent studies have demonstrated that under certain conditions actinide hydroxide and carbonate complexes can also be stabilized by formation of ternary complexes with $\mathrm{Mg^{2+}}$ and $\mathrm{Ca^{2+}}$, thereby enhancing the solubility of all actinide redox species.[6, 29, 30]

Naturally abundant organic complexants can be classified as small carboxylic acids, macromolecular humic or fulvic acids (HAs/FAs), or siderophores. These ligands are produced as degradation products of plants and other organisms or as microbial exudates. As hard Lewis acids, plutonium species usually coordinate to hard Lewis bases, such as oxygen-donor ligands (e.g., carboxylate groups). All microbial reactions with plutonium and their products are discussed in a separate chapter in this handbook (Chapter 25, “Plutonium Microbial Interactions in the Environment”). Complexation with small organic ligands can be relatively weak, as with acetic or propionic acid that is found, for example, in pore waters of clay rock. Stable complexes form with chelating ligands, such as αhydroxy carboxylic acids (e.g., isosaccharinic acid as cellulose degradation product, hydroxamic acid belonging to the microbial exudates group of siderophores, or HA/FA).

HAs/FAs are abundant in soil, peat, lignite, and all kinds of natural aquatic systems. Plutonium in the environment is found in many places to be associated with degradation products of flora and fauna (e.g., in the Chernobyl area,[31-33] in the case of remobilized plutonium from contaminated soil,[34] for plutonium released from nuclear reprocessing plants,[35, 36] in nearshore sediments and coastal soils,[37] in soil after weathering of plutonium particles released by the atomic bomb explosion in Nagasaki,[38] in groundwater close to nuclear weapon test sites,[39] during mobilization of fallout plutonium in sandy aquifers,[40] and in forest soil [32]). Binding to humic matter can contribute to both mobilization and immobilization of plutonium depending on whether the HAs/FAs are associated with the solid phase or are colloidally dispersed in water.

Humic substances can act as scavengers and serve as pseudo-colloidal carriers for most metals in freshwater systems.[41] Modes of interaction of plutonium ions with HAs/FAs can be manyfold (Table 5),[42] including complexation, redox reactions, and colloid formation. HAs/FAs do not exhibit a discrete stoichiometric composition, but rather consist of a range of chemical compositions, depending on their origin. Nevertheless, geochemical approaches exist to estimate metal-ion-complex speciation in aqueous systems containing HAs/FAs. Models vary widely with regard to accounting for the heterogeneity of humic/fulvic functional groups, their colloidal nature, and their affinity toward cations as a function of geochemical conditions.[43-46] A detailed discussion on model concepts and their strengths and drawbacks is available from Ref. 42. Notable open questions relate to the type of Pu(IV) complexation to HAs/FAs. Pu(IV) is in general considered as poorly soluble and rather immobile. The potential mobilization by HA/FA is thus of notable interest. Usually carboxylate groups, and to a lesser extent phenolic groups, are assumed as binding ligand entities. In addition to binary complexes, under relevant pH conditions, the derived complexation constants also suggest the formation of ternary complex species, such as $\mathrm{Pu(IV)(OH)}_x\mathrm{HA/FA}$ (e.g., see Refs. [47-50]). Pu(III) and notably Pu(IV) HA/FA complexes are characterized by a remarkable kinetic stability, and dissociation might be very slow.

Redox-active entities in natural HAs/FAs, such as hydroquinone groups or humic-/fulvic-bound Fe(II), can reduce the higher oxidation states Pu(V) and Pu(VI) to Pu(IV) or Pu(III). Upon reduction of oxidized plutonium species at elevated total plutonium concentrations, solubility limits of Pu(IV) species can be exceeded and hydrated PuO_2 nanoparticulate oxide species can form. By forming coatings at colloid surfaces, organic matter can contribute significantly to the colloidal stabilization of such species (see references in Table 6). Organic matter being immobilized at mineral surfaces can in principle interact with plutonium species in the same way. Ongoing discussions deal with metal ion partitioning between mineral surfaces, organic coating on mineral surfaces, and dissolved organic matter (DOM). Notably, in soil, the interaction mechanisms of organic matter, plutonium, and mineral surfaces are very relevant. The kinetics of sorption/desorption and surface speciation strongly depends on the nature of the organic matter (e.g., HAs/FAs, siderophores). Kinetic effects apparently play a dominant role in many experimental laboratory studies, leading to the observation that, for example, the metal ion, HA, and mineral addition/mixing sequence determines the final distribution of the metal ion between solid and aqueous phases.[51, 52] Another issue involves understanding the selective sorption of specific HA fractions to mineral surfaces; these HA coated surfaces exhibit different binding strengths to plutonium and thus change plutonium partitioning. Finally, uncertainties regarding the exact nature of metal ion binding to the HAs/FAs exist. It is not always clear whether plutonium forms surface complexes with the mineral surface, binds to the adsorbed HAs/FAs, or forms ternary mineral–plutonium–humic complexes.

2.4 Colloid Formation and Migration

Colloidal plutonium species have been identified in effluents from nuclear installations (e.g., Sellafield, United Kingdom), in contaminated reservoirs of the Techa River; in groundwaters at Mayak PA in the Ural mountains, in waters within the Chernobyl 30-km exclusion zone; in the Ob and Yenisey Rivers, including their estuaries; and in seawater contaminated by nuclear waste dumping.[53-56] Colloidal species can include intrinsic Pu colloids, organic macromolecular complexes, and inorganic colloid associations. The nature of the colloidal species will impact the overall migration behavior of plutonium.

The slow and inhibited plutonium dissociation from plutonium–humate/fulvate complexes mentioned above is possibly due to conformational changes in the organic complex upon metal–ion complexation. This may explain the finding that HA-/FA-mediated colloidal actinide transport in natural water can take place, even in diffusion-controlled aquitards, such as clay rock.[57, 58] However, HAs with molecular masses up to 20 kDa or hydrodynamic radii up to 2.8 nm are assumed to be retained because of physical filtration in nanoporous media, such as Boom clay.[59] In advective flow systems in porous media, fractured rock, or surface water, HAs can play an important role as a colloidal carrier for plutonium transport (e.g., see Ref. 60).

In the absence of organic colloidal matter, inorganic colloids, such as iron oxyhydroxides and clay particles, may also contribute to Pu(IV) mobilization (see Table 6). Moreover, plutonium in the tetravalent state is well known to form polynuclear and colloidal nanoparticulate oxy/hydroxo species.[61] The role of these species in plutonium mobility in environmental systems has been the subject of considerable debate. For example, plutonium oxyhydroxide nanoparticles have been found to be colloidally stable over a wide range of geochemical conditions, even at elevated ionic strength, but dissolve as soon as the total plutonium concentration falls below solubility limits.[62] Alternatively, plutonium oxyhydroxide nanoparticles have also been observed to behave as more or less chemically inert colloids over a wide range of chemical conditions. In the latter case, they contribute to plutonium mobilization.[63, 64] The observation of different plutonium oxyhydroxide colloid behavior arises from different generation/synthesis modes: the high crystallinity of $[Pu_{38}O_{56}]^{40+}$ nanoparticles[63] may lead to high stability (as is known to occur for high-fired hydrophobic plutonium oxide), whereas hydrophilic particles with surficial amorphous and hydroxidic composition are usually more reactive. Thus, colloidal transport behavior depends significantly on the plutonium nanoparticle source and release conditions. Colloidal transport of plutonium is observed at many contaminated sites, influencing the ecosystem transfer.

Table 5. Plutonium Interaction Modes with Humic Matter

System	Reaction	Reference(s)
HA solution, natural groundwater; $[Pu]_{tot} = 10^{-10}$–10^{-3} M; pH = 1–8	Pu(V,VI) reduction and Pu(III) oxidation to Pu(IV)	[65, 66, 67, 68, 69]
HA solution, natural groundwater; $[Pu]_{tot} = 10^{-3}$ M; pH = 1–7	Pu(IV) oxyhydroxide colloid formation with humic coating	[67]
HA solution or chemically immobilized at silica; $[Pu]_{tot}$ = ~10^{-8}–10^{-7} M; pH ≤ 4	Complex formation with proposed speciation: Pu(IV)–HA, $(Pu_4(OH_8))$–HA, $Pu(OH)_3$–HA, $Pu(OH)_2$–HA	[48, 49, 70, 71]
HA solution; $[Pu]_{tot} = 10^{-3}$ M; pH = 1	Complex formation: Pu(III)–HA	[72]
Humic matter bound to mineral surfaces in contact with HA-/FA-containing solutions	Formation of ternary surface complexes; plutonium partitioning between aqueous solution and solid depends on redox conditions and pH	Kaolinite,[73,74] γ-alumina or amorphous silica,[75]

		goethite,[51] montmorillonite[52]

Note: FA = fulvic acid; HA = humic acid.

Table 6. Examples of Colloidal Plutonium Transport (modified from Kersting et al.[4])

Plutonium-containing colloid type	Environmental medium	Reference(s)
Debris of nuclear weapon test site	Aquifer (pH=8.4, $I = 10^{-3}$ M): Nevada Test Site, United States	[76]
Colloids of amorphous iron oxyhydroxides	Surface/shallow groundwater: Mayak PA site, Lake Karachay, Russia	[77]
Colloids in effluents	Effluent from Sellafield, United Kingdom	[54]
Organic + mineral colloids + plutonium oxyhydroxide colloids	Surface soil and surface water at a contaminated site: Rocky Flats Plant, United States	[34, 78]
Groundwater colloids	Savannah River; US Department of Energy Hanford site	[79, 80]
Colloids released to the environment (in general)	Marine/surface water environment	[81]
Colloids in Ob and Yenisey estuaries	River and estuary water; isotope ratio reflecting weapons-grade origin	[56]
Colloids in river water	Rhône River, France	[82]
Clay mineral colloids	Meteoric-type groundwater; in situ experiments at the underground rock laboratory at the Grimsel Test Site, Switzerland	[83, 84]
Colloids in seawater	Arctic Sea, Gulf of Lion	[56, 54, 82]

2.5 Sorption to Mineral Surfaces

Modes of plutonium interaction with mineral surfaces strongly depend on the oxidation state and the type of mineral.[7, 8] Clay minerals, for instance, possess permanently charged basal planes because of isomorphic substitution of aluminum or silicon in tetrahedral silica and octahedral alumina layers. As a consequence, physisorption (outer-sphere sorption, ion exchange) dominates for tri-, penta-, and hexavalent actinide ions at low pH and low ionic strength. Inner-sphere surface complexation with mainly SiOH and AlOH functional groups at clay mineral edge sites predominates at intermediate to high pH. The affinity of Pu(IV) for hydroxide in solution and for mineral hydroxyl groups is so strong that outer-sphere sorption of the Pu^{4+} aquo ion becomes irrelevant. [85] Of all the plutonium oxidation states, Pu(IV) has been found to form the most stable inner-sphere surface complexes and therefore is predominantly found adsorbed at mineral surfaces. The Pu(III) species also forms strong inner-sphere surface complexes, although they are somewhat weaker than those of Pu(IV), at least in the pH region <6 (e.g., see Figure 4b). Pu(VI) and Pu(V) usually are not detected at mineral surfaces at environmentally relevant pH ranges because they are mostly redox-unstable under these conditions and reduction to Pu(IV) and Pu(III) occurs. Other oxide minerals (iron oxides, quartz, etc.) also offer hydroxyl groups, such as SiOH, FeOH, and TiOH, that can lead to inner-sphere surface complexation of plutonium (chemisorption) (Table 7).

Recent investigations have clearly shown that minerals are not chemically inert and that surface sorption reactions are not limited to purely outer-/inner-sphere reactions. As a redox-active metal ion, plutonium can undergo various types of surface-induced surface sorption processes, depending on the presence of redox-active Fe(II/III) or Mn(II/IV) in the mineral and the redox conditions in the mineral/water system.[86-88] The high thermodynamic stability of Pu(IV) surface complexes can induce a shift of the redox transition borderline (Figure 4), and under certain conditions surface-induced redox reactions take place even in the absence of redox-active mineral components.

Moreover, actinide surface precipitation, incorporation into the solid, or solid solution formation (e.g., at calcite, aragonite, and apatite surfaces) can also occur and have been observed experimentally for trivalent actinide ions spectroscopically (e.g., see Ref. 8 and references therein). Studies at the Oklo natural analogue site support the idea that coprecipitation or incorporation reactions might be very relevant for plutonium in the geosphere.[89] Evidence for extinct plutonium can be found for instance in apatite samples taken from the site, indicated by an enriched ^{235}U/^{238}U isotopic ratio in the mineral due to ^{239}Pu decay to ^{235}U.

Table 7. Selected Examples of Mineral Surface Reactions of Plutonium Studied in Recent Laboratory Experiments

Initial plutonium form	Redox conditions/ mineral	Sorption mechanism	Reference(s)
Pu(V)/Pu(IV) (10^{-11}–10^{-6} M)	Aerobic conditions/ montmorillonite	Slow surface-induced reduction in the case of Pu(V) to Pu(IV)	[90]
Pu(V) (10^{-11} M)	Lysimeter studies using sandy soil (pH = 4.5–6)	Partial reduction to Pu(IV) being retained at the solid phase	[91]
85 % Pu(IV), 11 % Pu(V), 4 % Pu(III) (10^{-11}–10^{-8} M)	Slightly reducing/ Na-illite	Redox state of surface-complexed plutonium depends on measured Eh	[88]
Pu(IV) (7×10^{-9} to 3.5×10^{-7} M)	Anaerobic and aerobic conditions/kaolinite	Redox state of surface-complexed plutonium depends on measured Eh	[92]
Pu(VI) (1.5×10^{-4} M)	Aerobic conditions/ hematite nanoparticles	Surface-mediated reduction (ATR-IR in situ study)	[93]
PuO_2 colloids (1–1000 nm size; 1.4×10^{-4} M)/Pu(IV) (10^{-11}–10^{-6} M)	Goethite	Surface sorption at $<10^{-7}$ M Pu(IV); surface precipitation of Pu(IV) at $>10^{-7}$ M (as Pu_4O_7); weak sorption of PuO_2 colloids	[94]
PuO_2 colloids (2–5 nm	Aerobic conditions (pH =	Isotactic growth of Pu_4O_7 at goethite	[95]

size; 1.4 × 10^{-6} M)/ Pu(IV) (7 × 10^{-6} M)	7)/quartz, goethite	surface; PuO_2 structure remains at quartz surface	
Pu(III)/$[Pu_{38}O_{56}]^{40+}$ nanoparticles (10^{-4} M)	Aerobic conditions (pH = 2.4–2.6)/muscovite	Surface-enhanced oxidation/polymerization of Pu(III); surface sorption of Pu(IV) oxide nanoparticles	[96, 97]
Pu(V)/Pu(VI) (10^{-14}–10^{-9}/10^{-6} M)	N_2 atmosphere and aerobic conditions (pH = 1–7)/ hematite	Surface-mediated reduction to Pu(IV); formation of PuO_{2+x} x nH_2O at $[Pu]_{tot} > 10^{-9}$ M	[87, 98]
Pu(V)/Pu(VI) (4 × 10^{-8} M)	Aerobic conditions (pH = 3, 5, 7)/quartz	Surface-mediated reduction to Pu(IV) irrespective of specific activity (no radiolysis effect)	[86]
Pu(V)/Pu(III) (10^{-5} M)	Reducing anoxic conditions (pH = 6–8)/ magnetite, chukanowite, mackinawite	Surface-adsorbed Pu(III) and Pu(IV) depending on Eh/pH conditions; surface precipitation of PuO_2 nanoparticles	[99]

Note: ATR = attenuated total reflection.

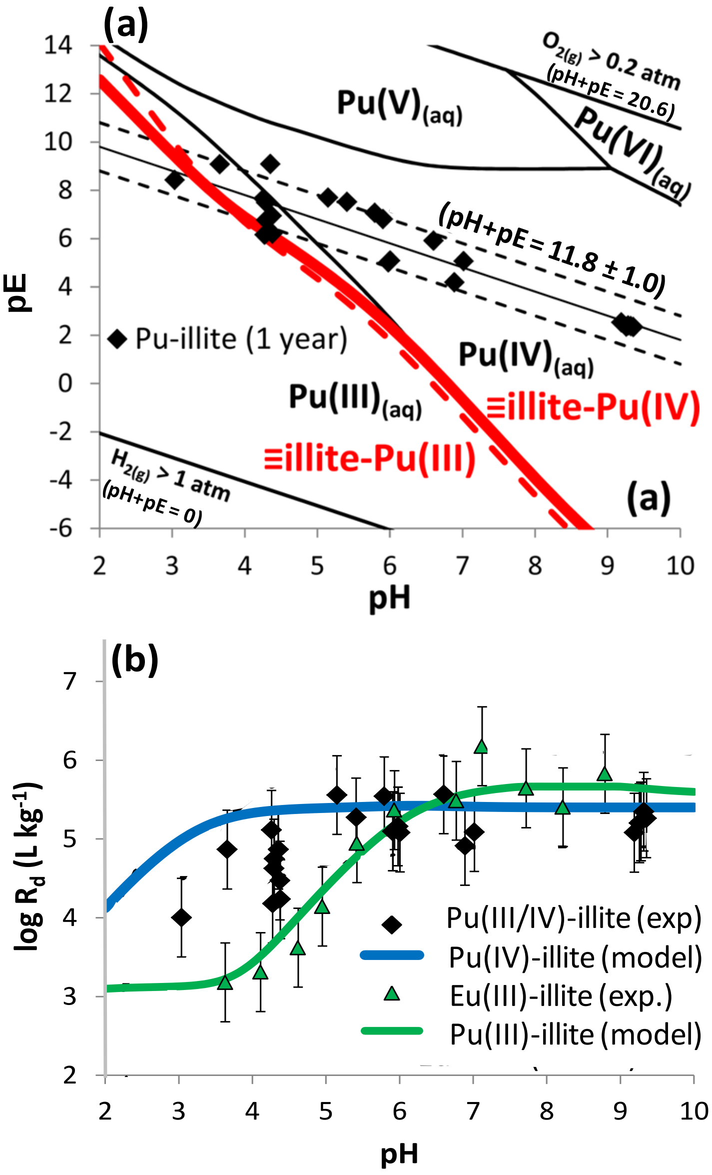


Figure 4. (a) Predominance pH−pE diagram for plutonium redox speciation in 0.1 M NaCl solution (black lines) and as surface-complexed plutonium species (red line and dashed line for different Pu(IV) surface complexation constants); black diamonds correspond to measured pH−pE data in experiments. Relevant redox conditions for this study (pH + pE = 11.8 ± 1.0) are shown as straight (solid and dashed) lines. (b) Data for plutonium uptake onto illite (R_d is given as the solid–liquid distribution ratio in L/kg) as a function of pH compared with model calculations for Eu(III) (green line) taken as a chemical homologue to Pu(III), and Pu(IV) (blue line) (Reprinted (adapted) with permission from Ref. 88. Copyright 2016 American Chemical Society).

2.6 Plutonium-Containing Particles

According to the International Atomic Energy Agency (IAEA) Coordinated Research Program,[12] radioactive particles in the environment are defined as localized aggregates of radioactive atoms that give rise to inhomogeneous distribution of radionuclides significantly different from that of the matrix background. In aquatic systems, particles are defined as entities having diameters larger than 0.45 µm–2 mm, whereas larger entities are referred to as fragments. Colloids/nanoparticles or pseudocolloids are defined as localized heterogeneities ranging in size from about 1 nm to 0.45 µm (i.e., entities that do not settle in still water because of mutual repulsion and Brownian movement). Hence, radionuclide species with nominal molecular mass less than 1–10 kDa (diameters less than about 1 nm) referred to as LMM species are assumed to be mobile and potentially bioavailable (can cross biological membranes). In air, radioactive particles are classified according to their aerodynamic diameters; particles less than 5-10 µm are considered respiratory.[12, 100] Because plutonium is a refractory element, a major fraction of the plutonium released during nuclear events (such as nuclear weapons tests, safety trials in which nuclear weapons or other plutonium sources are destroyed using conventional explosives, and reactor accidents) as well as from effluents from nuclear installations is present as radioactive particles. These radioactive particles may range in size from submicrometers to fragments (often referred to as "hot particles") and will be discussed further in the following sections.

Radioactive particles are formed as a result of destruction (e.g., explosions, fires) or weathering (e.g., corrosion processes) of nuclear or radiological materials, such as fuel or weapon matrices, radiological sources, and so forth. During high temperature and pressure conditions (e.g., nuclear weapon tests, reactor explosions or fire), the particles will be enriched in refractory elements, such as plutonium, and depleted in volatiles (e.g. several activation or fission products such as iodine-, cesium- and strontium-isotopes). Thus, the elemental composition of the plutonium-containing particles will reflect the emitting source (e.g., burn-up), either PuO_2 or mixed oxide (MOX) (Pu–U oxides) as a matrix or plutonium in UO_2 as an actinide product of neutron captures in uranium fuel. During the Chernobyl reactor explosion inert U-O-Zr particles containing plutonium were released, (high temperature and pressure, no oxygen, interaction with zircaloy), while the U fuel particles containing plutonium released during the subsequent fire was oxidized (U_3O_8) and easily soluble. Hence, particle properties, such as size distribution, crystallographic structure, and oxidation states, will also depend on the release conditions.[12]

2.7. Bioavailability and Uptake in Living Organisms

Plutonium interaction with microbes has been observed and is reviewed in several recent publications [10, 11, 101, 102] and discussed in detail in Chapter 25, "Plutonium Microbial Interactions in the Environment", in this handbook. A variety of geochemical reactions described above can be affected, hindered, or promoted by microbial activity. Microbial activity can generate exudate organic acids (such as citric acid) and sequestering agents (such as siderophores), potentially solubilizing and/or immobilizing plutonium by incorporation into cells. As a result, microbial activity may influence plutonium speciation and reactions in the geo- and biosphere. Likewise, stabilization and destabilization of colloidal plutonium is possible depending on the geochemical conditions and microorganisms present. Reduction and subsequent bioaccumulation by bacteria are considered appropriate strategies for in situ remediation of contaminated sites.[9, 103, 104]

To assess the environmental impact of plutonium, transfer factors are utilized for modeling purposes. These factors include the transfer coefficient TC (m^2/kg; for soil-to-plant transfer), the aggregated transfer coefficient TF_{agg} or T_{agg} (m^2/kg; for soil–plant–animal transfer), the bioconcentration factor BCF (L/kg) or concentration ratio (CR; Bq/ kg vegetation per Bq/kg soil on a wet weight basis used by the IAEA) for radionuclides accumulated in biota. As with K_d, these factors are often regarded as constants, without taking radionuclide speciation or other variable boundary conditions into account. However, these transfer factors depend on several factors (e.g., soil types, microbial activities, plant and animal species, dietary habits, trophic levels) and in particular on the radionuclide speciation. Large variations are also seen in the literature,[12] as summarized in Tables 8-10.

Uptake in the food chain is strongly influenced by the chemical speciation of plutonium in soil.[105] In general, plutonium transfer into plants increases with solution concentration and is determined by the prevailing oxidation state.[54] Bioavailability of relatively insoluble Pu(IV) can significantly increase in the presence of chelating ligands, such as citrate, EDTA, and so forth as well as soil water pH. LMM plutonium species can cross biological membranes directly or indirectly after interactions with ligands or carrier molecules. Therefore, organic ligands, such as citrate, may stimulate the uptake, whereas HMM organics, such as humic substances, can reduce uptake, as observed for other radionuclides. Root uptake and xylem transport of complexed species are usually responsible for plutonium uptake and distribution in plants.[106, 107]

Table 8. Soil-to-Plant Transfer given as Concentration Ratio**s** for Plutonium[a 18]

Plant group	Mean	Minimum	Maximum
Cereals	9.5×10^{-6}	2.0×10^{-7}	1.1×10^{-3}
Maize	5.2×10^{-5}	2.0×10^{-6}	3.2×10^{-4}
Leafy vegetables	8.3×10^{-5}	1.0×10^{-5}	2.9×10^{-4}
Nonleafy vegetables	6.5×10^{-5}	6.0×10^{-6}	2.0×10^{-4}
Leguminous vegetables	6.3×10^{-5}	3.7×10^{-5}	1.5×10^{-4}
Root crops	3.9×10^{-4}	7.0×10^{-5}	5.8×10^{-3}
Tubers	1.1×10^{-4}	3.8×10^{-6}	5.0×10^{-3}
Grasses	1.6×10^{-4}	5.0×10^{-5}	2.7×10^{-4}
Leguminous fodder	4.9×10^{-4}	1.1×10^{-4}	2.9×10^{-3}
Pasture	5.5×10^{-4}	6.3×10^{-5}	3.9×10^{-3}
Woody trees	1.4×10^{-4}	1.3×10^{-6}	2.1×10^{-2}
Shrubs	1.7×10^{-4}	6.4×10^{-5}	2.7×10^{-4}
Herbaceous plants	8.3×10^{-4}	2.7×10^{-5}	8.3×10^{-4}

[a]CR; Bq/ kg vegetation wet weight per Bq/kg soil dry weight

Table 9. Soil-to-Animal Products Concentration Ratio and Water-to-Fish Concentration Ratio for Plutonium[a 18, 108]

Species/compartment	Mean	Minimum	Maximum
Cow’s milk	1.0×10^{-5}		
Sheep’s milk	1.0×10^{-4}		
Beef	1.1×10^{-6}	8.8×10^{-8}	3.0×10^{-4}
Mutton	5.3×10^{-5}	2.0×10^{-5}	8.5×10^{-5}
Egg	1.2×10^{-3}	9.9×10^{-6}	2.3×10^{-3}
Roach	170	140	200

[a]CR: Bq/ kg product wet weight per Bq/kg soil dry weight and CR: Bq/kg fish wet weight per Bq/kg water

Uptake in fish and invertebrates occurs by ionic species interacting with external organs (gills, skin) or by digestive uptake. Because the fraction of LMM plutonium species in waters is usually low, direct uptake should also be relatively low, except for cases of long-term chronic exposures, such as in the Mayak PA reservoirs where the plutonium retained in fish bone and liver is expected to be relatively high. The plutonium CR for roach filet (170) in Mayak reservoirs[108] was found to be within the IAEA-reported range of 4–300 for freshwater fish.[18] Børretzen et al.[108] reported a CR value of 1450 for mussels, which is an order of magnitude higher than that previously reported for freshwater mollusks (100).[109] In filtering organisms, particles and colloids can be retained, and plutonium may accumulate because of changes in bioavailability in the gut (digestion) or through phagocytosis.

Table 10. Transfer of Plutonium to Animals, Aquatic Organisms, and Human Beings

Pathway	Transfer Factor	Reference
Soil-animal transfer [a]	0.03 (earthworm) 0.02 (rat, deer, duck, frog) 0.06 (bee)	[110]
Bioconcentration factor[b]	10^4–10^6 (invertebrates) ~150 (fish)	[111]
Plutonium transfer into human body by ingestion[c]	~ 5 10^{-4}	[111]

[a] Plutonium transfer given as concentration ratios (CRs) in Bq/kg animal (fresh weight)/Bq/kg soil (dry weight)
[b] Plutonium transfer given as bioconcentration factor (BCF) for the transfer from water to aquatic organisms in Bq/kg organism (fresh weight)/Bq/L water
[c] Plutonium transfer to the human body by food ingestion as fraction of intake

Plutonium particles can be retained in filtering organisms and act as a point source producing for instance burn marks as well as non-targeted effects (e.g., DNA damage), as demonstrated by Dounreay fuel particles in blue mussels.[112] Furthermore, plutonium particles can be taken up by grazing animals, as demonstrated by Chernobyl fuel particles given to goats.[113] Plutonium particles have also been recognized in feces from hare and snails in Palomares, Spain[114] and recent data from Palomares show that plutonium particles can be incorporated in the snail shell structure [115]. Retained particles will be unevenly distributed internally. Thus, development of microdosimetry is needed to properly assess uneven internal doses to biota from plutonium particles. Following dissolution of retained particles, plutonium species may over time be transported to accumulating organs in affected organism.

The physiological behavior of plutonium in the human body is discussed in detail in chapter 35 “Bioassay and Dosimetry of Plutonium”. Plutonium uptake is mostly attributed to inhalation, while the dietary uptake usually is low. Natural plutonium contributes to an average base load of <2 amol, which has increased by 5 orders of magnitude to 130 fmol since the beginning of atmospheric nuclear weapons testing period. This value is still very low, corresponding to <1 atom per 500 cells.[116] In a recent laboratory study, the uptake of plutonium into rat pheochromocytoma cells (PC12) could be visualized by X-ray fluorescence microscopy and μ–X-ray absorption near-edge spectroscopy (XANES), demonstrating that plutonium existed in the tetravalent state (Figure 5).[117]

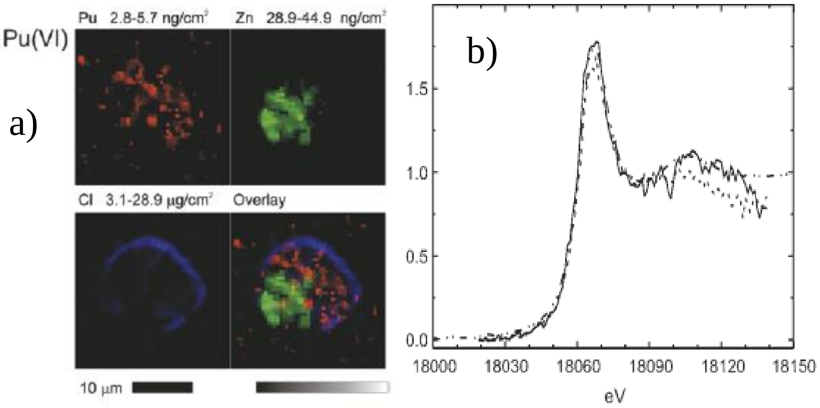


Figure 5. (A) X-ray fluorescence microscopy element maps for rat pheochromocytoma cells (PC12) showing internalized plutonium after exposure to Pu(VI). (B) The respective X-ray absorption near-edge spectroscopy (XANES) spectrum revealing plutonium to be Pu(IV) irrespective of the initial plutonium oxidation state (Reprinted (adapted) with permission from Ref. 117, Copyright 2016 American Chemical Society).

The small plutonium fraction transferred to the blood circuit existed as Pu(IV) and was reported to be mostly associated with the iron transporters ferritin and transferrin.[118, 119] More recent metalloproteomic investigations point to the important role of other proteins binding selectively (e.g., calcium, magnesium, and other divalent cations).[120] Main targets for plutonium in the body are the liver (60 %) and the skeleton (30 %).[121] For occupationally exposed persons, biological half-lives of plutonium for removal from the respiratory tract, the liver, and the skeleton are about 10 min to 19 years, 20 – 82 years, and 50 to 200 years, respectively.[122,123,124]

3. SPECIATION TECHNIQUES APPLIED TO THE ANALYSIS OF ENVIRONMENTAL PLUTONIUM

According to the IUPAC,[13] speciation analysis is defined as the “analytical activities of identifying and/or measuring the quantities of one or more individual chemical species in a sample”, whereas the phrase “speciation of an element” is defined as “the distribution of an element amongst defined chemical species in a system”.[13] In natural ecosystems, however, transformation processes and interactions over time will change plutonium species originally deposited in the environment.

Because of the usually low concentrations of plutonium in the environment, no direct species-specific spectroscopic techniques are available. Thus, fractionation of plutonium according to species categories must be performed before dissolution, chemical separations, and analysis using α-spectrometry or mass spectrometry (e.g. inductively coupled plasma mass spectrometry [ICP-MS], secondary-ion mass spectrometry [SIMS], accelerator mass spectrometry [AMS]). Concentrations of plutonium at the femtogram level can be analysed using AMS. Separation procedures, such as preconcentration of trace plutonium concentrations with scavenger precipitations (e.g. iron, manganese, and aluminum hydroxides), may, however, alter the original speciation. Furthermore, at trace concentrations, interactions with macrocomponents and total organic carbon/dissolved organic carbon (DOC) can influence the behavior of plutonium. As natural systems are often not well defined and chemical equilibria possibly not attained, predictions of plutonium species based on thermodynamic constants obtained in laboratory experiments of well-defined systems may not apply to the actual plutonium species present in complex natural environments.

3.1 Plutonium in Air

Air filters, varying in pore size and materials, are usually applied to remove particles with aerodynamic diameters exceeding the respective cut-off values such as 0.1, 1, 5, or 10 µm. More coarse filters were commonly used for gross α and gross β monitoring of fallout during the atmospheric nuclear weapon testing period. By re-examining air filters collected daily during the nuclear weapon testing period from 1956 to 1963, information on plutonium and the plutonium isotope ratios retained in the filters can be obtained, as demonstrated by Wendel et al.[125] The ^{240}Pu/^{239}Pu atom ratio in filters from 1962 in Norway reflected a low-yield weapon source, and in combination with air dispersion modeling and real-time meteorology data, the origin of the plutonium fallout could be identified as nuclear tests at the Semipalatinsk Test Site (STS). Today, cascade impactors are used more often than filters, as they allow for a series of size fractions with different aerodynamic diameters to be collected. Because of the low plutonium concentrations, sampling of large air volumes is usually needed.[126] Because wind erosion at contaminated sites is an issue, an alternative approach is to perform resuspension studies where dust-laden air is generated, allowing airborne components to be classified using a cascade impactor. Such an approach was used at the UK test sites in Australia[127] and showed that a fraction of plutonium with an activity median aerodynamic diameter value of about 6 µm could be inhalable.

3.2 Plutonium in Water

To obtain insight into the chemical state of plutonium in water, fractionation techniques must be applied prior to the use of appropriate detection systems. Several size and charge fractionation techniques are available for classifying radionuclide species in water (Table 11). Most data on plutonium in water refer to total plutonium in water (unfiltered) or to plutonium in filtered water where the pore size of the filter varies (1 µm, 0.45 µm, or 0.22 µm). Thus, the colloidal fraction of plutonium has often been miscategorized as dissolved and is often incorrectly represented as ionic species. Among size fractionation techniques, the filtration and tangential cross flow (hollow fiber ultrafiltration) techniques can be applied efficiently in the field. Size fractionation of radionuclide species should take place in the field because storage of samples can lead to sorption, aggregation, and sedimentation, changes in pH or redox conditions, as well as bacterial growth, that can change the original distribution of species.[16] The applicability of fractionation methods for the speciation of transuranic elements predominantly associated with particles and colloids in effluents from Sellafield has been demonstrated.[54] By combining fractionation methods with mass spectrometry (e.g., atom ratio by AMS), radionuclides associated with particles and colloids and those present as LMM species can be distinguished, as demonstrated for plutonium in the Ob and Yenisey estuaries.[128, 129] The atom ratio of plutonium isotopes (^{240}Pu/^{239}Pu) in particulate materials (>0.45-µm filter membrane) reflected global fallout, whereas plutonium associated with the colloidal fraction (0.45 µm–10 kDa) and LMM plutonium species (≤10 kDa) could be attributed to weapons-grade plutonium.[128, 129]

Many techniques are also available for fractionation of species according to their redox state, although most are not well suited to *in situ* measurement. Solvent extraction and coprecipitation procedures have been developed to identify plutonium oxidation states in natural water.[19, 130] Redox agents have frequently been added to samples (e.g., samples taken from the Irish Sea) to differentiate between Pu(III) and Pu(IV), which are particle-reactive, and Pu(V) and Pu(VI), which are mobile.[131] Similarly, H_2O_2 or UV irradiation has been used to decompose and destroy organic material in order to remobilize associated radionuclides and thus identify plutonium associated with organic matter. However, such procedures are also able to mobilize plutonium associated with other components, such as clay. Ion-exchange chromatography can be applied to distinguish between cationic, anionic, or neutral species in situ (Table 11). When ion-exchange chromatography is combined with filtration and hollow fiber ultrafiltration, information on size and charge categories of plutonium species in waters becomes accessible, as demonstrated for radionuclides in effluent from the La Hague reprocessing site in France.[132] Recently, diffusive gradients in thin films (DGT) have been used as an *in situ* fractionation technique for radionuclide species.[133] DGT provides a measure for the complexation strength and the complex lability of plutonium species in water and thus can be used to estimate the mobility and potential bioavailability of plutonium.

Various authors have reported the direct determination of plutonium polymeric species in solution using electrospray mass spectrometry.[134] Even more sensitive are methods in which separation and fractionation devices are coupled online with ICP-MS. Information on plutonium redox and complex speciation in aqueous solutions can be obtained at trace concentrations down to 10^{-12} M (sub-ppb) by coupling capillary electrophoresis and high-resolution ICP-MS.[135, 136] The combination of field-flow fractionation or size-exclusion chromatography and triple quadrupole ICP-MS allows the characterization of colloid-borne plutonium species at trace concentration ranges.[137] However, these mass spectrometry techniques are laboratory-based and require transport and storage of samples before analysis. The combination of *in situ* size and charge fractionation with laboratory analysis, where the fractions obtained in the field are transported to the laboratory for low level analyses of concentrations and atomic ratios, provides a strategy for minimizing artifacts due to speciation changes during storage and transport.

Table 11. Available Techniques for Size and Charge Fractionation of Plutonium Species in Water. [16, 138]

Size fractionation	Charge and redox fractionation
Filtration	Exchange chromatography (cation, anion, adsorption)
Tangential cross flow/hollow fiber ultrafiltration	Liquid–liquid extraction
Continuous flow centrifugation	Sequential extractions
Ultra centrifugation	Electrochemical methods
In situ dialysis (small volumes)	Crown ether chromatography
Dialysis/diffusion	Redox agents
Size exclusion/gel chromatography	Capillary electrophoresis
Field-flow fractionation	
Electrospray mass spectrometry	

3.3 Plutonium in Soils or Sediments

***3.3.1 Plutonium Particle Separation*.** Digital autoradiography is most useful to identify inhomogeneous distribution of radionuclides in soils and hot spots reflecting the presence of radioactive particles (Figure 6). Soil or sediment samples are often separated according to particle size into sand, silt, and clay fractions, and autoradiography can be applied to identify hot spots in the separated fractions of sediments. Imaging techniques such as digital phosphor imaging have proved most useful for locating radioactive particles in a sample. Using micromanipulators under the microscope, single micrometer sized particles can be isolated and extracted for further analysis.

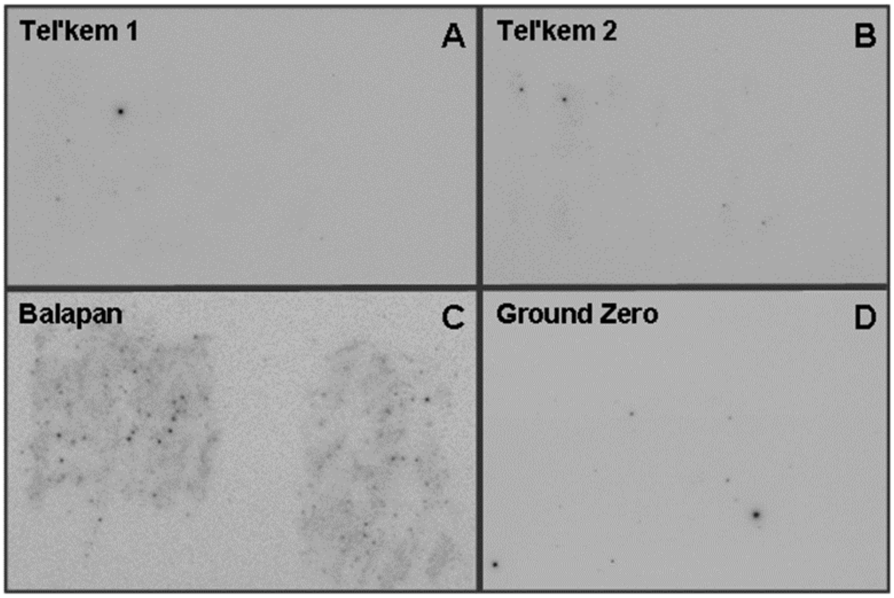


Figure 6. Digital phosphor imaging of soils (1-5 cm) from locations within the Semipalatinsk Test Site, Kazakhstan. (A) The outer rim of the Tel'kem 1 crater; (B) Outside of the Tel'kem 2 crater; (C) Within the fusion explosion crater of the Balapan Lake (Atomic Lake). (D) Ground Zero. [139, 140]

3.3.2 Plutonium and Sequential Extraction. Sequential extraction procedures involve reagents with increasing displacement and dissolution power.[141] Plutonium distribution in individual sequential extraction fractions can provide information on binding mechanisms and chemical states.[53, 142] Thus, the fraction of radionuclides that is potentially mobile due to physisorption (van-der-Waals or electrostatic attraction) can easily be distinguished from the fraction that is strongly fixed to soil components (chemisorption, released by redox agents). The procedure has been utilized for radionuclides in soils/sediments from many contaminated sites, including plutonium in sediments from Mayak reservoirs.[143, 144]

3.3.3 Plutonium Particle Characterization. A major fraction of plutonium released from nuclear sources, such as nuclear weapon tests and reactor accidents, is associated with radioactive particles,[12, 145] whereas colloidal or LMM species are also encountered in effluents from nuclear installations or as vectors for plutonium transported to the far field.[4, 54, 56, 76, 77, 146] To assess the environmental impact of plutonium released from nuclear sources and deposited in ecosystems, detailed information on the solid-state speciation of plutonium associated with particles, colloids, or other environmental surfaces, such as minerals, is required. Of particular importance are particle characteristics, such as particle size distributions, surface and particle matrix (three-dimensional) elemental composition, morphology, crystalline structure, density, and oxidation state, which influence particle weathering rates and the subsequent remobilization of radionuclides from particles present in soil–water and sediment–water systems.[140]

A number of analytical tools have been used for the solid-state speciation of plutonium in environmental samples (Table 12).[12, 147] Particles are located, isolated, and extracted based on their radioactive (e.g., imaging techniques such as digital autoradiography, repeated sample mixing or splitting combined with γ-spectrometry) or chemical (e.g., high atomic number backscattered electron imaging contrast and X-ray signals in electron microscopy) properties. Isolation and extraction procedures are most often followed by the use of microscopic methods, such as scanning electron microscopy or scanning transmission electron microscopy interfaced with X-ray microscopic techniques for the characterization of two-dimensional elemental composition.[12, 145] The elemental composition of micrometer-sized particles can also be determined by other X-ray emission techniques (i.e., μ–X-ray fluorescence, μ–particle-induced X-ray emission, and electron probe microanalysis) that differ in the type of primary beam used to eject core-level electrons from the target atoms.

Synchrotron radiation (SR) nanoscopic and microscopic X-ray techniques represent state-of-the-art technologies and X-ray absorption spectroscopy (XAS) is increasingly used to study the speciation of actinides. SR fluorescence analysis (μ-XRF) provides information on 2 dimensional or 3 dimensional (μ-tomography) elemental distribution within individual particles. Nano/micro-X-ray diffraction (XRD) gives information on the 2 dimensional or 3 dimensional crystallographic structures of solid particles[148], while nano or micro X-ray absorption near edge structure spectrometry (XANES) provides information on the oxidation state of matrix elements on nanometer or micrometer scales, respectively. In addition, extended X-ray absorption fine structure analysis could provide information on the coordination number and the distance to neighbouring atoms, if detailed knowledge on the particle composition is available. EXAFS has also been utilized for actinides in solution, in solid forms or at a solution–solid interface,[149] and Batuk et al. has recently reported EXAFS data for plutonium in particles from several contaminated sites.[148]

Computed tomography techniques (3 dimensions) combined with reconstruction algorithms allow information of the inner structure of a solid particle without physically sectioning the object; combination with XRF provides 3 D elemental distribution and combination with XRD provides 3 D density or crystalline structure distribution. Synchrotron-based X-ray microtomography has been used to characterize plutonium-containing particles from Mururoa and Thule.[150] Recently, laboratory-based X-ray absorption tomography with a resolution of a few hundred nanometers (nano–computerized tomography) has become available and proves most useful for characterization of particles with respect to density distributions, morphology, porosity and identification of high density material inclusions within larger particles.[140] The combination of synchrotron based μ-XRF, μ-XRD, μ-XANES applied to one single radioactive particle has proved most useful for uranium particles,[151-156] while so far less utilized for plutonium particles.

Alternatively, micro-Raman could potentially be used for particle characterization as demonstrated by Shinonaga et al. using this technique to characterize synthesized PuO_2 particles.[157] The results seems promising although no reports on the use of micro-Raman on environmental plutonium samples seems so far to be available.

Table 12. Analytical Tools for Solid-State Speciation Analysis of Plutonium Colloids and Particles in Environmental Samples (modified from Ref. 12 and 140)

Method	**Information obtained**
Identification and isolation of plutonium heterogeneities	
Size fractionation in water followed by radioanalytical and/or mass spectrometric techniques[79, 132, 158-162]	Size distribution
Cascade impactor with aerosol filters followed by radioanalytical and/or mass spectrometric techniques	Size distribution (AMAD)

techniques[127]	
Portable monitors in the field[163]	Hot spot identification
Imaging techniques based on ionizing radiation (e.g., autoradiography[140, 164, 165], beta-camera[166], alpha track analysis and fission track analysis[167])	Distribution of radioactivity, extent of heterogeneity of sample
Repeated sample splitting combined with light microscopy, γ-spectrometry, or autoradiography[168-170]	Heterogeneities (as indicated by elevated activities in subsamples)
Repeated sample mixing combined with γ-spectrometry[171]	Heterogeneities (as indicated by skewed frequency distribution of the counts)
Direct identification in SEM and confirmation by EDX[169, 170, 172, 173]	High atomic number elements (bright areas in BEI mode)
Characterization of plutonium associated with solids	
SEM with EDX[150, 170, 173]	Size distribution, surface morphology, elemental composition and distribution
Analytical TEM/STEM with EDX,[174] electron diffraction,[174] EELS[175, 176], HAADF	Size distribution of colloids, elemental composition, crystalline structure, chemical bonding, Z-contrast imaging
Nano- and microfocused XRF mapping[150, 170, 177-179]	Elemental composition and two-dimensional distribution (depth)
Confocal μ-XRF[139, 180, 181]	Elemental composition and three-dimensional distribution
Nano- and microfocused XANES[148, 150, 170, 182-185]	Oxidation state (distribution)
Nano- and microfocused EXAFS[148]	Coordination number, distance to and species of the neighboring atom of Pu
Nano- and microfocused XRD[148, 186]	Crystallographic structures
Nano- and microfocused x-ray tomography[150, 187]	Spatial distribution of density, elements, oxidation states

STXM[188, 189]	Elemental composition, high resolution elemental distribution, oxidation state (distribution)
μ-PIXE[127, 181, 190]	Elemental composition and distribution
SIMS[191, 192]	Size distribution, elemental and isotopic distribution (~1 μm resolution)
Nano-SIMS[77]	Size distribution, elemental and isotopic distribution (~100 nm resolution)
LA-ICP-MS[193, 194]	Elemental and isotopic composition and spatial distribution
Micro-Raman[157]	Spatial distribution of molecular species
Leaching experiments[127, 195, 196]	Solubility, weathering rates, bioavailability

Note: AMAD = activity median aerodynamic diameter; BEI = backscattered electron imaging; EDX = energy-dispersive X-ray spectroscopy; EELS = electron energy loss spectroscopy; HAADF = high-angle annular dark-field imaging; LA-ICP-MS = laser ablation inductively coupled plasma mass spectrometry; LAMMA = laser microprobe mass spectrometry; PIXE = particle-induced X-ray emission; SEM = scanning electron microscopy; SIMS = secondary-ion mass spectrometry; STEM = scanning transmission electron microscopy; STXM = Scanning transmission x-ray microscopy; TEM = transmission electron microscopy; XANES = X-ray absorption near-edge spectroscopy; XRD = X-ray diffraction; XRF = X-ray fluorescence.

Following non-destructive solid-state speciation techniques, leaching experiments can provide important information on particle behavior, linking particle characteristics to particle weathering rates and remobilization potential for particle associated radionuclides (and metals). Leaching can be performed with single abiotic agents (rain water, acids such as 0.16 M HCl to simulate stomach juice), biotic agents (real stomach juices) or sequentially using reagents of increasing displacement and dissolution power.

4. PLUTONIUM SOURCES IN THE ENVIRONMENT

Plutonium in the environment predominantly originates from nuclear weapon tests and emissions from nuclear fuel cycles, while only minute amounts of plutonium are associated with natural sources. The first injection of artificially produced plutonium into the atmosphere occurred in July 1945 with the detonation of the first plutonium device, containing 6 kg of plutonium, at the Trinity Site near Alamogordo in New Mexico, United States. The bomb dropped on Hiroshima on August 6, 1945, contained highly enriched uranium and the bomb detonated over Nagasaki 3 days later contained plutonium.[197] Since 1945, a series of sources associated with the nuclear weapon and fuel cycles have contributed to the release of artificially produced radionuclides, such as plutonium, into the environment. These releases occurred mainly as a result of atmospheric and underground nuclear weapons tests but also resulted from accidents with nuclear weapons, reactor accidents, releases from reprocessing and waste storage facilities, and accidents with nuclear-powered vehicles.

4.1. Natural Occurrence of Plutonium

Plutonium from natural sources (Table 13) generated by various processes is present in the environment at trace concentrations. One source for plutonium of natural origin (“naturogenic plutonium”)is the production of ^{244}Pu ($t_{1/2}$ = 8.00 × 10^7 years) in supernovae by nucleosynthesis via the r-process, based on the observation of an anomalous pattern of xenon isotopes produced by spontaneous fission of ^{244}Pu in meteorites.[198] Deposition of ^{244}Pu on earth from the impact of cosmic radiation or as a relic of supernova explosions before the formation of the earth has been postulated,[199] although the quantitative assessment is still under debate.[200] In 1971, Hoffman et al. analyzed ^{244}Pu in bastnaesite ((Ce, La, Nd, Y)[(F,OH)|CO_3]),[201] and in a recent study, other authors reported an upper limit for the content of ^{244}Pu in a similar sample based on the detection limit of AMS.[199] The same group measured about 4000 atoms of ^{244}Pu/cm^2 in a ferromanganese crust sample, the origin of which they attribute to a supernova event.[202] They derive a cosmic input of ^{244}Pu to the earth’s surface on the order of 3 × 10^4 atoms/cm^2 in a period 1–14 million years ago.

A second source for naturogenic plutonium on earth arises from continuously occurring neutron capture reactions of natural uranium, in which neutrons are generated by spontaneous fission of ^{238}U, from cosmic radiation (1 g natural uranium: 1 neutron/min; cosmic radiation: 0.1 neutron/(min cm^2)),[203, 204] and from (α,n) reactions.[205] Assuming an average ^{238}U content in the earth’s crust of 2.7 × 10^{-3} g/kg, a rough estimate gives an average ^{239}Pu concentration of 2 × 10^{-14}g/kg (100 amol/kg). A more recent investigation of uranium ore from the Canadian Cigar Lake site yielded atomic ^{239}Pu/^{238}U ratios of 2.4 × 10^{-12} to 44 × 10^{-12}.[206] Values for the total amount of ^{239}Pu in the earth’s crust remain rough estimates and will depend on exact production rates and the total mass of ^{238}U on earth. Available estimates come to several kilograms. During the operational phase of the natural fission reactor at the Oklo site in Gabon, Africa, 2 billion years ago, about 2 metric tons of ^{239}Pu was produced, which has subsequently decayed again to ^{235}U.[207] Some sediment samples have been found in which the ^{235}U content is slightly enriched, which indicates that enrichment of ^{239}Pu took place locally (see also section 6.5).[89]

Table 13. Sources for naturogenic plutonium on earth

Origin	Abundance	References
^{244}Pu from supernovae	Total: ~9 g $<1.5 \times 10^{-19}$ - 10^{-18} g ^{244}Pu/g in bastnaesite 3×10^{-25} g ^{244}Pu/g in the earth's crust	[201, 199]
Uranium ore	Total: several kilograms Atomic ratio of ^{239}Pu/^{238}U ~10^{-13}–10^{-11}	[116, 204, 205, 206, 208]

4.2. Characteristics of Plutonium Released from Anthropogenic Sources

Anthropogenic plutonium has been released into the environment from a number of sources: nuclear weapons tests, accidental releases from nuclear installations, accidents with vehicles carrying nuclear materials (satellites, aircraft), effluents from reprocessing and disposal facilities and intentional disposal and dumping of radioactive waste in the early nuclear era (Note: nuclear waste disposal and associated releases are described separately in Section 6). The fate of plutonium related to mobilization and transfer to the food chain depends, inter alia, on the nature of the plutonium species released and the receiving ecosystem.

4.2.1 Source and Release Conditions. Plutonium-containing particles can be formed as a consequence of explosions, fires, or corrosion processes of plutonium-containing materials, such as weapons or nuclear fuel. Particle formation and release during events under high-temperature and high-pressure conditions, such as nuclear weapon tests, will depend on the weapon's materials and composition (i.e., uranium or plutonium oxides, major metal components) as well as the yield and altitude of the shot. Fission and activation products, as well as transuranic elements form during detonation and subsequently undergo fractionation during cooling of the debris. Volatiles escape while refractory elements such as plutonium remain in fallout particles. High-yield thermonuclear plutonium weapons with uranium tampers produce the heaviest plutonium isotopes. Particle size distribution, morphology, and structure depend on the altitude of the explosion: near-surface detonations produce large, glassy, soil-containing radioactive particles, whereas small spherical particles are formed from high-altitude shots.[209]

Detonation of conventional explosives in plutonium-containing nuclear weapons occurred during accidents in Thule, Greenland and in Palomares, Spain. In those cases, the composition of emitted particles reflected mechanically destroyed weapon and containment materials. As a consequence of nuclear reactor accidents accompanied by explosion and fire, as was the case in Chernobyl, volatiles can escape, while particles released contain refractory elements such as plutonium. During the initial explosion in the Chernobyl reactor (high temperature, high pressure, no air) interactions with construction material took place and fuel particles consisting of U–O–Zr composites were released. During the subsequent fire (medium temperature, normal pressure, air present), uranium in the released fuel particles was oxidized.[151] The U-O-Zr particles released during explosion were inert, with very slow weathering rates and slow ecosystem transfer of particle-associated radionuclides. The weathering rates of the oxidized U fuel particles released during the subsequent fire were fast with rapid ecosystem transfer of associated radionuclides. Although the source (UO_2 spent fuel) was the same, the different release scenarios resulted in different particle characteristics, different weathering rates as well as different ecosystem transfer of the particle - associated radionuclides.

Releases under low-temperature conditions are most often associated with corrosion damage of the source containment. The characteristics of actinide species released under low-temperature and low-pressure conditions are different from those of actinide species released under high-temperature and high-pressure conditions. This is illustrated by the fact that uranium particles released because of corrosion of U–Al fuel misplaced in air ducts at the Windscale Pile were significantly different from uranium particles released during the Chernobyl accident.[53] Plutonium-containing particles and colloids have also been released to the sea as authorized discharges from reprocessing facilities, such Sellafield in the United Kingdom and La Hague in France.[54, 132] Such particles will also reflect the composition of the waste streams, including signatures of the associated industrial processes (residues from exchange resins).

Based on a particle archive representing a series of historical release events, analyses have demonstrated that the particle composition and the actinide atom/isotope ratios depend on the source (e.g., burnup, depletion of volatiles), whereas particle characteristics related to microstructures also depend on release conditions and dispersion processes.[12, 210] Thus, the plutonium (and uranium) isotope/atom ratio signals can be utilized for source identification (Figure 7).

4.2.2 Atom or Isotopic Ratios. Plutonium is a key material within both the civil nuclear fuel cycle and the military nuclear weapons cycle (e.g., as MOX). One kilogram of ^{239}Pu is equivalent to about 22 million kW h of heat energy; the complete fission detonation of 1 kg of ^{239}Pu could theoretically produce an explosion equal to about 20,000 metric tons of chemical explosive, such as TNT.[211] Plutonium isotopes and ^{236}U are formed by single and multiple neutron capture during reactor operation and nuclear weapon detonations. Consequently, the isotopic composition of plutonium is altered by both reactor operation and nuclear detonations, resulting in the accumulation of heavier plutonium isotopes as a function of the source, reactor type, burnup, and operating history, as well as neutron flux and weapon yield. The isotopic signatures of plutonium associated with nuclear explosions are therefore distinctly different from plutonium originating from nuclear weapons destructed by conventional explosives as a consequence of accidents (e.g., Thule, Palomares). Hence, plutonium (and uranium) isotope/atom ratios can be used to identify the origin of contamination (nuclear forensic), calculate inventories, or follow the migration in contaminated sediments and waters (Figure 7). The ratio ^{238}Pu/^{239,240}Pu is commonly reported in older literature; the ratios ^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu, ^{242}Pu/^{239}Pu, and ^{236}U/^{239}U are more commonly reported today, providing more detailed information. Based on the literature, Table 14 summarizes specific plutonium isotope characteristics for debris from nuclear detonations and various reactor types.

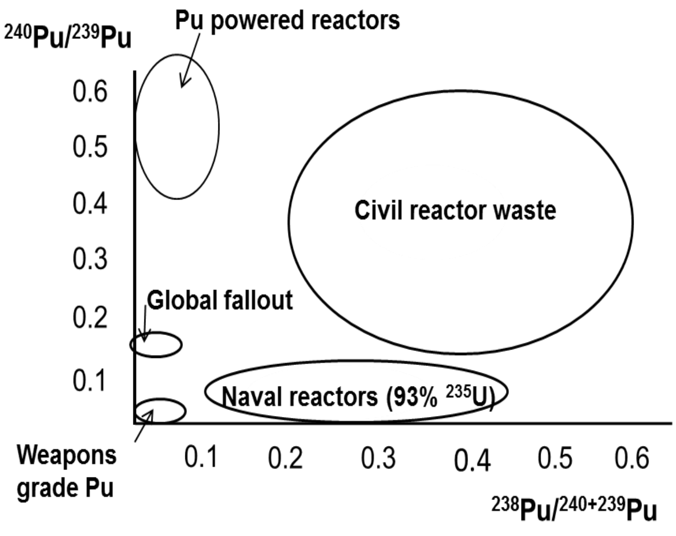


Figure 7. Principle scheme of sources and associated plutonium isotope ratio signals.[212]

Weapons-grade plutonium is characterized by a low level of ^{240}Pu with ^{240}Pu/^{239}Pu isotope ratios less than 0.05, whereas ^{238}Pu/^{239,240}Pu isotope ratios are fairly similar to those of global fallout (0.17–0.19), as seen in Figure 7. In contrast, both global fallout and spent nuclear fuel from civil reactors have higher ^{240}Pu/^{239}Pu isotope ratios than most weapons material. Because ^{240}Pu and ^{239}Pu are not easily distinguished by α-spectrometry, mass spectrometry techniques such as ICP-MS, thermal ionization mass spectrometry, SIMS, and AMS are required for the assessment of notably low-level plutonium isotope ratios.[125, 170, 213-215]

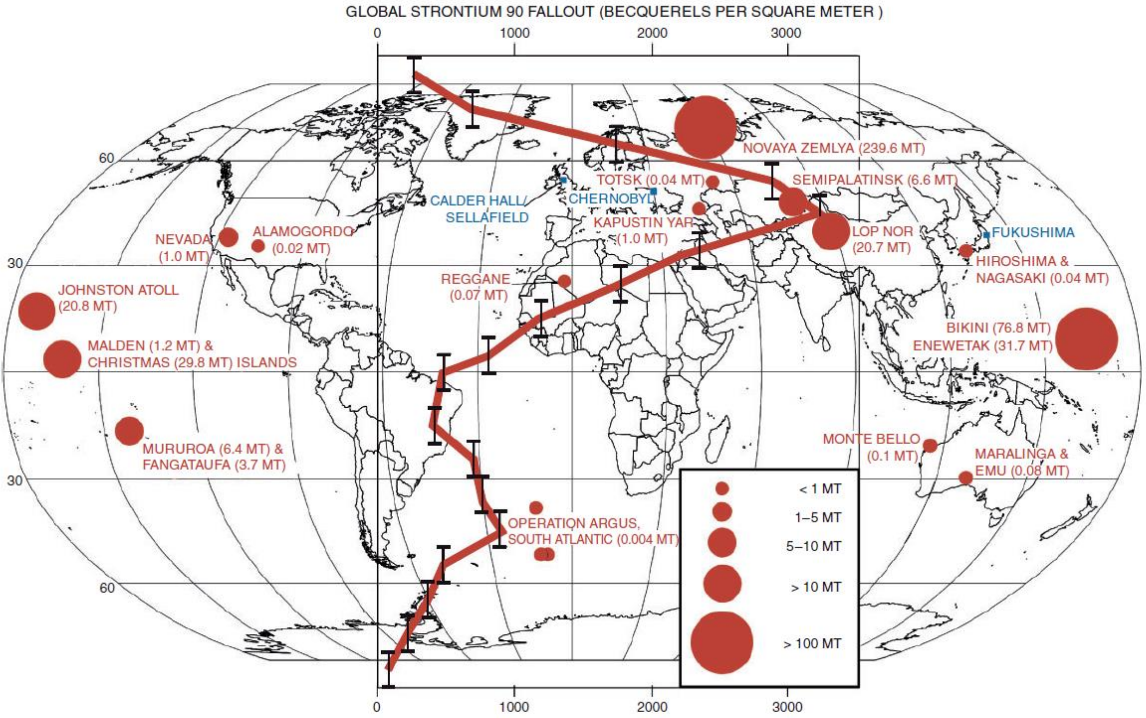
Table 14. Atom Ratios Characteristic for Debris from Nuclear Detonations and Various Reactor Types [i,125]

Source	^{240}Pu/^{239}Pu	^{241}Pu/^{239}Pu	^{242}Pu/^{239}Pu	^{236}U/^{239}Pu
Undetonated weapons plutonium	0.01–0.07[a]	—	—	—
Low-yield detonations, U-based	0.00015–0.053[b]	$(0.2–2.3) \times 10^{-4}$ [b]	—	—
Low-yield detonations, Pu-based	0.01–0.08[b]	$(0.2–6.7) \times 10^{-4}$ [b]	—	—
Low-yield detonations, Ground Zero Semipalatinsk	0.0438 ± 0.0001[c]	$(2.21 \pm 0.035) \times 10^{-4}$ [c]	$(7.89 \pm 0.26) \times 10^{-5}$ [c]	0.0244 ± 0.001[c]
Global fallout, Northern Hemisphere	0.182 ± 0.005[d]	$(1.12 \pm 0.85) \times 10^{-3}$ [d]	$(3.71 \pm 0.3) \times 10^{-3}$ [d]	0.235 ± 0.014[e]
Bikini Atoll, Ivy Mike	0.363 ± 0.004[f]	$(2.27 \pm 0.029) \times 10^{-3}$ [f]	0.019 ± 0.003[f]	—
Reactor debris, Chernobyl	0.13–0.53[g]	0.12–0.13[g]	0.034–0.048[g]	5.43–8.14[g]
Gas-cooled reactor, fuel burnup 3.6 GWd/t	0.23[h]	0.045[h]	0.006[h]	—
Pressurized heavy-water reactor, fuel burnup 7.5 GWd/t	0.41[h]	0.077[h]	0.023[h]	—
Advanced gas-cooled reactor, fuel burnup 18 GWd/t	0.57[h]	0.184[h]	0.093[h]	—
RMBK reactor, fuel burnup 27.5 GWd/t	0.67[h]	0.203[h]	0.108[h]	—
Pressurized water reactor, fuel burnup 33 GWd/t	0.43[h]	0.229[h]	0.096[h]	—

Note: [a] Refs. 215, 216, 217, [b] Refs. 218, 219, 220, 221, [c] Ref. 222; [d] Ref. 223; [e] Ref. 224; [f] Ref. 225; [g] Refs. 226-228; [h] Ref. 229;
[i] All isotope ratios decay corrected to December 1, 2011.

4.3 Nuclear Weapons Detonations

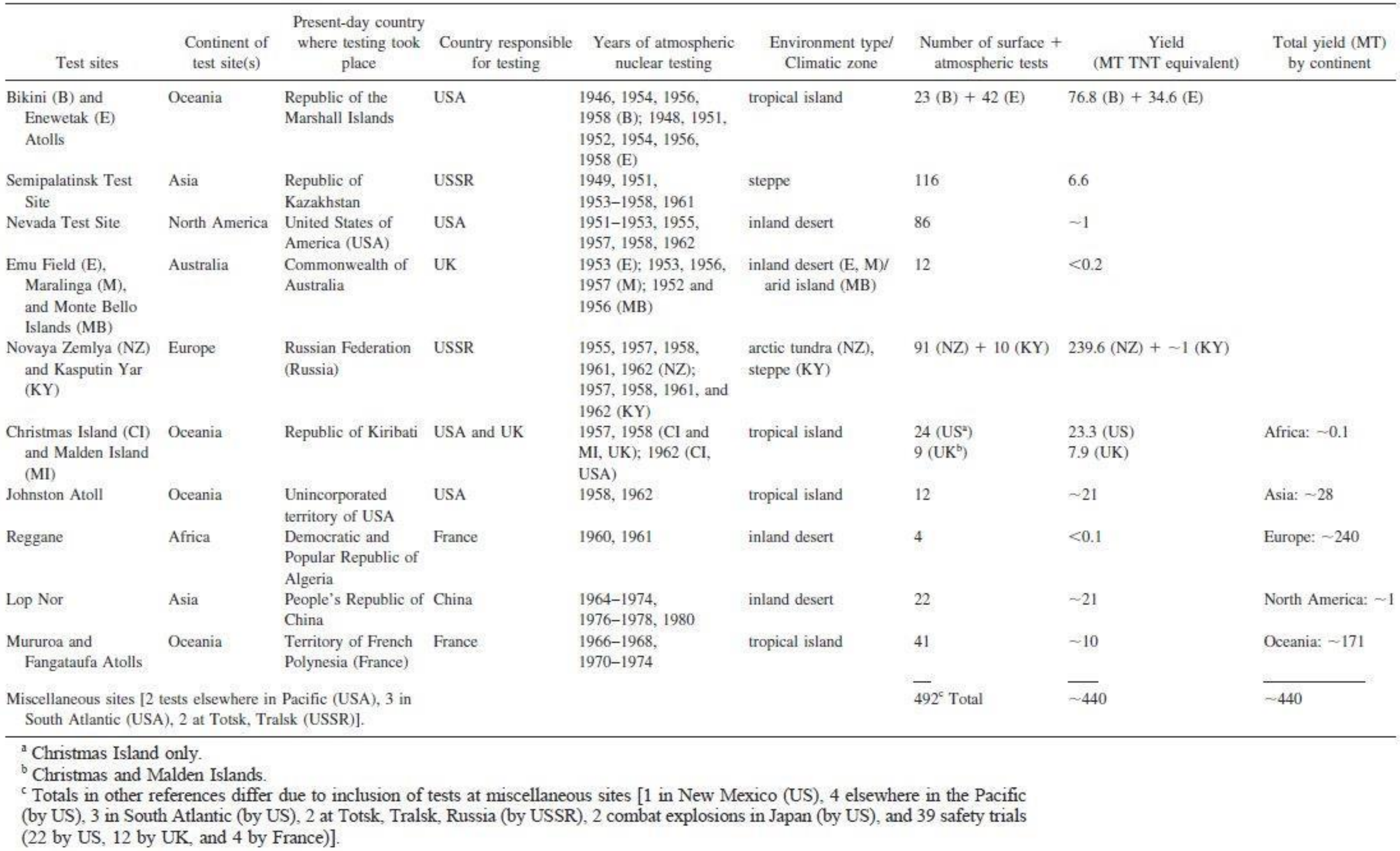
Since the discovery of plutonium, more than 2,400 nuclear weapons tests have been performed worldwide. Atmospheric nuclear explosions are by far the largest contributor of plutonium to the environment, performed at many locations (Figure 8) with nuclear weapons having different yields (Table 15). The dominant nuclear weapon states, the United States and the former Soviet Union, carried out a total of 1,054 [230] and 969 [202] nuclear weapons tests, respectively. France has carried out 210 tests, the United Kingdom 57 tests, China 44 tests, India 6 tests, Pakistan 6 tests, and North Korea 5 tests (including their most recent test in 2016).[231] Nuclear weapon tests can be broadly characterized as atmospheric, leading to local and global fallout, and underground, leading to local subsurface contamination. The military use of nuclear weapons only occurred on two occasions. Both nuclear weapons were used during the *Second World War*. The first bomb was dropped on Hiroshima, Japan, on August 6, 1945, and contained enriched uranium (80 % ^{235}U). The second bomb was dropped on Nagasaki, Japan, on August 9, 1945, and was a plutonium-containing weapon.



Source: UNSCEAR (2000)

Figure 8. Distribution of atmospheric nuclear weapon explosions including fission and fusion yields (red) and nuclear accidents and radionuclide discharges (blue). Superimposed is the latitudinal variation of global ^{90}Sr fallout in becquerels per square meter as an indicator for nuclear fallout. Two sites, Novaya Zemlya and the French Pacific atolls, contributed significantly to global fallout.[1]

Table 15. Summary of atmospheric nuclear testing performed by different countries [232, 233]



Test sites	Continent of test site(s)	Present-day country where testing took place	Country responsible for testing	Years of atmospheric nuclear testing	Environment type/ Climatic zone	Number of surface + atmospheric tests	Yield (MT TNT equivalent)	Total yield (MT) by continent
Bikini (B) and Enewetak (E) Atolls	Oceania	Republic of the Marshall Islands	USA	1946, 1954, 1956, 1958 (B); 1948, 1951, 1952, 1954, 1956, 1958 (E)	tropical island	23 (B) + 42 (E)	76.8 (B) + 34.6 (E)	
Semipalatinsk Test Site	Asia	Republic of Kazakhstan	USSR	1949, 1951, 1953–1958, 1961	steppe	116	6.6	
Nevada Test Site	North America	United States of America (USA)	USA	1951–1953, 1955, 1957, 1958, 1962	inland desert	86	~1	
Emu Field (E), Maralinga (M), and Monte Bello Islands (MB)	Australia	Commonwealth of Australia	UK	1953 (E); 1953, 1956, 1957 (M); 1952 and 1956 (MB)	inland desert (E, M)/ arid island (MB)	12	<0.2	
Novaya Zemlya (NZ) and Kasputin Yar (KY)	Europe	Russian Federation (Russia)	USSR	1955, 1957, 1958, 1961, 1962 (NZ); 1957, 1958, 1961, and 1962 (KY)	arctic tundra (NZ), steppe (KY)	91 (NZ) + 10 (KY)	239.6 (NZ) + ~1 (KY)	
Christmas Island (CI) and Malden Island (MI)	Oceania	Republic of Kiribati	USA and UK	1957, 1958 (CI and MI, UK); 1962 (CI, USA)	tropical island	24 (US[a]) 9 (UK[b])	23.3 (US) 7.9 (UK)	Africa: ~0.1
Johnston Atoll	Oceania	Unincorporated territory of USA	USA	1958, 1962	tropical island	12	~21	Asia: ~28
Reggane	Africa	Democratic and Popular Republic of Algeria	France	1960, 1961	inland desert	4	<0.1	Europe: ~240
Lop Nor	Asia	People's Republic of China	China	1964–1974, 1976–1978, 1980	inland desert	22	~21	North America: ~1
Mururoa and Fangataufa Atolls	Oceania	Territory of French Polynesia (France)	France	1966–1968, 1970–1974	tropical island	41	~10	Oceania: ~171
Miscellaneous sites [2 tests elsewhere in Pacific (USA), 3 in South Atlantic (USA), 2 at Totsk, Tralsk (USSR)].						492[c] Total	~440	~440

[a] Christmas Island only.

[b] Christmas and Malden Islands.

[c] Totals in other references differ due to inclusion of tests at miscellaneous sites [1 in New Mexico (US), 4 elsewhere in the Pacific (by US), 3 in South Atlantic (by US), 2 at Totsk, Tralsk, Russia (by USSR), 2 combat explosions in Japan (by US), and 39 safety trials (22 by US, 12 by UK, and 4 by France)].

4.3.1 Atmospheric Detonations. Five major nuclear weapon states have been involved in atmospheric nuclear testing: the United States, Russia, France, China, and the United Kingdom. In all, these countries performed 502 atmospheric nuclear weapons tests.[231] With 219 detonations, the former Soviet Union performed the largest number of atmospheric tests. The United States conducted 210 atmospheric tests (excluding the bombs dropped on Hiroshima and Nagasaki) and 5 underwater tests between 1945 and 1962.[230] Of these, 100 tests were conducted at the Nevada Test Site (NTS) (renamed the Nevada National Security Site [NNSS]). The remaining atmospheric tests were conducted in the Pacific Ocean (2 [+2 underwater]), at Bikini Atoll (22 [+1 underwater]), at Enewetak Atoll (41 [+2 underwater]), at Johnston Island (12), at Christmas Island (24), Republic of Kiribati in the South Atlantic Ocean (3), at Nellis Air Force Range, Nevada (5), and in Alamogordo, New Mexico (1). The Trinity test, conducted in Alamogordo, New Mexico, was the first test of a nuclear weapon. Note that the number of atmospheric tests conducted by the United States varies slightly between Ref. 234 and the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR)[231] because of differences in categorization of atmospheric tests.

The former Soviet Union performed atmospheric nuclear weapon tests primarily at the Semipalatinsk Test Site (STS) today located in Kazakhstan (116), at Novaya Zemlya (91), at Kasputin Yar (10) and at Totsk, Tralsk. The United Kingdom performed atmospheric nuclear tests in Australia at the Maralinga (7) and Emu (2) sites and at the Montebello Islands (3), as well as at Christmas Island (6), and Malden Island (3) in the Republic of Kiribati. The 45 French atmospheric tests were performed in Algeria (4) and in Mururoa (37) and Fangataufa (4), French Polynesia in the Pacific Ocean. The 22 Chinese atmospheric nuclear tests were performed at Lop Nor. Following the atmospheric test ban treaty in 1963, the vast majority of testing was performed underground. Only France and China continued atmospheric testing, until 1974 and 1980, respectively. Detailed information can be found in Table 32 of Ref. 231.

The UNSCEAR estimated a global release of plutonium isotopes from atmospheric nuclear testing to be 6520 TBq of ^{239}Pu (2842 kg), 4350 TBq of ^{240}Pu (518 kg), and 1.42×10^5 TBq of ^{241}Pu (37 kg).[231] In general, the pattern of fallout plutonium found in soil and sediment is often similar to that of radiocesium, indicating relatively low and slow mobility of both radionuclides. Plutonium concentration profiles in sediment, ice, and coral cores have been proposed to be used for dating purposes.[235] However, one has to consider that plutonium can be mobilized by particulates and colloids. Notably in organic-rich environments, such as peat bogs, plutonium mobility can be enhanced.[236] Complexation by HA may propagate plutonium to sediment layers that were formed before the nuclear age. In this case, plutonium dating may be erroneous or not feasible.

Concentrations of plutonium dispersed from global fallout into the environment, predominantly within the Northern Hemisphere, are mostly low, and correlate with global precipitation patterns. Elevated plutonium levels are generally seen at accident sites (e.g., Chernobyl). Aerosol records in the stratosphere and the near-surface atmosphere are a good indicator of the evolution of plutonium deposition in the environment.[237] Maximum plutonium concentrations in air were clearly associated with atmospheric weapon testing and dropped significantly in both the stratosphere and the surface air until 1986 (Figure 9). However, since then, no real decrease has been observed and the measured concentrations are characterized by seasonal variations. Apparently, plutonium persists in the air because of resuspension from soil. Interestingly, relatively high plutonium concentrations were measured in the stratosphere between 2007 and 2011, and these concentrations were higher than those in the troposphere.[238] This indicates that aerosol residence times are longer in the stratosphere, where deposition rates are slower than in the troposphere. Global dust outbreaks and biomass burning are also believed to contribute to the persistence of plutonium in air for long time scales.

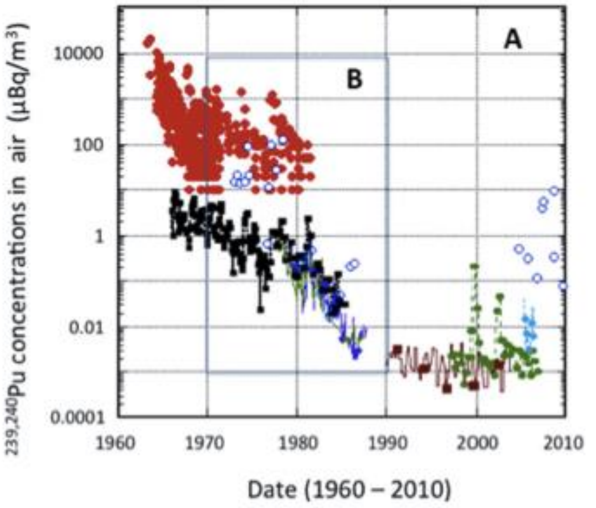


Figure 9. Temporal change of plutonium in the air.[237] Closed red circles: plutonium in the stratosphere (20–40 km height); open blue circles: plutonium in the lower stratosphere (10.1–14.2 km height). Other data points relate to surface air collected at various points in the world (Copyright © 2015, Rights Managed by Nature Publishing Group)

4.3.2 Underground Detonations. Most underground tests had a much lower yield than atmospheric tests, and the debris remains contained so that exposures beyond the test sites occurred only if radioactive gases leaked or were vented.[231] A total of 1,881 underground tests (including 5 in North Korea) were carried out by seven countries (the United States, the former Soviet Union, France, China, the United Kingdom, Pakistan, India, and North Korea).

The United States conducted 828 underground nuclear tests at the NNSS and an additional 11 tests in various locations throughout the United States.[234] A total of 750 underground nuclear tests were performed by the former Soviet Union and 160 tests were performed by France.[231] Most nuclear weapon states concluded their nuclear weapons test programs in the 1990s: the United States in 1992, the former Soviet Union in 1990, the United Kingdom in 1991, France and China in 1996, and India and Pakistan in 1998.[197] More recently, five underground nuclear tests were conducted by North Korea between 2006 and 2016.

4.3.3 Peaceful Nuclear Explosions.

Between 1961 and 1989, the former Soviet Union and the United States performed more than 150 so-called peaceful nuclear explosions (PNEs) for civil economic reasons such as deep seismic sounding; creating lakes, channels, and underground storage cavities, extracting gas and oil, or extinguishing burning gas or oil wells.[231] The PNEs are not qualitatively different from weapons tests but are much smaller in terms of yield and releases beyond sites. The largest PNE was the Sedan nuclear test performed at the Nevada Test Site (NTS, now NNSS) in 1962, creating the Sedan crater, the largest manmade crater in the world (Figure 10A). At the Semipalatinsk Test Site, the elliptical 130 × 40 m Tel’kem 2 test crater created by three bomb explosions is filled with fresh water (Figure 10B).[210]

Figure 10. (A) The Sedan crater at the Nevada Test Site, United States. (B) The Tel’kem 2 crater at the Semipalatinsk Test Site, former Soviet Union. Both were created by nuclear explosions.[210] Figure A reproduced from Ref. 234 with permission from the US Department of Energy.

4.3.4 Safety Tests.

At many test sites, experiments with nuclear materials, such as nuclear weapons, liquids, and solid materials containing radionuclides, including plutonium, were performed in the field for safety reasons. Materials were dispersed at ground level using conventional explosives or fires. Radiologic contamination from these safety tests is heterogeneously distributed, with hot spots containing significant levels of plutonium particles as observed in Mururoa, French Polynesia,[239, 240] and in Maralinga at the Taranaki site, Australia.[127, 241] All test sites remain contaminated with predominantly long-lived fission and activation products, while plutonium contamination is of most concern where safety tests with plutonium sources were performed.

4.3.5 Military Use of Nuclear Weapons. More than 70 years have elapsed since the atom bombs exploded in 1945 at Hiroshima and Nagasaki, the hitherto only case when nuclear weapons were used within a military conflict. About 210,000 people died immediately and many survivors were injured. No weapon-derived plutonium deposition was discovered in Hiroshima, where uranium enriched in ^{233}U was used as fissile material. About 1.2 kg of plutonium underwent fission in Nagasaki, another 14 kg was released into the environment, and 37.5 g was deposited directly in the Nagasaki area.[242, 243] Investigations in the Nagasaki area revealed that isotopic ratios in soil were different from those for global fallout.[244] Isotopic ratios for ^{238}Pu/^{239,240}Pu were 0.05–0.06, for ^{239,240}Pu/^{137}Cs were 0.2–0.3, for ^{241}Am/^{239,240}Pu were 0.04–0.05, and for ^{240}Pu/^{239}Pu were 0.08–0.13, clearly indicating that the origin of the fallout was the bomb dropped in this area. A later analysis of the ^{240}Pu/^{239}Pu isotope ratio yielded a refined value of 0.0283 ± 0.0002 for Nagasaki fallout plutonium.[245]

In field surveys, the highest contamination levels were found in the Nishiyama area. About 95–97 % of the plutonium originating from local fallout found in soil samples has remained in the soil at 0–10 cm depth for decades (Figure 11).[243] A maximum concentration of 1990 Bq/kg plutonium in soil was discovered east of the city,[242, 244] where "black rain" precipitated. Less than 10 % of the deposited plutonium in waterlogged soil and reservoir sediment appears to be mobile.[38, 246] Mobility is mostly due to plutonium binding to colloidal natural organic matter. Interestingly, investigations of plutonium concentrations in tree rings from the site decades after the detonation revealed lower bioavailability of local fallout plutonium than that of later global fallout.[247, 248] The underlying reason is not yet understood but might probably partly be due to a higher fraction of less bioavailable plutonium particles released by the local bomb explosion as compared to the plutonium speciation in the global fallout.

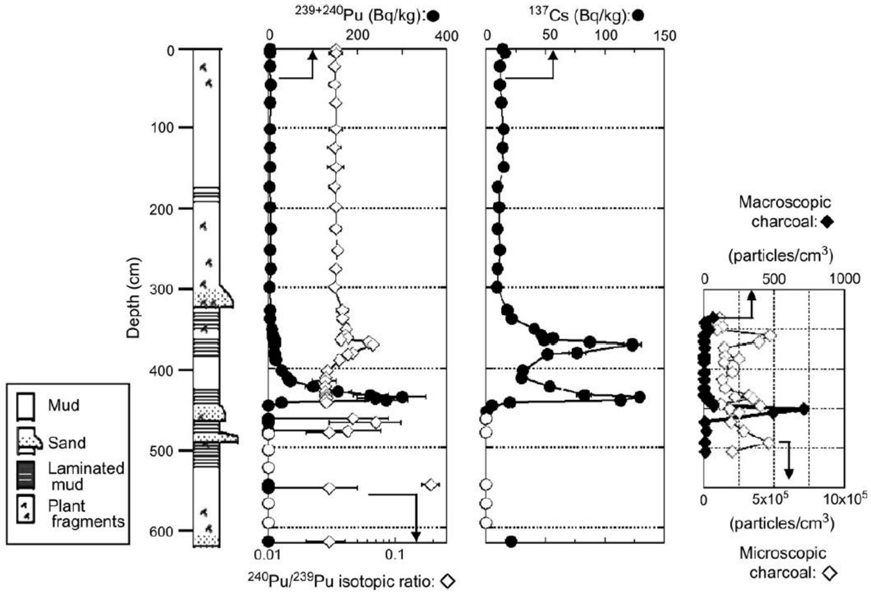


Figure 11. Depth profile of radionuclides from local and global radionuclide (cesium, plutonium) fallout in sediment core from Nagasaki (Nishiyama reservoir). The higher plutonium and cesium peaks at 411–450 cm represent the signature of the Nagasaki bomb detonation fallout coinciding with charcoal particles of "black rain". The increased activities found at a depth of 364–384 cm can be attributed to global fallout radionuclide deposition (Reprinted from Ref. 245. Copyright (2008), with permission from Elsevier).

4.3.6 United States Nuclear Weapons Testing

Most US atmospheric and underground weapon tests were carried out at the Nevada Test Site (NTS) and in the Marshall Islands. The NTS was recently renamed the Nevada National Security Site (NNSS). In addition, the United States carried out 27 PNEs between 1961 and 1973: 4 in Colorado and New Mexico and 23 at the NNSS, where the Sedan crater was created in 1962 (Figure 10). The Plowshare Program that was initiated to utilize nuclear explosions for peaceful purposes during the 1960s and 1970s concluded in 1975.[197, 234, 231] All US nuclear testing locations (excluding Atlantic and Pacific Ocean locations) are shown in Figure 12.

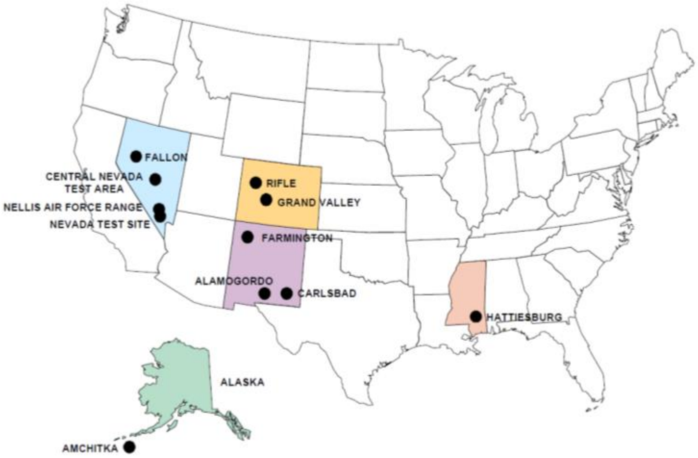


Figure 12. US nuclear test locations (excluding Atlantic and Pacific Ocean locations). Reproduced from Ref. 234 with permission from the US Department of Energy.

Nevada Test Site. At the NTS (now the NNSS), 100 atmospheric tests were performed during 1951–1962 and 828 underground tests were performed during 1951–1992 (Figure 13).[249] Between 1961 and 1992, 52 nuclear tests, the majority of which were located at the NNSS, were designated as resulting in offsite radiologic releases.[250] The NNSS is located in an arid desert environment. Nuclear tests were performed in a variety of geologic environments, including rhyolitic tuff, alluvium, granite, and carbonate, both above and below the groundwater table. However, most were performed in alluvium or rhyolitic volcanic rock. Approximately one-third of the underground nuclear tests were performed below the groundwater table in rhyolitic tuff.

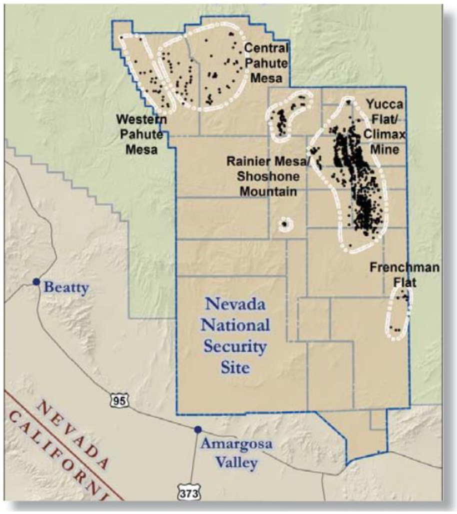


Figure 13. Location of tests at the Nevada Test Site, now the Nevada National Security Site. Reproduced from Ref. 249 with permission from the US Department of Energy.

In surface soils, localized heterogeneities reflected the presence of radioactive particles,[251] and a large variety of fused or partially fused particles as well as large agglomerates consisting of individual small particles differing in color, specific activity, density, and magnetic properties had been identified already in the 1960s. According to Crocker et al.,[209] the particle size distribution depended on device and shot conditions; small spherical, dense particles with activity distributed throughout were observed from high-altitude shots, whereas large irregularly shaped particles containing soil components were observed from ground surface shots. Although measurements were based on gross αs and βs, it is believed that the particles consisted of uranium and plutonium matrices.

Approximately 4.9×10^{18} Bq (decay corrected to 1992) of radioactivity remains in the subsurface of the NNSS, consisting of fission products, activation products, actinides, and tritium.[252] Most of the refractory radionuclides, including plutonium, associated with underground nuclear tests were incorporated into melt glass that formed at the bottom of the underground test cavities.[76] For more information on the phenomenology of underground nuclear tests, see Kersting and Zavarin[253] and references therein.

Because the release of radionuclides from underground tests is typically localized, the exposure dose has not contributed significantly to the total human exposure. Nevertheless, the residual inventory in the subsurface as a result of underground nuclear testing is substantial. For example, underground nuclear testing at the NNSS has left behind 1500 TBq (2.3 kg) of ^{238}Pu, 5900 TBq (2600 kg) of ^{239}Pu, 1600 TBq (180 kg) of ^{240}Pu, 22,000 TBq (5.7 kg) of ^{241}Pu, and 0.6 TBq (4.1 kg) of ^{242}Pu in the subsurface.[252] The release of plutonium into groundwater and the subsequent potential human exposure have been the subject of a number of detailed studies (e.g., Ref. 76). To date, no remediation strategy but only long-term monitoring has been proposed; alternative strategies have been shown to be both financially and logistically infeasible.

In 1999, Kersting et al. measured low levels of plutonium (2.3×10^{-2} Bq) associated with the colloidal fraction of the groundwater 1.3 km downgradient from the original plutonium source.[76] The colloidal fraction consisted of clays and zeolites. Subsequent sampling and plutonium–colloid partitioning measurements have revealed consistent plutonium association with colloids in NNSS groundwater. Thus, it appears that colloid-facilitated transport is the dominant plutonium transport mechanism at this site. Recently, plutonium was detected an additional 0.8 km downgradient from the well originally sampled by Kersting et al.[254] These new data confirm that plutonium is migrating from Western Pahute Mesa in a southwesterly direction in low, but measureable concentrations.

Although colloid-facilitated plutonium transport appears to be the dominant mechanism leading to plutonium migration at the NTS, a unique condition was identified in the tunnel systems of Rainier Mesa (Figure 13). Here, perched vadose zone waters are characterized by high concentrations of dissolved organic matter (DOM) resulting from anthropogenic activities associated with tunnel construction for nuclear testing. Sixty-one nuclear tests were performed in the vadose zone in the zeolitized fractured volcanic tuff in Rainier Mesa.[234] Water samples contained DOM concentrations as high as 15–19 mg of carbon/L (compared to the local spring water concentrations of 0.2 mg of carbon/L).[39] Plutonium concentrations measured in tunnel water ranged from 3.3×10^{-4} Bq/L to 2 Bq/L, significantly higher than those in other contaminated water samples at the NNSS. In addition, less than 10 % of the plutonium detected in the vadose zone water was associated with the colloidal fraction (20–1000 nm).[39] Under the high-organic-groundwater conditions at Rainier Mesa, plutonium migration appears to be associated with the DOM and not with an inorganic colloidal fraction of the groundwater.[254]

The monitoring program at the NNSS includes the analysis of plutonium in groundwater from a large number of wells located on or near the NNSS.[254] Generally, plutonium is detected only in wells drilled directly into the nuclear test source or where significant radiological plumes were identified (e.g., the plume downgradient of the Benham test). Based on 50 recent measurements, only two locations were identified at which plutonium concentrations exceeded the maximum contaminant level for α-emitting radionuclides in drinking water set by the US Environmental Protection Agency (0.55 Bq/L) and reached ~ 2 Bq/L. Based on these analyses, it appears that plutonium release into groundwater as a result of underground nuclear testing is minor. However, continued monitoring is warranted because of the large plutonium inventories present at the site.

Marshall Islands. A total of 66 nuclear tests were conducted by the United States at Bikini (23) and Enewetak (43) Atolls in the Republic of the Marshall Islands, including large-scale thermonuclear bomb tests, ground surface nuclear weapons tests, and safety tests.[234] The atolls were contaminated with actinides and fission products. Simon et al. [255] investigated contaminated surface soils from Rongelap Atoll to determine the spatial distribution of plutonium contamination using α-spectrometry and nuclear track detectors. Significant heterogeneity was observed for the distribution of transuranium elements, and autoradiography of samples from ground surface shots showed large spherical particles (0.5–1 mm) as well as irregular millimeter-sized particles contaminated at the surface. The concentration of ^{239,240}Pu and ^{241}Am increased with decreasing particle size. The presence of low-solubility plutonium particles had already been reported in the 1960s,[209] along with the claim that the characteristics of plutonium-containing particles, such as size distribution, shape, and color, were dependent on the type of weapon device and the shot conditions. Spherical plutonium particles associated with high-altitude shots were inert toward leaching with water, whereas particles associated with debris from coral-surface bursts were relatively soluble in water.

Fragments containing pure plutonium matrices found at Runit Island, Enewetak Atoll, probably originated from the 1958 Quince safety trial.[187] Based on detailed investigation of plutonium-containing particles (Figure 14) collected in the Runit Island soils,[256] two types of particles could be distinguished; small particles with a plutonium matrix and particles in which plutonium was heterogeneously distributed in a glasslike structure. No uranium was observed in the investigated particles. The low ^{240}Pu/^{239}Pu atomic ratio (<0.065) and the low fission product level indicated that the particles were fuel fragments, most likely originating from a safety test or low-yield test. The ^{241}Am/^{239}Pu atomic ratio (3.7×10^{-3}) in particles indicated a 1956 safety test to be the origin.

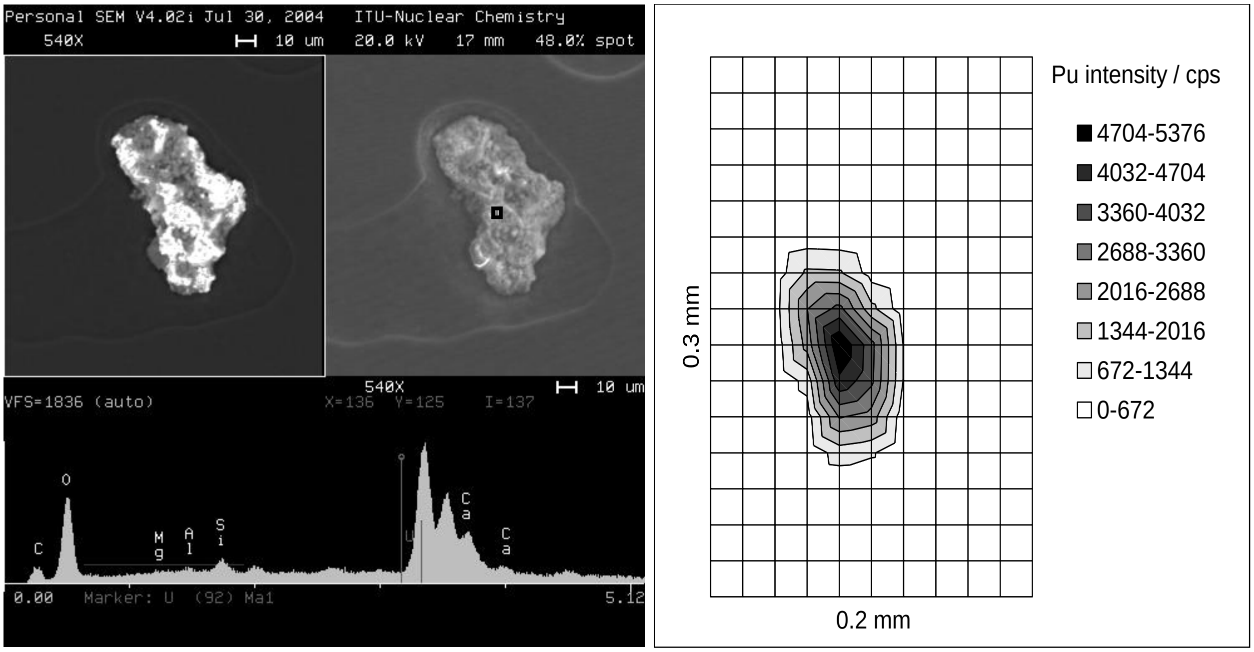


Figure 14. Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDX) spectra of a particle from Runit Island.[256] (A) Two SEM images and the corresponding EDX spectrum; the black square on the particle image (upper part, middle) marks the position where the EDX spectrum was measured. (B) Plutonium Lα X-ray fluorescence intensity distribution in the particle.

In accordance with the measurements of Simon et al.[255] from the Rongelap samples, more than 99 % of the activity was associated with particles smaller than 150 µm. The smallest fraction studied (<40 µm) contained the highest activity. Cleanup of the debris started in 1969, and after a preliminary radiological survey in 1970, the public was allowed to return to Bikini Atoll. However, because of estimated high doses to the public, the population was relocated again in 1978.[255]

Johnston Atoll. During 1958–1975, 12 atmospheric tests (rocket-launched and airplane-dropped) were performed at Johnston Atoll in the Pacific Ocean. In 1962, three nuclear warhead–carrying Thor missiles were aborted and physically destroyed; one on the launch pad and two at altitudes of 9 and 33 km, resulting in contamination of weapon-grade plutonium- and uranium-containing particles throughout the atoll.[174]

"Off-Site" Underground Nuclear Tests. Aside from the NNSS, a number of sites across the United States were used for underground nuclear weapons tests, mostly PNEs. These sites included Amchitka, Alaska; Carlsbad, New Mexico, Central Nevada, Fallon, Nevada, Farmington, New Mexico, Grand Valley, Colorado, Hattiesburg, Tennessee, and Rifle, Colorado. Each site was the location of one to three tests. Thus, the radiological inventories at these sites are small. The US Department of Energy retains responsibility over the environmental management of these sites and has supported the evaluation of contaminant migration.[257]

4.3.7 Former Soviet Union/Russia Nuclear Weapons Testing

Semipalatinsk Test Site. From 1949 to 1989, 456 nuclear weapons tests, with a total yield of 6.62 Mt were performed in the atmosphere (86), above and at ground surface (30), and underground (340) at the Semipalatink test Site (STS), which is located in an arid desert region near Kurchatov City in North Kazakhstan (Figure 15).[258] Uranium was taken from Tajikistan to Mayak (Chelyabinsk-45), where the first reactor operated from December 1948. Half a year later, in August 1949, the former Soviet Union's first nuclear bomb was produced and successfully tested at STS. The first Soviet hydrogen bomb was detonated at the STS in August 1953. After 1963, weapons tests moved underground into the Degelen Mountains (areas G and B: 318 tests; area M: 22 tests).

The atmospheric tests at Ground Zero resulted in widespread contamination of actinides and fission products, and glassified soils can still be seen at the site. Spherical, uniformly colored, reddish-brown or black radioactive particles with optical diameters up to about 15 μm originating from the STS tests were identified in Japan in 1961–1962.[259, 260] Tropospheric transport of radioactive debris from specific low yield nuclear detonations at the STS to Norway has also been demonstrated based on plutonium atom ratios in air filters, air transport models, and real-time meteorological data.[125] Thus, long-distance transport of radioactive debris from the STS to Europe may have occurred at least periodically during 1950–1960 and played a more important role in the radionuclide depositions in Europe than previously assumed.

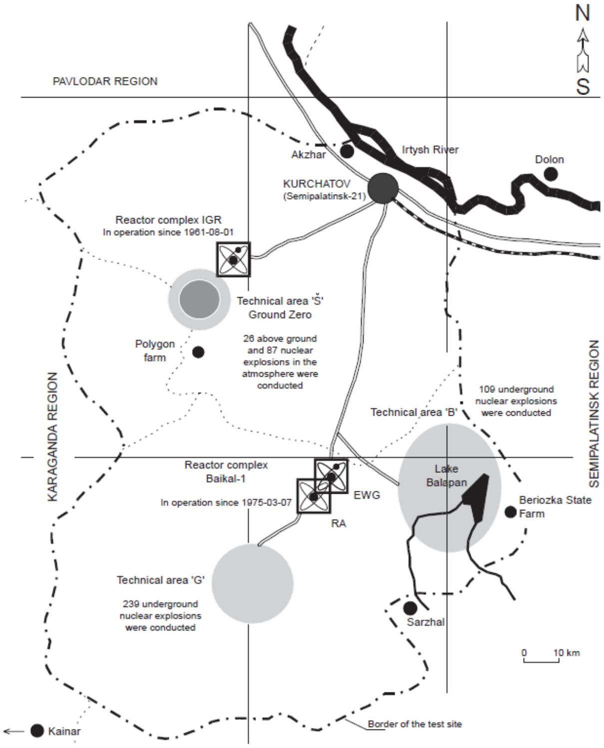


Figure 15. Map of the Semipalatinsk Test Site. Reproduced from Ref. 258

An IAEA survey[258] concluded that the surface contamination of γ-emitting radionuclides was relatively low within most of the STS territory. Localized contamination was seen at Ground Zero, PNE sites, and at the Degelen Mountain because of venting from underground tests. Information on plutonium contamination has been scarce, although Dubasov et al.[261] reported plutonium associated with particles or fragments with activity levels exceeding 50 kBq/kg. Releases from individual tests could also be traced by using the ^{240}Pu/^{239}Pu ratios.[262] Digital phosphor imaging of dried and homogenized surface soils from several detonation sites, such as Ground Zero and the PNE sites, demonstrated highly heterogeneous radioactive contamination.[263] Glasslike vitrified particles were observed in soil samples from the Ground Zero (Figure 16), Balapan,[264] and Degelen[265] sites.

Within the test site, PNEs as well as safety tests were performed. Four different PNE tests were performed; Chagan, Tel’kem 1, Tel’kem 2, and Sary-Uzen. The Chagan test resulted in the formation of Lake Balapan (the Atomic Lake), with plutonium levels up to 20 kBq/kg. The circular Tel’kem 1 (one nuclear device) and the elliptical 130 ×

40 m Tel’kem 2 (three nuclear devices) test craters (Figure 10B) are also filled with fresh water. At the Tel’kem 1 and Tel’kem 2 craters, radioactive particles with uranium and plutonium coexisting in highly concentrated small grains (tens of micrometers in size) were found, as seen in Figure 17.[264]

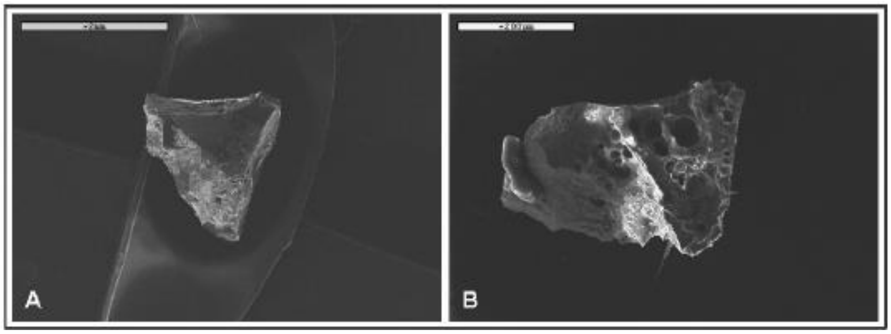


Figure 16. Electron micrographs of large vitrified radioactive particles isolated from Ground Zero, Semipalatinsk Test Site. Low ^{236}U/^{235}U and ^{240}Pu/^{239}Pu atom ratios were determined by accelerator mass spectrometry.[139]

Plutonium concentrations in sediments from Lake Balapan, Tel’kem 1, and Tel’kem 2 are reported to be 2–3 orders of magnitude higher than those in sediments from the surrounding uncontaminated sites. The plutonium concentrations in the <0.45-μm filtered water were 0.0008, 0.1, and 0.059 Bq/L at Balapan Lake, Tel’kem 1, and Tel’kem 2, respectively.[266] Furthermore, the ^{239,240}Pu concentration in filtered well water (<0.45 mm) was 0.0007 to 0.1 Bq/L, median suspended particulate ^{239,240}Pu concentrations were 0.00008 Bq/L, and filtered stream water ^{239,240}Pu concentrations were 0.0006 to 0.03 Bq/L, similar to plutonium concentrations reported in Degelen tunnel waters.[267] Based on present knowledge, the plutonium concentrations in water at both the STS and the NNSS are at trace levels and generally below the radiological limits for drinking water. These low levels reflect the fact that a major fraction of plutonium still is present as inert particles with very low weathering rates.[268]

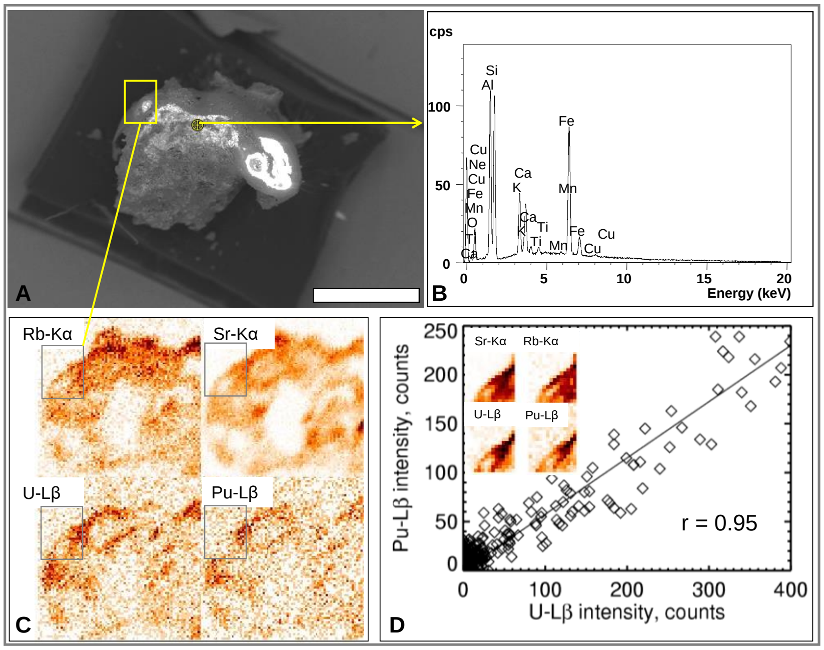


Figure 17. Radioactive particle (not vitrified) isolated from Tel'kem 1 crater soil. The particle contains uranium, plutonium, and ^{241}Am. (A) Scanning electron microscopy (SEM) image of the particle (bar 1 mm). (B) No uranium and plutonium signals are observed at the particle surface by SEM energy-dispersive X-ray spectroscopy. (C) Elemental maps of rubidium, strontium, uranium, and plutonium in the interior part of the particle obtained by confocal μ–synchrotron radiation X-ray fluorescence (SRXRF). (D) Correlation between uranium and plutonium intensities in the individual μ-SRXRF pixels, within the shown rectangles; the correlation between Pu-Lβ and U-Lβ intensities was 0.6.[12]

Novaya Zemlya Test Site. During 1954–1990, 136 nuclear detonations with a total energy yield of about 265 Mt were carried in the atmosphere (91), on ground (39) and under water (6) at Novaya Zemlya Island.[231] Novaya Zemlya is situated between the Barents Sea and Kara Sea in the High North (Figure 18). Although information on plutonium contamination is scarce, contamination with actinides and fission products has been localized to the three major test areas: Chernaya Guba (1955–1962 and 1972–1974), Matochkin Shar (1963–1990), and Sukhoy Nos (1958–1961), which was the site of the 50 Mt Tsar Bomba test performed in 1961. It is assumed that most of the contamination originates from specific events, such as releases from the underwater test in 1955, releases from surface tests at Chernaya Guba in 1957 and 1961, and fallout from the low-altitude atmospheric weapons test in

1957. Venting from underground tests was also observed in Scandinavia in 1990.[269] Three underwater weapons tests (1955, 1957, 1961) and dumping of waste (1991) took place at Chernaya Guba.[270]

According to Smith et al.,[271] sediments from Chernaya Guba were contaminated (up to 8.5 kBq of ^{239,240}Pu/kg and 430 Bq of ^{241}Am), and the total inventory was estimated to be 3 TBq. Localized radioactivity and sample heterogeneity indicated the presence of radioactive particles. During the Kara Sea expedition in 1992, sediment samples were collected from southeast of the Kara Gate. Elevated levels of plutonium were observed, the activity was heterogeneously distributed, and oxidizing agents were needed to leach plutonium from the sediments.[272] The elevated plutonium level was attributed to the nuclear tests at Novaya Zemlya, in particular the Chernaya Guba tests.

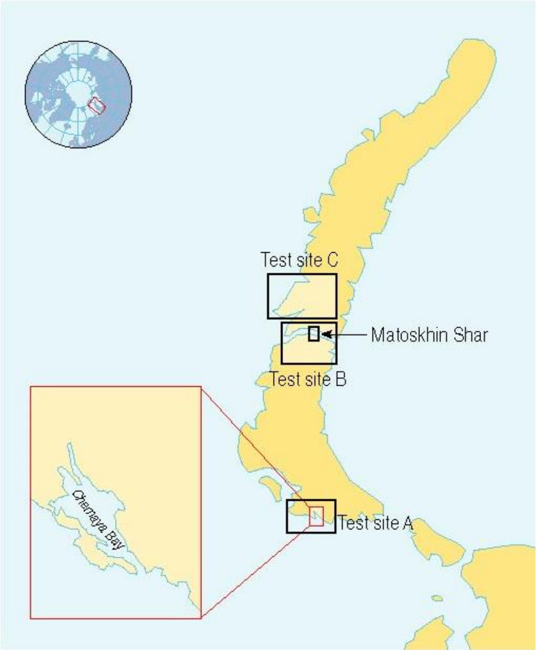


Figure 18. Novaya Zemlya test sites and general boundaries of the testing subareas on the islands.[273]

After the disintegration of the Soviet Union, the test sites have been utilized for subcritical hydronuclear experiments with up to 100 g of weapons-grade plutonium each.[274] Additionally, 129 PNEs have been conducted in different parts of the former Soviet Union, including missile testing in the atmosphere, an atmospheric nuclear explosion near Totsk (Orenburg, Russia), and a near-surface explosion near Aral’sk (Kazakhstan). Information on plutonium released by PNEs in the affected areas is scarce.

4.3.8 United Kingdom Nuclear Weapons Testing

During 1952–1963, 12 atmospheric nuclear weapons tests, with yields up to 100 kt, were conducted by the United Kingdom in Australia (Figure 19).[275] The first test was carried out in 1952 at the Montebello Islands, close to the western coast of Australia. Two more tests followed at Montebello Islands in 1956. Two tests were performed at Emu Field in the Great Victoria Desert in 1953, and seven tests were performed at Maralinga (near Emu), starting in 1956. In addition, several hundred subcritical and safety tests were performed at Emu and Maralinga. Most shots were at low altitude (towers), and actinide contamination was localized. UK performed also 9 atmospheric tests at the Christmas Island and Malden Island, Republic of Kiribati.

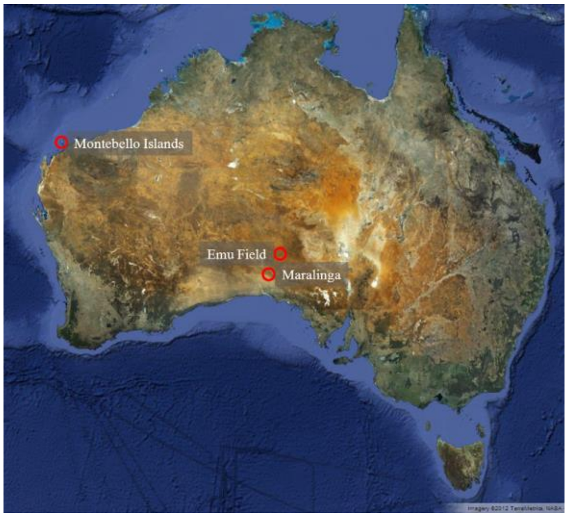


Figure 19. Former British nuclear test sites in Australia.[276]

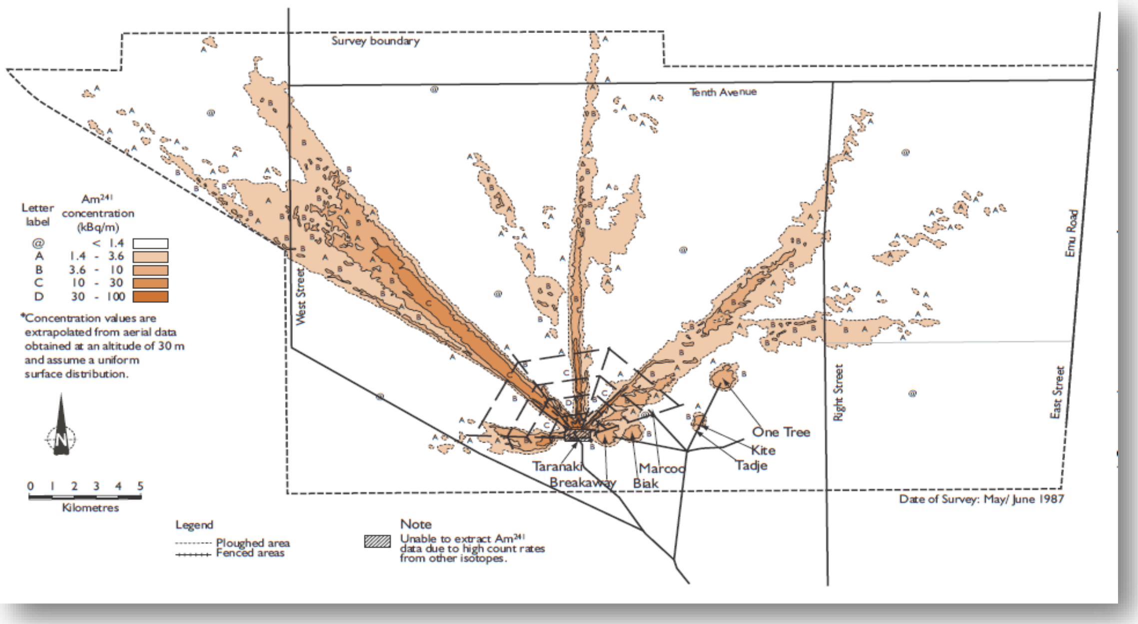


Figure 20. Contamination map of the Maralinga test sites based on a 1987 aerial survey of ^{241}Am (as an indicator of plutonium). The largest plumes are associated with the approximately 22 kg of plutonium dispersed from safety tests conducted at the Taranaki site. The most contaminated areas were remediated in the 1990s.[277]

The major contamination of plutonium at Maralinga (Figure 20) is attributed to the safety trials involving plutonium, in particular the 12 Vixen B trials exploring the effect of TNT explosive detonation of nuclear weapons performed at the Taranaki site.[241, 278] About 22 kg of plutonium and about the same amount of uranium were dispersed to altitudes up to 800 m. Because of wind transport, actinides were dispersed many kilometers downstream from the sites. Based on several investigations of the plutonium contamination,[241, 278] plutonium was present as coatings on remnants of the experimental assemblies (e.g., wires, plastics), as particles up to several hundred micrometers (250–500 µm), as finely dispersed particles (less than 6–7 µm), and as plutonium-contaminated soil particles.[12] One of the largest fragments collected at Taranaki was a 25 × 12 cm steel plate containing 7 GBq of ^{239}Pu.[279] Leaching experiments using a simulated lung fluid demonstrated the presence of inert particles with low solubility, whereas in 0.16 M HCl, mimicking stomach fluid, the solubility varied from 1 to 96 % over a period of 40 days.[127]

4.3.9 France Nuclear Weapons Testing

Algeria. The first French nuclear tests were performed in Algeria, before the test sites in French Polynesia were established. From 1960 until 1966 France performed 17 nuclear tests at the Reggane Oasis and two sites (Adrar Tikertine and Taourirt Tan Afella) in the In Ekker region, Sahara Desert, Algeria.[280] First, there were 4 atmospheric tests at the Reggane Oasis in 1960 and 1961 followed by 13 underground tests from 1961 to 1966 performed in tunnels dug into the Taourirt Tan Afella granite mountain. In addition, 35 experiments were performed on plutonium pellets (ca 20 g Pu per experiment) at the Reggane Oasis between 1961 and 1963. Between 1964 and 1966, five plutonium dispersal experiments involving 20 to 200 g Pu per experiment were performed at Adrar Tikertine. [280]

Following the IAEA 1999 mission, the report [280] documented that the general contamination was low, except for the contamination following the Béryl test in 1962 (residual ^{239,240}Pu activity of 1–2 TBq) and at the plutonium experimental sites. At these sites, radioactive hot spots including particles with diameters less than 50 μm with activity levels up to 10^6 Bq/kg contained most of the plutonium activity.[280] The number of samples was small, however, and the results were probably not representative of the plutonium contamination, especially at the safety trials.

Mururoa Atoll and Fangataufa Atoll, French Polynesia. During 1966–1996, 178 nuclear weapon tests were performed by France at the atolls of Mururoa and Fangataufa in French Polynesia: 41 atmospheric tests during 1966–1974 and 137 underground tests until 1996.[239] In addition, 15 safety trials in which nuclear devices were detonated with conventional explosives to simulate accidents were performed in the Colette region of Mururoa Atoll. Safety trials included the dispersion of about 3.5 kg of ^{239}Pu (metal and oxides).

Based on a 1996 field investigation, an IAEA report[147] showed that the activity concentration levels at the atolls were generally below action levels, except for the plutonium particles originating from the safety trials in the Colette region of Mururoa Atoll. The concentration of ^{239,240}Pu in soil samples ranged from 0.6 to 770 Bq/kg, with hot spots reflecting the presence of plutonium particles at Kilo (Figure 21), the western zone of Fangataufa Atoll. Plutonium concentrations in vegetation ranged between 20 and 250 mBq/kg wet weight. The total inventory of plutonium

(^{238}Pu, ^{239}Pu, and ^{240}Pu) in both lagoons was estimated to be about 30 TBq. The ^{238}Pu/^{239,240}Pu ratio was 0.0044 (n = 18), reflecting weapons-grade plutonium.

The major plutonium contamination was identified in the Colette region at the northern part of Mururoa Atoll and originated from the five safety trials performed on the coral bedrock from 1966 to 1974.[240, 258] According to Danesi et al.,[240] plutonium particles with activities up to 1 MBq and ranging in size from 200 μm to several hundred micrometers were identified at the Colette site. The morphology of the particles varied from glassy, relatively smooth compact surfaces to conglomerates of small particles with rough appearances, and more than 99% of the mass and more than 95 % of the activity were present in particles larger than 250 μm. ^{241}Am peaked at 5.6 kBq and the ^{239}Pu/^{241}Am ratio ranged from 3–67. The activity levels of ^{239}Pu and ^{241}Am in a series of particles ranged from 5 kBq to about 1 MBq and from 0.2 to 5.6 kBq, respectively. One individual particle from Mururoa Atoll was characterized by Eriksson et al.[150] as a plutonium inclusion (~100 μm) attached to a coral matrix. Microtomographic studies revealed that plutonium was heterogeneously distributed within the coral-based particle. According to Danesi et al.,[281] leaching experiments with simulated serum demonstrated the presence of inert particles with low solubility (less than 0.07 %).

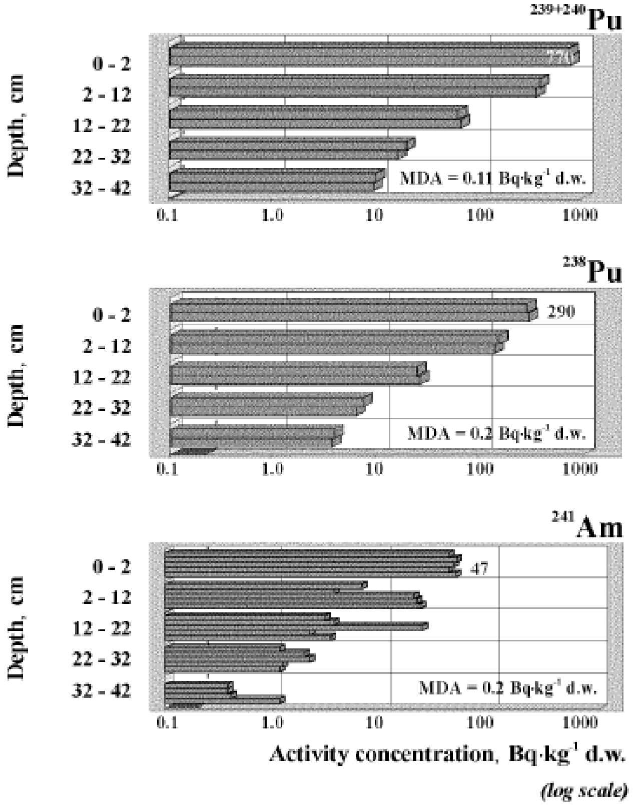


Figure 21. Plutonium and americium activity concentrations in vertical soil profiles from Kilo, Fangataufa Atoll.[240] MDA = minimum detectable activity.

4.3.10 China Nuclear Weapons Testing

During 1964–1996, China carried out 45 atmospheric and underground nuclear tests at the Lop Nor Nuclear Weapons Test Base in northwestern China.[232] The first Chinese hydrogen bomb was detonated in 1967. The atmospheric weapons tests ceased in 1980, and 20 tests were performed underground after that time. The former Soviet Union assisted China in the development of nuclear weapon technology, and it is reasonable to believe that the weapon construction was similar to that of weapons tested at the STS and the Novaya Zemlya site. Fallout from the first test in 1964 (small-scale land surface burst) was identified in Japan 3–4 days after the test as spherical (7–22 μm) radioactive particles.[282]

No information about the local contamination at Lop Nor is available in the open literature. However, regional plutonium deposition has been reported. Heterogeneous soil contamination with ^{240,239}Pu (13–546 Bq/m^2) was observed in the Jiuquan region, downwind from Lop Nor, with ^{240}Pu/^{239}Pu atom ratios ranging from 0.059 to 0.186.[283] Lacustrine sediments in lakes downwind of Lop Nor have also been contaminated by plutonium with a low ^{240}Pu/^{239}Pu atom ratio, probably originating from low-yield nuclear tests at Lop Nor.[284]

4.3.11 India, Pakistan, and North Korea Nuclear Weapons Testing.

During 1974–1998, India carried out six underground nuclear tests at the Pokhran Test Range in the Thar Desert, Rajastan.[285] The first test, Pokhran-I in 1974, was named Smiling Buddha. The Pokhran-II series carried out in 1998 included five nuclear tests (one fusion and four fission devices). Following these tests, sanctions against India were installed. Pakistan conducted six underground nuclear tests during May 28–30, 1998. Between 2006 and 2016, North Korea conducted five underground nuclear tests at its Punggye-ri Nuclear Test Site. In October 2006, a nuclear test was reported by North Korea. Based on seismic responses and measurements of radioactive noble gases, the test was assumed to be real. North Korea reported additional nuclear weapons tests in 2009, 2013, and 2016. In all cases, the tests are assumed to be performed in desert areas, but no information on plutonium contamination is presently available in the open literature.[286]

5. ACCIDENTALLY RELEASED PLUTONIUM AND ENVIRONMENTAL CLEANUP

Globally, and especially in the Northern Hemisphere, anthropogenic actinides such as plutonium originate primarily from nuclear weapons tests. The following section describes events in which plutonium was released into the environment from sources other than nuclear weapons tests.

5.1 Accidental Releases from Nuclear Power Plants

Today, more than 440 nuclear reactors are in operation, and despite the Chernobyl and Fukushima accidents, new nuclear power plants are under construction or planned. Accidents have mostly occurred in prototype and Generation I reactors. Generation III plants exhibiting significantly higher safety standards have been and are being constructed, and Generation IV reactors are in a planning state.

5.1.1 United Kingdom: Windscale Piles.

During 1951–1957, two air-cooled graphite-moderated uranium reactors (Piles 1 and 2) operated at the Windscale works site on the east coast of England. The piles were producing plutonium for the UK weapons program (Figure 22). The reactor fuel in each reactor pile consisted of 180 metric tons of uranium metal. Atmospheric releases of spent fuel particles were already observed in the mid-1950s. Because of oxidation and corrosion of spent U–Al fuel elements misplaced in the air-cooled ducts leading to a discharge stack with an inefficient filtering system, fuel particles containing actinides and fission products were continuously dispersed and released to the local environment. Over the years, the total release has been estimated to be about 20 kg of uranium as particles containing plutonium, up to 700 μm in length.[287, 288] Based on electron microscopy, the fuel particles had a flakelike structure, significantly different from those observed in Chernobyl fallout.[55, 289]

Figure 22. The Windscale Piles at Sellafield, United Kingdom, in 1950, looking northwest. Pile 1 is in the background. Reproduced from Ref. 290.

In October 1957, a fire in Pile 1 led to the largest accidental release of radioactivity in the history of the nuclear industry in the United Kingdom.[291] Part of the core was overheated and fuel and graphite burned in the air-cooled ducts, as described in detail by Arnold.[292] In the ensuing fire, volatiles, some of the fission products and activation products were released into the atmosphere.[290] The majority of the radiological emissions of 3.8×10^{15} Bq consisted of ^{133}Xe, ^{3}H, and ^{131}I.[290] Following the fire, about 0.02 TBq (8.7 g) of ^{239}Pu was released, probably associated with irradiated fuel particles. These particles were observed as localized heterogeneities by autoradiography of samples taken from the stack filters, contaminated surfaces, outside the reactor, and contaminated soils.[293, 294] Particles in the size range 20–500 μm were observed up to 4 km from the site, but were considered of little relevance to public health.[295] The radioactive plume containing volatiles (e.g. ^{131}I) was transported east over Belgium, Holland, and

Germany and north to Scandinavia.[296] Both reactors were permanently shut down following the fire and the majority of the fuel was removed from both reactors.

5.1.2 Canada: Chalk River Laboratories.

Chalk River Laboratories of Atomic Energy of Canada Limited on the Ottawa River has two large nuclear research reactors: NRX, which operated from 1947 to 1991, and NRU, which continues to operate (Figure 23). Accidents occurred at the NRX reactor in 1952 and at the NRU reactor in 1958. Trace concentrations of radionuclides, presumably including plutonium, were released into the environment from the "once-through" cooling system of the research reactor. Trace levels of radionuclides (primarily ^{137}Cs and ^{60}Co) are detectable as far as 2 km downstream from the site and can be attributed to the Chalk River Laboratories reactors. So far, no plutonium releases have been officially reported.[297]

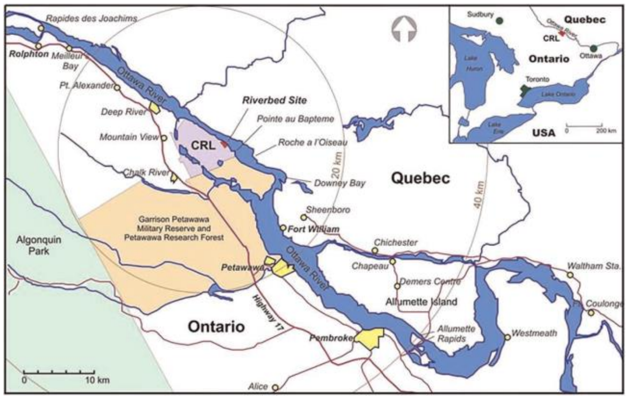


Figure 23. Chalk River Laboratories in Ontario, Canada.[297]

5.1.3 United States: Three Mile Island.

On March 28, 1979, the Three Mile Island Unit 2 reactor, located near Middletown, Pennsylvania, partially melted down. This remains the most significant commercial nuclear power plant accident in the United States. Because of solid containment construction, the releases were mainly restricted to volatiles: an estimated 1.3×10^{15} Bq of ^{85}Kr and 5.9×10^{11} Bq of ^{131}I were emitted from the fuel elements. Actinides were not released in measurable quantities, but remained in the intact and melted core. The melted core debris was shipped to the Department of Energy Idaho National Laboratory (INL).[298, 299]

5.1.4 Former Soviet Union/Ukraine: Chernobyl.

The most serious accident and the most extensive release of radioactivity into the environment in the history of nuclear power occurred at the Chernobyl nuclear power plant, located approximately 100 km north of Kiev, Ukraine. At the time of the accident, about 5.37×10^{6} Bq (8×10^{-6} g) of ^{238}Pu, 4.54×10^{6} Bq (2×10^{-3} g) of ^{239}Pu, and 6.33×10^{6} Bq (8×10^{-4} g) of ^{240}Pu per gram of UO_2 were inventoried in the reactor fuel.[300] On April 26, 1986, two explosions destroyed the core of Reactor 4, and the subsequent fire severely damaged the reactor building. Large amounts of volatile radionuclides, such as noble gases, ^{131}I, ^{134}Cs, and ^{137}Cs, as well as 3–4 metric tons of irradiated UO_2 fuel were released during the explosion and the subsequent graphite fire. Approximately 10 days after the accident, the reactor core was covered by Pb containing cement. Based on the most comprehensive survey and monitoring program, Kashparov et al.[302] estimated that about 1.5 % of the core inventory was released: 20 TBq of ^{238}Pu, 15 TBq of ^{239}Pu, 23 TBq of ^{240}Pu, 3000 TBq (1.4 kg) of ^{241}Pu, and 0.04 TBq of ^{242}Pu.[268] This estimate is 2-3 times lower than the previous widely-cited estimates.[301, 302] About 98 % of the transuranium elements (approximately 190 metric tons of irradiated UO_2 fuel with more than 700,000 TBq total activity) was captured in the cement sarcophagus.[300, 303]

Following the initial explosion, wind carried the radioactive plume west towards Poland and Scandinavia. Radionuclides emitted into the air by the subsequent fire were transported to the north and then east and south, contaminating large areas in Europe (Figure 24). About 70 % of the radioactivity released was deposited in Belarus. In the Baltic Sea, an estimated 0.001.5 TBq of ^{239,240}Pu was deposited as a result of the Chernobyl event, which accounted for <10 % of the total plutonium inventory in the Baltic Sea (~0.0165 TBq, as a result of global fallout from the atmospheric nuclear testing source term).[304] The highest airborne plutonium activity measured over Austria was 9×10^{-5} Bq of ^{239,240}Pu/m^3 on May 3, 1986.[305]

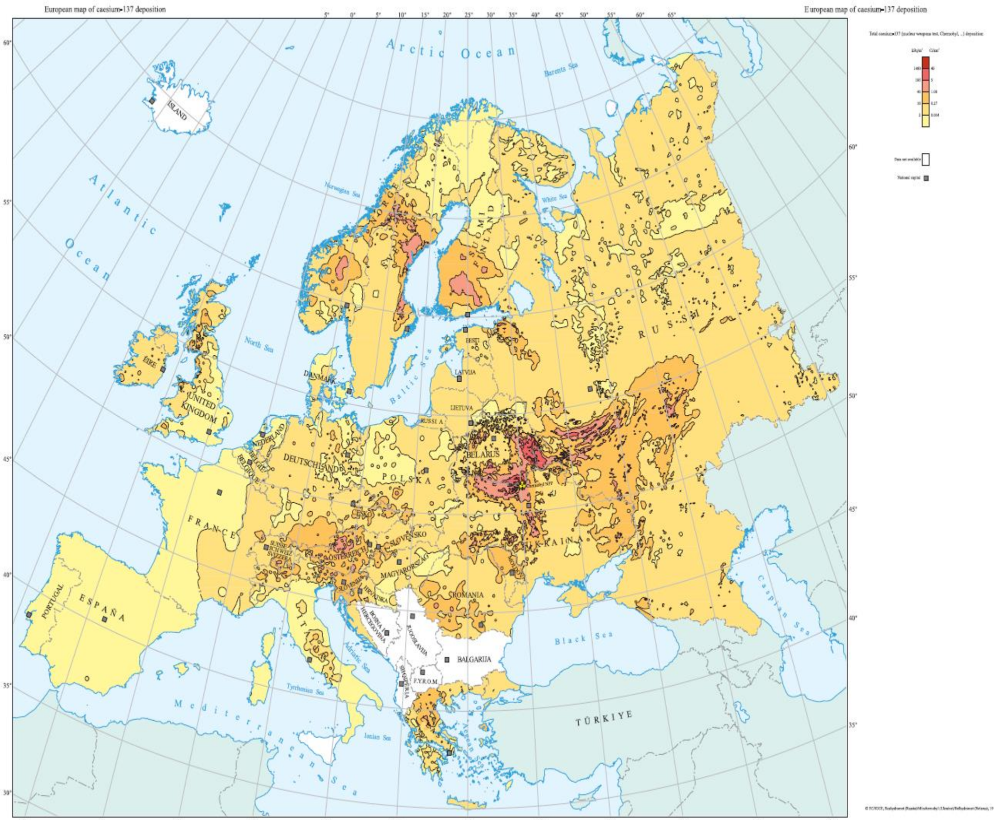


Figure 24. Cesium-137 deposition across Europe as a result of the Chernobyl accident.[306]

In 2000, Kashparov et al.[307, 308] produced detailed integrated maps of the radionuclide deposition, including the terrestrial density of plutonium contamination, at the Chernobyl nuclear power plant (Figure 25).

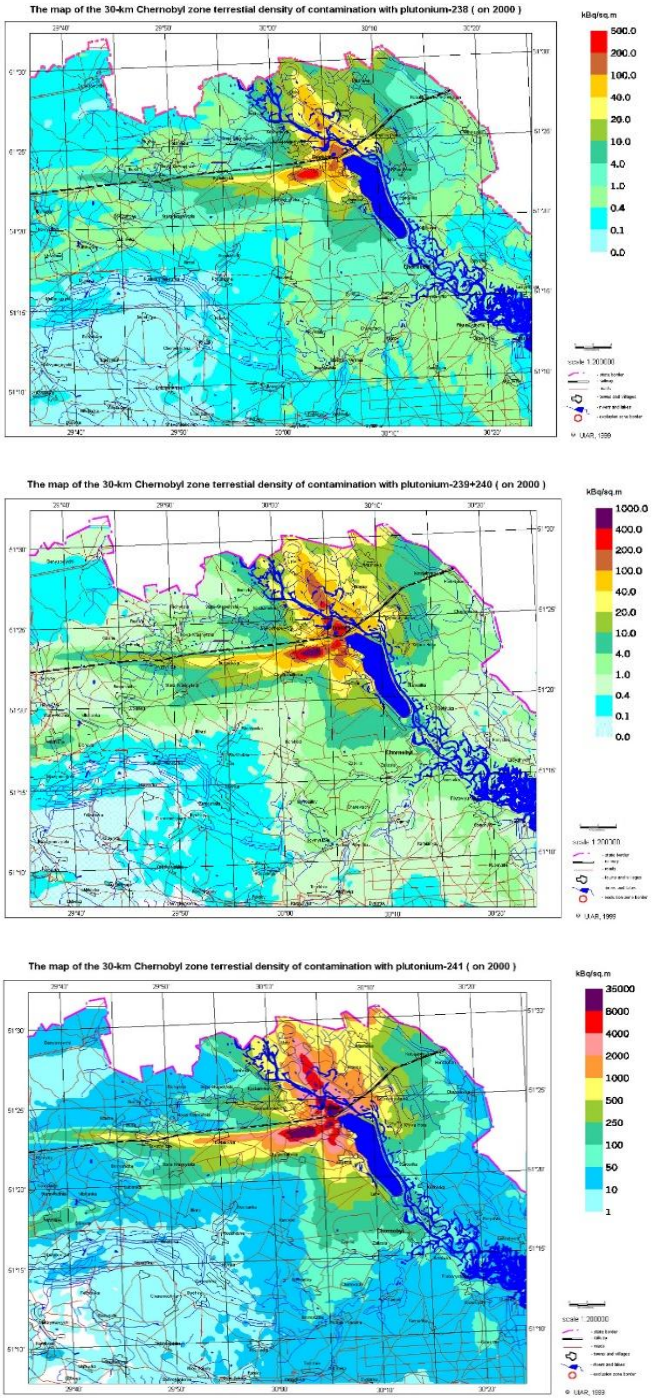


Figure 25. Integrated map of the terrestrial density of contamination of the Chernobyl nuclear power plant near zone with ^{238}Pu (A), ^{239,240}Pu (B), and ^{241}Pu (C) in kBq/m^2 in the year 2000.[308]

Radioactivity levels of plutonium reached 0.09 TBq/km^2 within a 1-km radius around the Chernobyl site, gradually decreasing to about 0.07 TBq/km^2 within a radius of 15–30 km. Recently, the contamination level of ^{239,240}Pu in soils was reported to be as high as 0.74 TBq/km^2 within the 30-km exclusion zone.[303]

A substantial fraction of refractory radionuclides was released into the atmosphere as radioactive particles, which were detected repeatedly,[309-311] even in Scandinavia about 2000 km away from the site.[55, 312] Six classes of particles have been identified, ranging from pure fuel particles to condensation particles where volatile radionuclides deposited on available particle surfaces (e.g., fly ash) during release and transport.[303] Grains of irradiated UO_2 fuel containing fission and activation products as well as transuranics, ranging from submicrons, to fragments were released from the damaged reactor.[313] The majority of the released plutonium was deposited as particle aggregates and fragments particulate in the close vicinity of the Chernobyl reactor (Figure 25).

During the explosion, the apparently reduced uranium fuel particles containing actinides, fission products, and activation products released during the initial explosion were quite inert (e.g. UZrOx) with very low weathering rates. In contrast, uranium in the fuel particles released during the subsequent fire was oxidized (e.g., to U_3O_8), so these particles were more soluble with higher weathering rates, as illustrated in Figure 26.

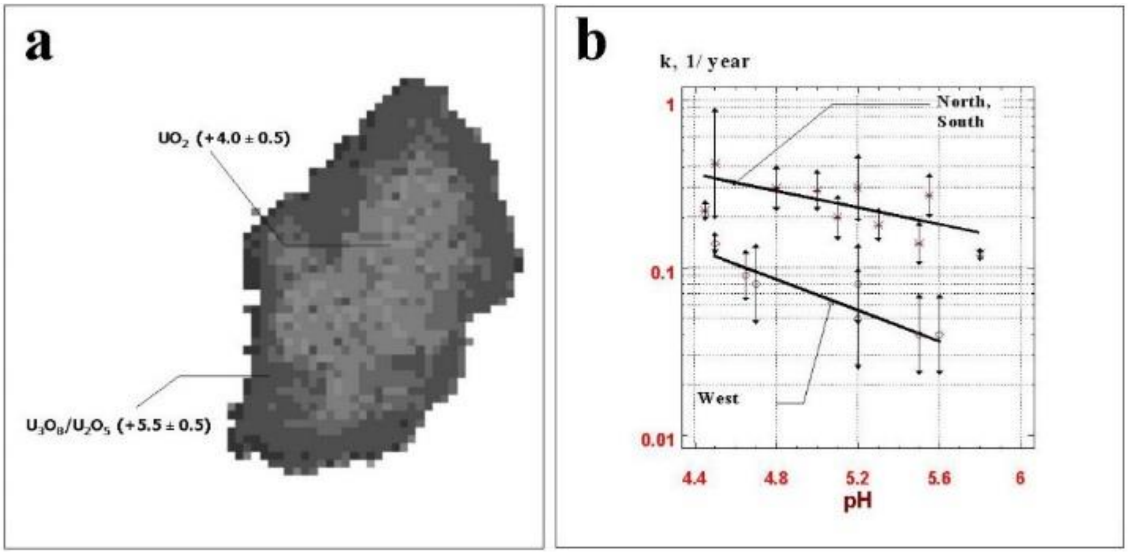


Figure 26. (A) Oxidized fuel particle (UO_2 cores with oxidized U_3O_8 and U_2O_5 layers) released during the reactor fire obtained from two-dimensional uranium L_3 micro–X-ray absorption near-edge spectroscopy.[314-316] (B)

Weathering rate constants as functions of pH for fuel particles released during the explosion (lower line) and during the fire (upper line).[317]

The particle weathering rate constant (k, 1/y) of uranium fuel particles in Chernobyl ranged from 0.04 to 0.4 1/y, reflecting the fact that the weathering rates were related to particle characteristics as well as soil pH.[317] Although all particles were released from the same source, i.e., the Chernobyl reactor, the different release scenarios resulted in inert fuel particles (explosion-related) with low weathering rates and low ecosystem transfer to the West of the reactor and quite soluble oxidized uranium fuel particles (fire-related) with high weathering rate and rapid ecosystem transfer to the North of the site.

Many investigations into plutonium migration patterns at the Chernobyl site have been reported. For example, soils from a 30-km exclusion zone surrounding the Chernobyl nuclear power plant were studied over a 10-year period after the accident (Figure 25).[318] The majority of plutonium in sandy and podzolic soils was located in the top surface layer, whereas vertical migration of plutonium to a depth of 10–15 cm was observed in peat soils. Results of sequential extraction demonstrated that plutonium was released from the slowly dissolving "hot" particles and subsequently associated with mobile organic substances within the peat soils. Similarly, plutonium in lake and river water within the 30-km exclusion zone surrounding Chernobyl appeared to be dominated by association with DOM.[33] Levchuk et al. studied the migration of plutonium from a disposal trench from the Red Forest area near Chernobyl.[319, 320] Plutonium was found in groundwater at significant distances from the trench. Using ultrafiltration, it was demonstrated that a large fraction of plutonium in groundwater appeared to be soluble. It was suggested that, as in other locations, plutonium migration was occurring because of association with LMM natural organic compounds.[320]

5.1.5 Japan: Fukushima.

On March 11, 2011, a 9.0-magnitude earthquake occurred near Honshu, Japan. The earthquake and subsequent tsunami, which flooded more than 500 km^2 of land, resulted in the loss of more than 20,000 lives and destroyed property, infrastructure, and natural resources. It also led to the worst accident within the nuclear power industry since Chernobyl.

Fukushima Daiichi power plant situated at the North Pacific coast, north of Tokyo, includes 6 boiling water reactors (BWR). At the time of the accident, on 11 March 2011, reactors 4, 5 and 6 were shut down in preparation for re-fueling, while storage of fuel in pool still required cooling. Immediately after the earthquake, the reactors 1-3 were shut down and emergency generators were in function. Because of flooding of 10 out of 12 emergency generators (2 survived serving units 5 and 6), loss of off-site and on-site electrical power occurred and compromised safety systems at the Fukushima Daiichi Nuclear Power Station (FDNPS). Insufficient cooling led to three hydrogen – air explosions, and radioactivity releases from reactors 1, 2 and 3 occurred from March 12-15. Due to loss of coolant of the storage pool, overheating of spent fuel rods occurred in 15 March. The loss of coolant and the hydrogen explosions led to severe core damage to three of the four nuclear reactors on the site and to damage of fuel storage vessels. This resulted in the release of large amounts of volatile radioactive material (e.g., noble gases and iodine, cesium, and strontium isotopes) into the environment (Figure 27).[321, 322]

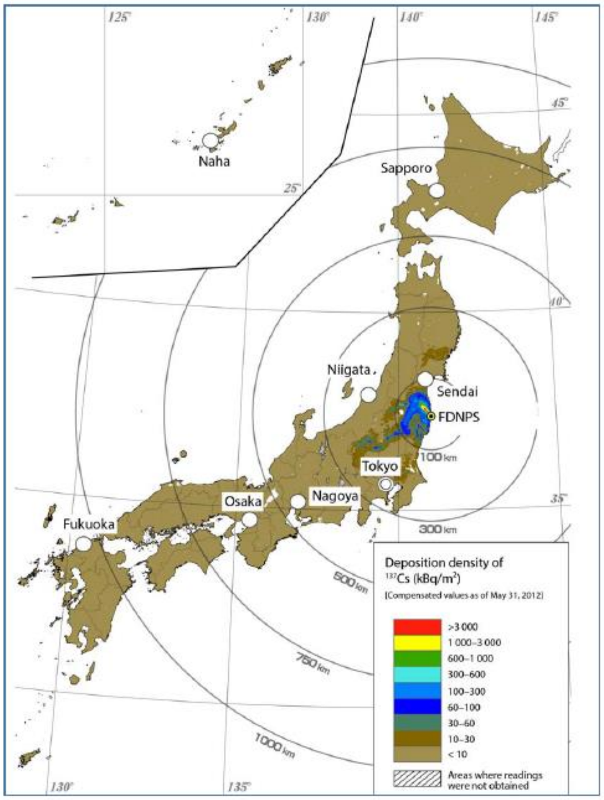


Figure 27. Cesium-137 deposition across Japan as a result of the Fukushima Daiichi Nuclear Power Station (FDNPS) accident.[322]

Most of the fuel assemblies in the FDNPS reactors were UO_2. However, in the Reactor unit 3, 32 MOX fuel assemblies containing ~6 % plutonium were present. In total, the three operating reactors contained 256,000 kg of nuclear fuel. Spent fuel pools in the four damaged reactor buildings contained an additional 461,000 kg of nuclear fuel. The largest spent fuel pool, located in the Unit 4 reactor building, contained 1331 spent nuclear fuel assemblies.[302]

Following the accident, most emphasis was put on contamination associated with radioactive Cs- and I- isotopes. A recent review of plutonium contamination as a result of the FDNPS accident summarized the rather limited information available.[302] Although ^{239,240}Pu activity in most surface soils appears to be consistent with background levels associated with global fallout, a few Pu isotope ratio measurements suggest that some plutonium was released into the environment as a result of the FDNPS accident. Black-colored road dust material highly contaminated with radionuclides including plutonium originating from the FDNPS accident has been reported in Japan after the Fukushima accident.[323] Analysis of ^{241}Pu in soil litter and river sediment samples indicated that plutonium from the FDNPS accident had migrated ~45 km from the site.[324] Following hydrogen explosions, plutonium should potentially be released as fuel particles. So far plutonium is not observed in the low-level radioactive cesium-bearing particles claimed to have originated from the damaged Fukushima reactors.[325, 326] Due to run-off from the reactor site, emphasis has also been put on the marine environment. So far, plutonium contamination of the marine environment appears to be rather limited, and the ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu atom ratios in sediment cores 5 km from the FDNPS site are not distinguishable from those of global fallout and Pacific Proving Ground close-in fallout background.[327]

A comparison of the plutonium inventories and releases from the Chernobyl and Fukushima accidents indicates that plutonium releases at Fukushima were orders of magnitude lower than those at Chernobyl (Table 16) and that only trace quantities of plutonium were potentially released from the Fukushima accident (during the venting of Units 1 and 3).[328] It was estimated that ~2-5 × 10^{-5} % of the core plutonium inventory was released into the environment at Fukushima, compared to ~ 1.5 at Chernobyl.[302, 329,303] The amount of plutonium remaining in the damaged reactor cores and spent fuel pools at Fukushima, thus, exceeds that at Chernobyl by far.[302, 330] At Fukushima, it is assumed that the majority of plutonium contamination is localized within a few tens of kilometers of the FDNPS site.[302, 331]

Table 16. Plutonium Inventory and Relative Percent Release into the Environment from the Fukushima Accident.

	Fukushima[302]			Chernobyl[303]	
	Inventory[a]	Released		Inventory	Released
	Bq	Bq	%	Bq	%
^{238}Pu	1.1×10^{16}	$(2.9–6.9) \times 10^{9}$	$(2–5) \times 10^{-5}$	$(8.2\text{-}13) \times 10^{14}$	1.4±0.5
$^{239+240}$Pu	8.3×10^{15}	$(1.0–2.4) \times 10^{9}$	$(1–3) \times 10^{-5}$	$(2.1\text{-}2.8) \times 10^{15}$	1.4±0.5
^{241}Pu	7.0×10^{17}	$(1.1–2.6) \times 10^{11}$	$(2–4) \times 10^{-5}$	$(1.7\text{-}2.1) \times 10^{17}$	1.4±0.5

[a] Reactor 1, 2, 3

5.2 Releases from Nuclear Reprocessing, Research and Disposal Facilities

Beside releases from weapon tests and reactor accidents, plutonium releases to the environment have resulted from intentional discharges of liquid-waste streams from industrial-scale nuclear reprocessing facilities to seas, lakes, rivers, and unlined soil trenches. The most prominent nuclear material processing facilities have been the Hanford, Rocky Flats, and Savannah River Sites in the United States; Sellafield and Dounreay in the United Kingdom; La Hague and Marcoule in France; and PA Mayak (formerly Chelyabinsk-65), the Mining and Chemical Combine (MCC) (formerly Krasnoyarsk-26), and the Siberian Chemical Combine (SCC) (formerly Tomsk-7) in the former Soviet Union. Most of these facilities were established to process spent nuclear fuel for the separation of plutonium for nuclear weapons programs, although facilities such as Rocky Flats were designed for the processing of plutonium for the manufacture of weapons. Most of the radioactivity releases reported in the open literature concern ^{137}Cs, ^{90}Sr, ^{24}Na, ^{131}I, and some other fission products; reliable data on actinide releases remain fragmented.

During reprocessing of spent nuclear fuel to recover uranium and plutonium for civil or military use, the spent fuel is brought into solution. Reports on uranium fuel particles found in the vicinity of reprocessing sites indicate that the dissolution of fuel may have been incomplete and that residual fuel fragments and particles are released through discharges, making up an important part of the source term.[332-335] The following sections summarize information about the most prominent nuclear energy production, reprocessing, and manufacturing facilities that have contributed to the release of plutonium into the environment.

5.2.1 United Kingdom: Sellafield Nuclear Installation.

The site at Sellafield (formerly Windscale) is the largest nuclear complex in the United Kingdom.[336] Spent fuel elements were initially stored in various open water-filled ponds and later stored in enclosed ponds awaiting reprocessing. The storage facilities have increased in complexity over time.[336] Discharges of radioactive effluents have taken place since the inception of the complex in 1951.[337] Most of the low-level radioactive liquid wastes, including plutonium, were released via effluent pipelines reaching 2.5 km into the Irish Sea. The majority of this liquid waste was from reprocessing operations and fuel storage ponds. Peak releases occurred in the 1970s and early 1980s, after which significant improvements in predischarge treatment (e.g., flocculation, evaporation) led to substantial reductions in plutonium releases to the Irish Sea (Figure 28). Based on the data from Ref. 336, total plutonium released via effluent discharges is 120 TBq (0.2 kg) of ^{238}Pu, 620 TBq (270 kg) of ^{239}Pu, and 22,000 TBq (5.7 kg) of ^{241}Pu.

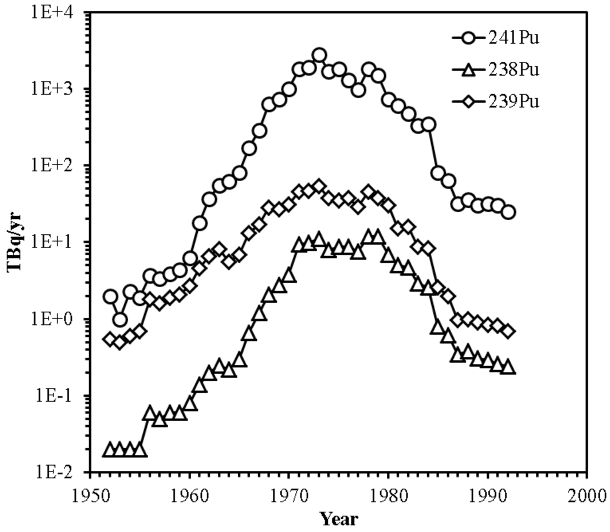


Figure 28. Effluence releases of plutonium from the Sellafield site to the Irish Sea. Data from Ref. 336.

Annual atmospheric releases from the Sellafield site have been documented using air sampling data and transport simulation.[336] Direct atmospheric release of plutonium was dominated by releases from reactor stacks. Releases were distinguished between near-surface sources (~10 m) and stack releases (~80 m) (Figure 29). Between 1952 and

1992, 3.6 TBq (1.6 kg) of ^{239}Pu and 23 TBq (6 g) of ^{241}Pu were released at about 80 m above ground and 0.076 TBq (30 g) of ^{239}Pu and 1.1 ^{T}Bq (0.3 g) of ^{241}Pu were released at about 10 m above ground. Both sources of atmospheric release are more than 2 orders of magnitude smaller than the liquid releases to the Irish Sea.

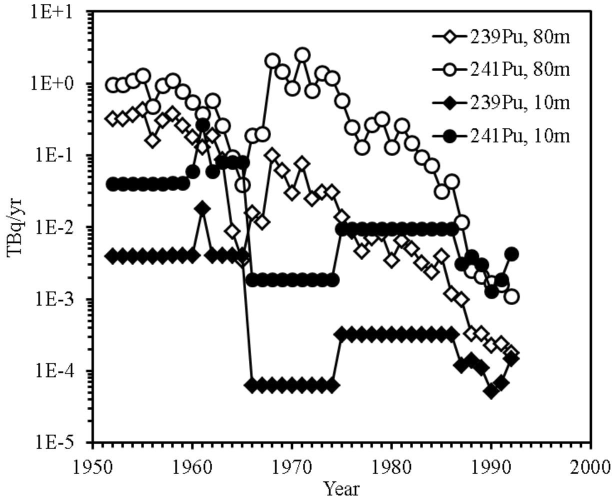


Figure 29. Atmospheric releases of plutonium from the Sellafield site from 1952 to 1992 at 10 m and 80 m above ground surface. Data from Ref. 336.

The discharges from Sellafield into the Irish Sea amounted to about 1300 TBq between 1950 and 1992, including significant amounts of ^{238,239,240}Pu (720 TBq.)[54] The releases of α-emitters from Dounreay and La Hague (discussed later in this section) were about 0.5 % and 1.5 % of the release from Sellafield, respectively. Speciation studies of the Sellafield and La Hague effluents demonstrated that a major fraction of the radionuclides were released as particles and colloids.[54, 132] The fate of plutonium released from the Sellafield site has been the subject of numerous investigations (e.g., Refs. 337, 338). They include modeling the partitioning and distribution of plutonium in the vicinity of the Sellafield site,[339] exposure pathways,[340] and the biogeochemical mechanisms controlling plutonium redistribution in seawater and sediments. For example, Nelson and Lovett[21] determined the concentration of plutonium and its oxidation states in samples of seawater in the coastal waters and in the open part of the Irish Sea. Broadly, the dissolved form of plutonium has been found to be predominantly in the Pu(V,VI) oxidation state, whereas plutonium bound to colloidal and suspended particles was in the reduced forms of Pu(III, IV).[341]

The fractionation and speciation of plutonium in bottom sediments from the Ravenglass Estuary in the northeastern Irish Sea were studied by Lucey et al. and others.[338, 342] The vertical distribution profile of plutonium in bottom sediments exhibited an increase in total plutonium concentration with depth and correlated with the intensity of plutonium's release in this region.[342] Hundreds of large radioactive particles with radioactivity inventories in the MBq range have also been identified in the coastal beaches at Sellafield, reflecting previous releases and the 1957 accident. Radioactive particles with uranium matrices have also been isolated from Irish Sea sediment cores by Jernström et al.[256] and from Ravenglass Estuary sediments by Lind et al.[139] The origin of these uranium matrix particles is assumed to be the fuel-rod decanning process at Sellafield. Radioactive particles in the Irish Sea sediment were also studied by Hamilton[343] in the 1990s, and it was recognized that a significant part of the actinides were attached as coatings to iron minerals, such as magnetite and hematite.

Over time, sediments in the Irish Sea, especially those in the mud patch outside the pipeline, have acted as a sink for radionuclides released in effluents. The sediments are heavily contaminated, partly because of sedimentation of particles. However, because of remobilization of plutonium, these contaminated sediments act as a diffuse source, and Sellafield-derived plutonium is being transported out of the Irish Sea via the North Channel and towards the North Sea.[26, 341]

5.2.2 United Kingdom: Dounreay Nuclear Power Development Establishment.

The UK Atomic Energy Authority's former fast-reactor research establishment at Dounreay, Caithness, northern Scotland, was opened in 1955, and about 10 PBq total activity was discharged until decommissioning in 1994.[344] Hundreds of highly radioactive (MBq) particles have been found on the foreshore at the facility and on neighboring beaches during the years (about 10 -15 particles per yr). Accidental releases of small pieces (typically 0.2–2 mm) of fuel material to the marine environment occurred during reprocessing operations involving irradiated spent fuel, which took place during 1960–1970.[332] The radionuclide composition in these particles is dominated by the U–Al matrix, and the particles also contain fission products and transuranic elements, such as plutonium and ^{241}Am.[345]

5.2.3 France: Marcoule Nuclear Site.

The Marcoule site was created in 1955 for plutonium weapon production and fuel reprocessing. Reprocessing of nuclear fuel for military purposes at Marcoule resulted in significant releases between 1961 and 1969 and between 1975 and 1991. Annual discharges into the Rhône River of (0.7–4) × 10^9 Bq of ^{238}Pu and up to 7 × 10^{10} Bq of ^{239,240}Pu in the 1960s and of approximately 6 × 10^9 Bq of ^{238}Pu and 2 × 10^{10} Bq of ^{239,240}Pu between 1978 and 1991 were reported.[346] Effluent treatment after 1991 led to a decrease of 2 orders of magnitude in the industrial plutonium discharge to the Rhône River[347] (Figure 30). The reprocessing facility is now undergoing a complex dismantling and cleanup effort.

The Rhône River also receives plutonium from the weathering of surface soils within its basin. These inputs have decreased from 1.8 × 10^{10} Bq/y of ^{239,240}Pu and 5 × 10^8 Bq/y of ^{238}Pu in 1960 to 8 × 10^8 Bq/y of ^{239,240}Pu and 3 × 10^7 Bq/y of ^{238}Pu at present. Between 1945 and 1998, the Rhône River received a total of 0.54 TBq (~0.2 kg) of ^{239,240}Pu and 0.09.5 TBq (~0.2 g) of ^{238}Pu, of which more than 80 % was derived from the Marcoule site.[347]

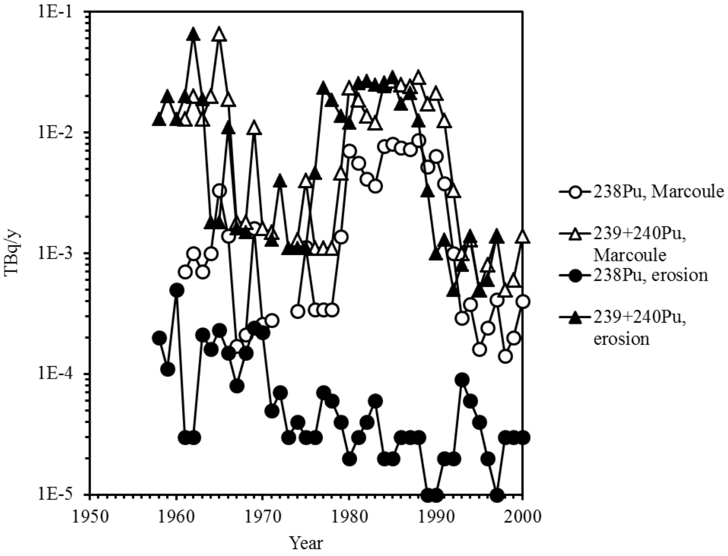


Figure 30. Plutonium release history from the Marcoule site. Data from Ref. 347.

Eyrolle and others have studied the nature of plutonium migration in the Rhône River from the Marcoule site.[346-350] The waters that drain from the Rhône basin generally contain an isotopic signature associated with global fallout. However, within the Rhône River proper, plutonium isotopic ratios at certain locations are indicative of a Marcoule source term (^{238}Pu/^{239,240}Pu activity ratio of ~0.3, which is substantially higher than that for present-day global fallout [^{238}Pu/^{239,240}Pu activity ratio of 0.03–0.05]). As in many plutonium-contaminated areas globally, plutonium in water has a tendency to be associated with colloidal phases.[349] It is estimated that up to 80 % of plutonium in the Rhône River water is associated with particulate matter. This has led to the conclusion that river sediment should be considered a delayed diffuse source that is slowly migrating downstream. The inventory of ^{239,240}Pu deposited in the river sediments since 1945 is estimated to be 0.17 TBq (~0.05 kg).[347]

5.2.4 France: La Hague Nuclear Installation.

The La Hague site provides the first stage in the recycling of spent fuel taken from nuclear reactors. The site is located 25 km west of Cherbourg, France, at the English Channel. Site operations include storage, separations, actinide recovery for use as nuclear fuel, and waste conditioning, including vitrification. Current reprocessing capacity is 1700 tons of spent nuclear fuel per year.[351] The major concerns for radioactivity release into the environment are related to β- and γ-emitting radionuclides (actinides are less of a concern). Until 1985, the total amount of ^{238,239,240}Pu discharged from La Hague to the English Channel was estimated to be 3 TBq. However, the ^{106}Ru, ^{137}Cs, ^{90}Sr, and ^{125}Sb source terms are substantially greater (5×10^3, 9×10^2, 7×10^2, and 10^3 TBq, respectively) (Figure 31).[352, 353] Radionuclide discharge rates decreased substantially in the 1990s. In 2007, AREVA reported the release of liquid discharge containing 2.13×10^{-2} TBq of α-emitting radionuclides, 1.2×10^4 TBq of ^{3}H, 1.4 TBq of iodine isotopes, and 1.0 TBq of ^{137}Cs.[354] The effluent contained radionuclides associated with particles and colloids that could remobilize in contact with water from the English Channel following the release.[132]

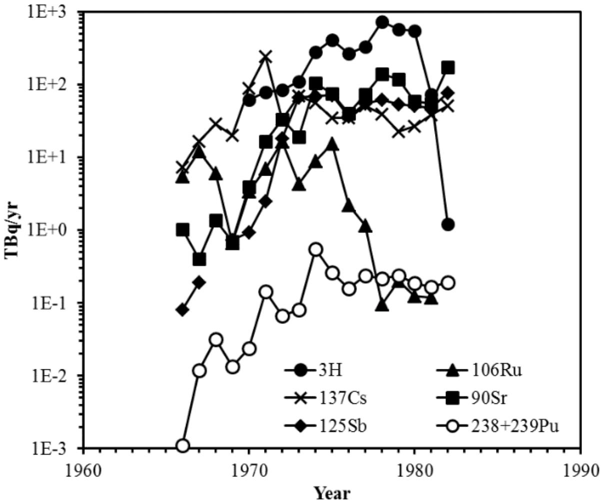


Figure 31. Effluence releases of major radionuclides and plutonium from the La Hague site. Data from Ref. 353.

5.2.5 Japan: Tokai Nuclear Installation.

The Tokai Reprocessing Plant was the first such plant in Japan. Until 2009, the plant had reprocessed 1100 metric tons of spent fuel. Low-level radioactive wastes have been released into the atmosphere (via 90-m stacks) and deposited into the Pacific Ocean via a pipeline extending 3.7 km into the ocean since 1977. Recent evaluation of effluent releases suggests that discharges from the Tokai plant were (with the exception of ^{3}H) several orders of magnitude lower than those from Sellafield and La Hague (Figure 32).[355] Between 1977 and 2007, approximately 4 × 10^8 Bq of plutonium was released from this site.

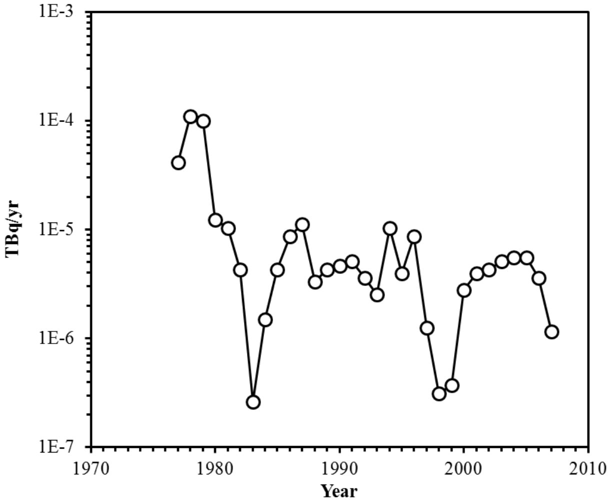


Figure 32. Effluence releases of plutonium from Tokai Reprocessing Plant, Japan. Data from Ref. 355.

5.2.6 India: Trombay, Bombay, and Tarapur.

The discharges of radionuclides from the Trombay, Bombay, and Tarapur facilities in India, which include research reactors and a fuel reprocessing plant, are reported to be modest. The dominant radionuclides present in the waste include ^{137}Cs, ^{144}Ce, ^{106}Ru, ^{95}Zr, ^{90}Sr, uranium, and only traces of ^{239}Pu.[356]

5.2.7 Former Soviet Union: Mayak PA (formerly Chelyabinsk-65).

The nuclear weapon program within the former Soviet union were based on three major nuclear complexes; Chelyabinsk-65 and Tomsk-7 situated at the Ob River and Krasnoyarsk- 26 situated at the Yenisey River (Figure 33).

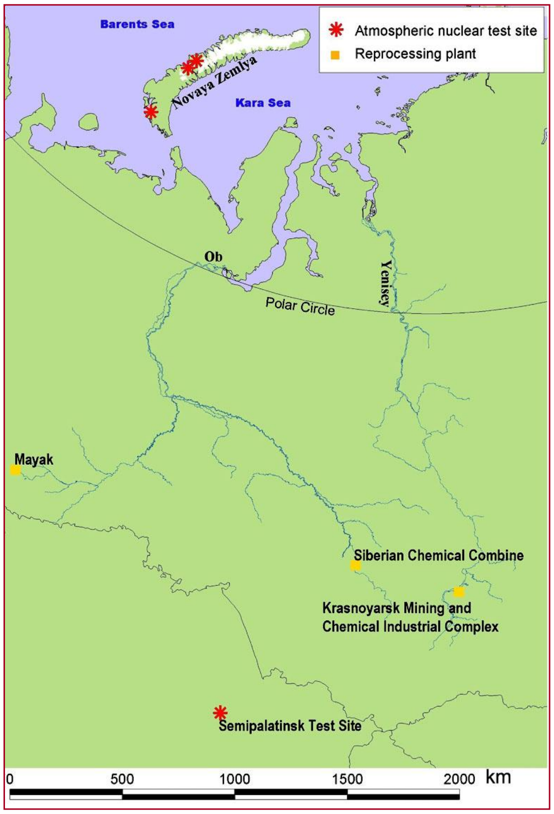


Figure 33. Map of the Ob and Yenisey Rivers and the adjacent Kara Sea. The three major Russian nuclear installations as well as Semipalatinsk Test Site in Kazakhstan are indicated.[214]

The Mayak Production Association (PA), established in 1948, was the first of the nuclear weapon production sites in the former Soviet Union. A number of review articles and reports related to the release of radioactivity from these sites into the environment have been produced.[329, 357, 358] The Mayak PA site is located about 2800 km from the Kara Sea near the Kyshtym village and about 70 km north of Chelyabinsk City in the southern region of the Ural Mountains in Russia. The site is situated along the Techa River, a tributary to the Tobol, Iset, and Ob Rivers. The site included both nuclear reactors and reprocessing plants to produce plutonium for the Soviet nuclear weapons program. In 1987, reprocessing of civil nuclear fuel was initiated. The site includes a variety of radioactive waste storage facilities.[281] Routine and accidental discharges have led to severe radioactive contamination of the area surrounding Mayak PA.

The state of contamination at the Mayak PA and the surrounding area and radionuclide migration to the Kara Sea have been studied extensively (see Refs. 14, 77, 359-363 and references therein). Three principal situations led to the contamination of the Mayak PA and surrounding areas:

- Routine direct discharge of liquid radioactive waste into the Techa River from 1948 to 1951 and into Lake Karachay from 1951 onward
- A 1957 waste tank explosion that led to contamination of about 20,000 km^2 of land (identified as the Kyshtym accident)[291]
- A 1967 event in which strong winds resuspended and distributed contaminated sediments from the shores of Lake Karachay into the surrounding environment

It is estimated that 7.6 × 10^7 m^3 of waste resulted from the production and reprocessing of plutonium and that a total of 3 × 10^7 TBq of liquid and solid radioactive waste was accumulated at the site. Approximately 10^5 TBq of intermediate-level waste (ILW) was discharged directly into the nearby Techa River between 1946 and 1956. The majority of this waste was discharged between 1950 and 1951 and deposited along the river, especially in the Asanov swamps, 35 km downstream the Techa River.[359, 360] The population in the village Metlino, situated at Techa downstream Mayak, was relocated in 1951. At 78 km downgradient from the Mayak site, sediments of the Techa River contained 9 × 10^{-4} Bq/kg of ^{239}Pu, whereas ^{137}Cs and ^{90}Sr concentrations were 1 and 2 orders of magnitude higher, respectively.[360] A number of reservoirs and bypass channels were developed over the years to capture radioactivity migrating in the upper Techa River and avoid transport to the downstream rivers. Radioactivity at these locations has been estimated to be 12,000 TBq and consists primarily of ^{137}Cs and ^{90}Sr but also of ^{60}Co, ^{241}Am, and plutonium isotopes.[359] There are some indications that discharged radioactivity migrated more than 2000 km to the Kara Sea. [56, 364]

Since 1951, waste effluent has been discharged into nearby Lake Karachay (also referred to as V-9 or reservoir number 9). This lake, which has no outlets, was originally an upland marsh with high organic content.[365] The discharged waste effluents were weakly alkaline $NaNO_3$ brine solutions with a pH between 7.9 and 9.3. Approximately 4×10^6 TBq of nuclear waste had been discharged into Lake Karachay by 1993.[359] The dominant radionuclides are ^{90}Sr, ^{137}Cs, and ^{106}Ru. Annual discharges were later reduced to 10^4 TBq. The lake is underlain by fractured andesitic to basaltic metavolcanic rocks into which radionuclides infiltrate. Concentrations of plutonium in the waste effluent at Lake Karachay were approximately 1,000 Bq/L, and the infiltration into groundwater is massive. The groundwater movement has been followed over the years utilizing a monitoring system consisting of a network of boreholes. Colloidal transport of radionuclides in groundwater was already observed in 1996.

In 1957, a 300 m^3 tank containing radioactive waste in nitric acid solutions exploded at the Mayak site as a result of loss of coolant,[291, 360] the so-called Kyshtym accident. The explosion released about 7.4×10^5 TBq of short-lived fission products, which were dispersed by wind and contaminated a 10 x 300 km NE trace, totally 20,000 km^2 area.[359] A small fraction of ^{90}Sr (2.4 % of the total) and an even smaller fraction of ^{137}Cs (0.04 % of the total) were released together with trace amount of ^{239,240}Pu.[291] Following the release, the population in many affected settlements was relocated.

In 1967, after a significant drought lowered the water level of Lake Karachay, strong winds transported contaminated sediments from the shore as windborne dust. Approximately 22 TBq of radioactivity was dispersed across areas that had been previously contaminated by releases to the Techa River and the Kyshtym accident. In this case, ^{137}Cs and ^{90}Sr were the dominant radiological contaminants, and only trace amounts of plutonium isotopes were also dispersed.

The total amount of plutonium released into the environment at the Mayak site is uncertain. Bradley[329] estimated that 1.2 TBq (decay corrected to 1995) of ^{239,240,241}Pu was released into the rivers and lakes from the once-through plutonium production reactors. Based on field work in 1994 and 1996, however, the plutonium inventory in Reservoirs 10 and 11 was estimated to be at least 40 TBq, significantly higher than previously anticipated.[143,357] However, much larger sources of plutonium exist at the site. According to the results of an inspection in 2002, all components of the open part of Lake Karachay (water, silts, and loams from the reservoir bed) contain approximately 10^6 TBq of β-emitters and 4×10^4 TBq of α-emitters, including plutonium.[366] It is important to note that the majority of radionuclides are found in silts and loams of the reservoir beds. During the operating time of the facility, a layer of so-called technogenic silts appeared in the reservoir; these are hydroxide and hydrocarbonate compounds of metals (aluminum, iron, and, to a lesser extent, manganese and others) with some organic, primary lake silts and sand. The concentration of ^{239,240}Pu in these silts is about 10^7–10^8 Bq/kg dry mass.[143, 212] In 2015, the open surface of Lake Karachai was finally closed using concrete blocks.

Among the reservoirs created to avoid transport into downstream rivers, Reservoir 17 and 10 are among those most contaminated. Reservoir 17 (refered to as V-17) was used as a storage for intermediate level wastes from 1949. The total beta-radioactivity is estimated as 4.4×10^4 TBq, mostly associated with bottom sediments. Reservoir 10 is the largest lake and was built in the 1950s while Reservoir 11 was built downstream reservoir 10 in the 1960s. Plutonium activity and atom ratios in sediments from Reservoir 10 downstream from Mayak[75,78] are shown in Figure 34. The plutonium isotope signal in the deep sediment of Reservoir 10 reflected weapons-grade plutonium, whereas the signal in upper sediment layers reflected the signature of civil fuel reprocessing, which was initiated in 1987. Thus, the Pu isotopic ratios in sediments demonstrated a change in discharge composition with time, coinciding with the change from reprocessing of weapons-grade plutonium to reprocessing of civil fuel.[143, 220] Activity levels and isotope ratios in reservoir sediment samples suggested that about 10 TBq of the plutonium isotopes in Reservoir 10 could originate from the early weapons production operation of the plant and that the majority of the plutonium (30 TBq) could originate from later civil discharges.[367]

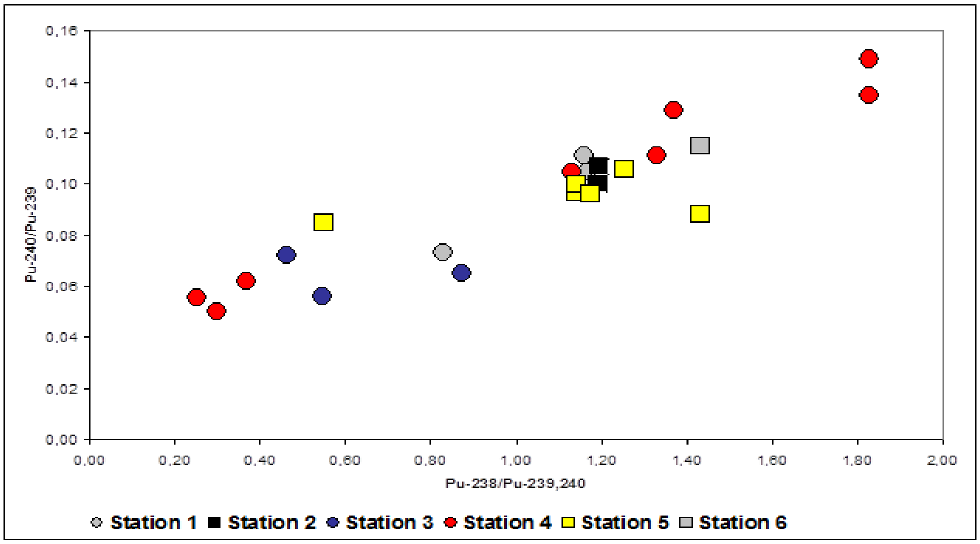


Figure 34. Plutonium activity ratios (x axis) versus atom ratios (y axis) in sediment cores taken across Reservoir 10. The different colors indicating the stations across the reservoir and the different points within each stations reflect the different depths in core (selected slices down to 50 cm); isotopic ratios decrease with the depth in core.[143]

Novikov et al.[77, 362] examined the concentration and nature of plutonium in Lake Karachay and the associated contaminated groundwater. In the near field, the concentration of plutonium both in Lake Karachay and in groundwater samples from the nearest wells exceeded the solubility of PuO_{2+x}(s,hyd), favoring the formation of intrinsic plutonium colloids.[368] However, more than 90 % of the plutonium detected 4 km from Lake Karachay was associated with the iron oxyhydroxide colloidal fraction in groundwater (Figure 35). Thus, it appears that at Mayak, as at other contaminated locations including surface waters, plutonium transport is predominantly facilitated by colloids (see also Refs. 369, 370).

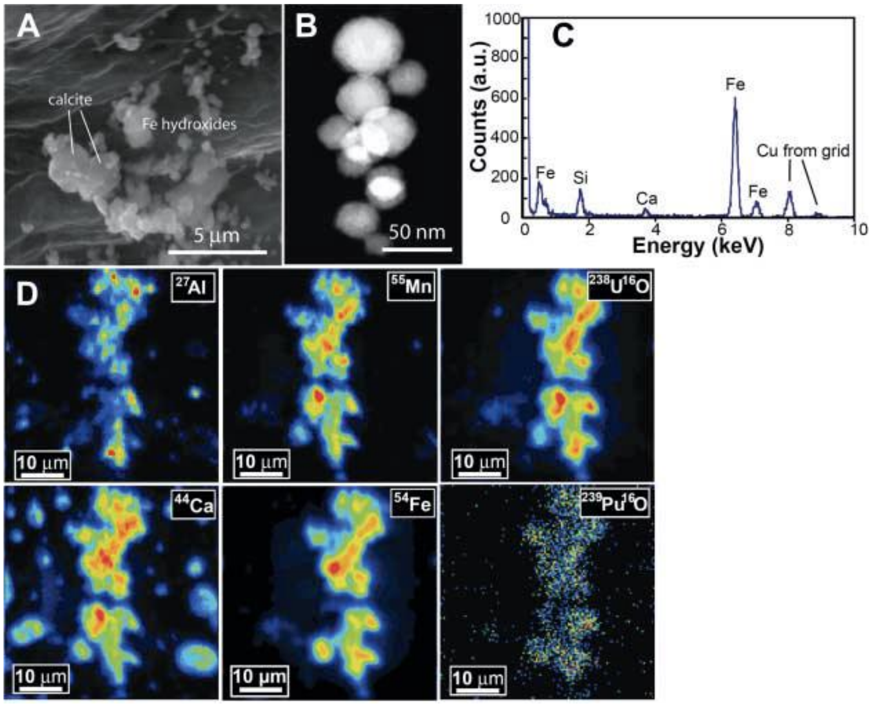


Figure 35. Plutonium associated with iron oxyhydroxide colloids in a groundwater sample close to Lake Karachay, Russia, as evidenced by transmission electron microscopy (A), electron diffraction (B), and nano–secondary-ion mass spectrometry (SIMS) investigations (D); (C) shows the element composition of the colloidal particle as analyzed by EDX (taken from Ref. 77).

5.2.8 Former Soviet Union: Mining and Chemical Combine (formerly Krasnoyarsk-26).

The Krasnoyarsk nuclear site was established in 1958 as part of the former Soviet Union's nuclear weapon program. The facility is located 50 km north of the city of Krasnoyarsk on the eastern side of the Yenisey River. Much of the facility was built underground to ensure survival in the event of a nuclear attack. Radionuclides from the Krasnoyarsk reactor were partly released via the effluent directly into the Yenisey River during the early days. In addition, accidents and flooding of cooling reservoirs contributed to downstream contamination, and waste streams were directly injected into the deep subsurface. However, information on the contamination status at the site is scarce.

The main sources of radioactive contamination in the Yenisey River are the once-through plutonium production reactors at the MCC Krasnoyarsk. Bradley estimated that 1 TBq (decay corrected to 1995) of ^{239,240,241}Pu was released into the Yenisey River from the reactor cooling water, and the ^{137}Cs and ^{90}Sr releases were much larger (18 and 17 TBq, respectively).[329]

In addition to the reactor cooling waters released directly into the Yenisey River, several open reservoirs at the Krasnoyarsk site contain significant amounts of plutonium (700 TBq total radioactivity, with plutonium constituting a significant portion of this radioactivity). The state of remediation of these reservoirs has not been reported. The contamination from the Krasnoyarsk facilities is believed to extend hundreds of kilometers downstream the site and far into the Yenisey floodplain. Research has been conducted to evaluate the concentrations and speciation of plutonium in the Yenisey River and downgradient to the Kara Sea.[371-379] Size fractionation of plutonium species in water samples from the lower parts of the Yenisey and Ob Rivers, their estuaries, and the adjacent Kara Sea revealed ^{240}Pu/^{239}Pu atom ratios equivalent to those from global fallout in the particulate fraction (>0.45 µm) (Figure 36). However, the ^{240}Pu/^{239}Pu atom ratios present as colloids and LMM species were lower than those from global fallout, indicating the presence of low-burnup weapons-grade plutonium. This plutonium fraction most likely originates from nuclear sites situated upstream from the sampling sites.

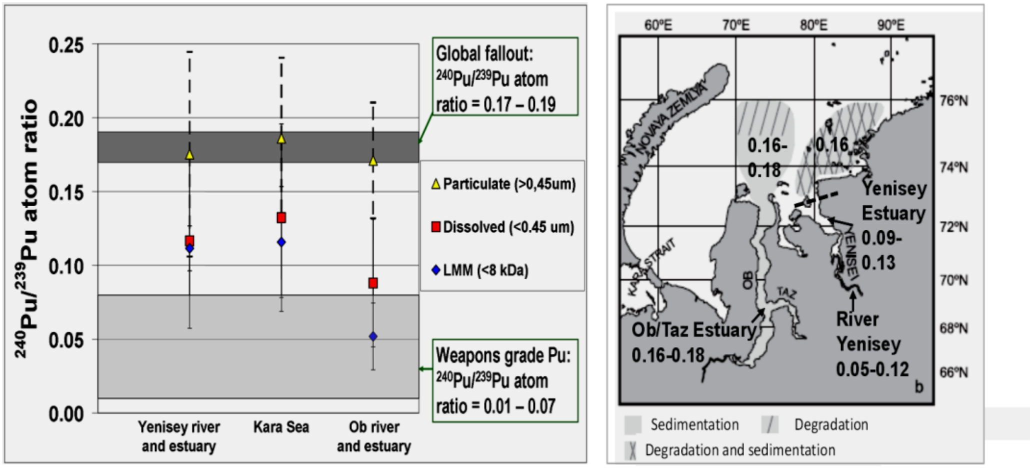


Figure 36. Speciation and source identification of plutonium in the Siberian Ob and Yenisey Rivers as well as the Kara Sea. (A) Pooled ^{240}Pu/^{239}Pu atom ratios in the particulate, dissolved, and low-molecular-mass (LMM) water fractions.[139] (B) ^{240}Pu/^{239}Pu atom ratios in sediments of the same area[214] and a map showing the sedimentation regime of the two rivers.[380]

Plutonium in the Yenisey River was found to exhibit low mobility, which may be due to the presence of plutonium-containing uranium fuel particles and other forms of radioactive particles from Krasnoyarsk-26 releases, including particles claimed to originate from three accidents.[154, 333] Gritchenko et al. [373] distinguished two types of radioactive particles. The first type has rarely been observed in the Yenisey River (~50 particles total). These particles tend to be large (tens to hundreds of micrometers), with activities in the order of 10^6 Bq/particle, be dominated by ^{137}Cs, and include only traces of plutonium. The distribution of these particles in the Yenisey floodplain was estimated to be 70 particles/km^2. The second type of particle is smaller (10–100 μm), contains a more complex mixture of radionuclides, and is much more abundant (10^{10} particles/km^2). Thus, these smaller particles account for a much larger fraction of the total radiological inventory of the Yenisey sediments. Both types of particles are attributed to the Krasnoyarsk facility.[373] The isotopic compositions obtained from γ and mass spectrometry (ICP-MS and AMS) analyses vary substantially between individual isolated particles, indicating several different source terms. Bulk Yenisey floodplain soil samples collected ~10 km downstream of the discharge point feature low ^{240}Pu/^{239}Pu weapons-grade signatures, whereas individual particles isolated from sediment samples collected from the same area, exhibit high ^{240}Pu/^{239}Pu atom ratios indicating a high-burnup fuel origin.[154]

Skipperud et al.[144] and Stepanets et al.[372] examined the speciation of plutonium in the sediments of the Yenisey and Ob Rivers. Based on sequential extraction analyses, the major fraction of plutonium in bottom sediments from the Ob and Yenisey Rivers appeared to be associated with organic matter. However, the plutonium appeared to be more strongly bound in the estuaries of both rivers. The authors postulated that the organic-bound plutonium either becomes more strongly bound in the presence of seawater or is exchanged from the organic matter and sorbs to amorphous iron/manganese oxyhydroxides over time. Plutonium concentrations ranged from 36 Bq/g near the Krasnoyarsk site to 0.34 Bq/g in the Yenisey Estuary.[379]

5.2.9 Former Soviet Union: Siberian Chemical Combine (SCC) (formerly Tomsk-7).

The Tomsk-7 site (now named Seversk), located 25 km from the city of Tomsk, was the largest plutonium weapon production and reprocessing site in the former Soviet Union. Construction of the site has operated since 1948. The site included reactors, several facilities for processing and enrichment, storage facilities, and a deep subsurface injection site for radioactive waste. The site was built to produce plutonium for the Soviet weapons program, but the reactors also provided electric power for the site and the cities of Seversk and Tomsk.[329] Nuclear materials from both Mayak and Tomsk have been reprocessed in the facilities at Tomsk-7. Radioactive waste at the Tomsk-7 site has been managed in a variety of ways, including burial of solid waste and discharge of liquid waste into surface ponds/reservoirs (estimated to be 4.7×10^6 TBq). The reservoirs have since been covered.[381] In addition, deep-well injection of radioactive waste has been used as part of the waste disposal program ($3\text{-}4 \times 10^7$ TBq).

More than 20 accidents that resulted in significant releases of radioactivity into the environment have occurred at Tomsk-7.[381, 382] However, information regarding the scale of plutonium contamination is limited, so estimates of plutonium contamination are quite uncertain. Environmental releases of plutonium from Tomsk-7 include (but are likely not limited to) the following:

- A single once-through plutonium production reactor that operated from 1955 to 1990 released radioactivity directly into the Tom River. The total release of ^{239,240,241}Pu was estimated to be 0.74 TBq (~0.1 kg).
- Tomsk-7 workers reported that up to 850 kg of plutonium was discharged into reservoirs.[329]
- A criticality accident in a storage tank containing uranium solution occurred in April 1993. The tank contained 0.31 kg of plutonium and 8733 kg of uranium. The explosion contaminated tens of square kilometers, and the contamination included radioactive particles.[383] It was estimated that 2.8 g of plutonium was released. Maximum plutonium contamination of the soil was 17 Bq/kg.[383]
- Deep-well injection (200–450 m deep) of about 30,000,000 metric tons of waste has occurred at the site ($\sim 4 \times 10^7$ TBq). Efforts were made to recover transuranic elements from the waste before injection. The plutonium inventory in wastes is not known.
- Gauthier-Lafaye et al.[381] reported high actinide inventories (5,900 Bq/m^2 of ^{239,240}Pu) in soil collected on the bank of the Romashka canal, which historically received aquatic discharges from Tomsk-7. The isotope signatures were in agreement with those of weapons-grade plutonium material.

5.2.10 Canada: Chalk River Laboratory.

During the course of the operation of the Chalk River Laboratory of Atomic Energy of Canada Limited, small quantities of radioactive particles with trace amounts of americium, and therefore probably also plutonium, were discharged to the Ottawa River through a process sewer discharge pipe.[384, 385]

5.2.11 United States: Rocky Flats Plant.

The Rocky Flats Plant (currently the Rocky Flats National Wildlife Refuge), located northwest of Denver, Colorado, was established in 1951 for the fabrication of uranium and plutonium components for the US nuclear weapons program (Figure 37).[386] During the plant's operation, a variety of accidents led to the release of radioactivity into the environment. Fires in 1957 and 1969 contaminated several buildings used to handle radioactive material, and radioactive plumes were emitted into the atmosphere. From 1958 to 1968, releases of plutonium into the environment resulted from the leakage of drums that contained plutonium-contaminated waste oil (19,000 L). It was estimated that 0.2 TBq of plutonium was lost to the soil from the leaking drums. The contaminated soil was later resuspended and transported by wind, contaminating a much larger area of Rocky Flats than the original storage area (903 Pad) (Figure 38). The contaminated surface soils were further redistributed as a result of topsoil erosion and surface water runoff. The plant was shut down in 1989, leaving behind a legacy of plutonium- and uranium-contaminated surface water, shallow groundwater, and soil.

After shutdown of the site, a long and complex environmental remediation program was developed to return the site to its preindustrial state, and the site was renamed the Rocky Flats Environmental Technology Site in 1994 to reflect the change in mission to environmental cleanup. Extensive studies were performed to understand the nature of the contamination and the processes controlling radionuclide migration at the site. Analysis of the colloidal fraction of the soil at Pad 903 and elsewhere by extended XANES showed that the plutonium existed as highly insoluble PuO_2.[182] In 1993, plutonium concentrations in ponds constructed to control and monitor surface discharges from the site ranged from 4×10^{-5} to $1 \text{ x } 10^{-1}$Bq/L, exceeding the discharge limit set for the site (6×10^{-3} Bq/L).[387] Water sampling and analysis performed from 1998 to 2000 at discharge ponds and storm runoff locations at the site showed plutonium concentrations ranging from 4×10^{-4} to 7×10^{-3} Bq/L.[388] Sediment samples from the ponds contained up to 5.6×10^{3} Bq/kg of plutonium.[387] It was determined that particulate forms of plutonium account for a significant fraction of the plutonium in surface waters.[388] Thus, it appears that soil erosion and particulate resuspension control the migration of plutonium at the site. Based on a detailed analysis of the particulate materials and plutonium associations, it was shown that more than 90 % of the plutonium in surface waters was associated with organic compounds (macromolecule, >6 kDa, ~ >1 nm) and not inorganic colloids.[388, 389] Thus, at Rocky Flats, plutonium was transported associated with organic nanocolloids or macromolecules and not with inorganic mineral colloids.

Figure 37. Rocky Flats Environmental Technology Site in 1995 compared to the same site in 2005 (inset). Reproduced from Ref. 386.

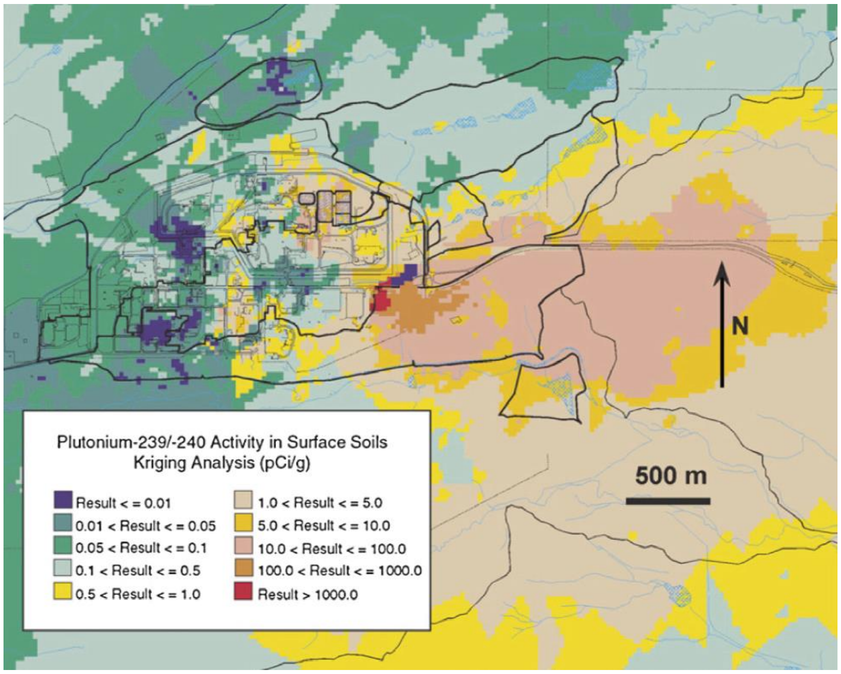


Figure 38. Plutonium distribution in surface soils across the Rocky Flats Environmental Technology Site. Reproduced from Ref. 386.

5.2.12 United States: Hanford Nuclear Reservation Site.

In 1943, the US government chose the Hanford Nuclear Reservation Site for the production of weapon grade plutonium for military purposes. The Hanford site is located in semiarid south central Washington state, along the Columbia River.[390] A total of nine nuclear reactors were built along the Columbia River, and four reprocessing plants were located in the 200 Area of Hanford (Figures 39 and 40). These facilities produced nearly two-thirds of the plutonium used for government purposes.[391] Most of the uranium metal used at Hanford was prepared at Fernald, Ohio, and Weldon Spring, Missouri. The first eight nuclear reactors were single-pass reactors that used Columbia River water for cooling. Water that returned to the Columbia River contained significant amounts of activation products and much smaller amounts of fission products. The irradiated uranium fuel was, after a short hold time, transported to the 200 Area for reprocessing. Approximately 100,000 metric tons of uranium was reprocessed at Hanford. The Plutonium Finishing Plant, located in the 200 West Area, produced weapons-grade plutonium from the reprocessed fluids. Approximately 67 metric tons of plutonium was recovered from the reprocessing plants at Hanford.[392]

The Hanford operations created a vast amount of radioactive and chemical waste. From 1944 to the 1980s, Hanford generated nearly 2,000,000 m^3 of high-level waste containing 7×10^6 TBq of radioactivity. The majority of the waste is contained in 177 waste tanks ranging in size from 210 to 4400 m^3, many of which have leaked. Although more than 96 % of the radioactivity is from ^{137}Cs and ^{90}Sr, the tanks also contain large inventories of protactinium (10 TBq), uranium (40 TBq), thorium (1 TBq), neptunium (5 TBq), plutonium (8,000 TBq), americium (5,000 TBq), and curium (10 TBq). Additional radioactive waste is stored in water-filled pools or buried in landfills (2×10^5 TBq). For example, a burial ground located 13 km north of the 300 Area is estimated to contain 25 TBq, including 5–10 kg of plutonium.

Radionuclides were both intentionally and accidentally released into the air, water, and soil at the site. Early in the history of Hanford, mildly contaminated liquids were simply released directly onto the ground. However, this practice quickly became unacceptable. Some contaminated liquids were also pumped into wells; this practice was later discontinued as well. Slightly contaminated waters were discharged into a variety of ponds, unlined ditches, tile fields, cribs, and so forth. The eight single-pass reactors released 4 × 10^6 TBq of short-lived radionuclides and smaller amounts of long-lived radionuclides directly into the Columbia River. The total amount of radioactivity distributed in the soil and groundwater at the Hanford site is estimated to be ~10^5 TBq.

Most of Hanford's air releases occurred during the routine facility operations of separating uranium from plutonium in used reactor fuel and from the reactors themselves (~10^6 TBq). Most reactor air releases were ^{41}Ar, whereas the reprocessing plant air releases were ^{131}I, ^{103}Ru, ^{106}Ru, ^{90}Sr, ^{239}Pu, and ^{144}Ce.[391]

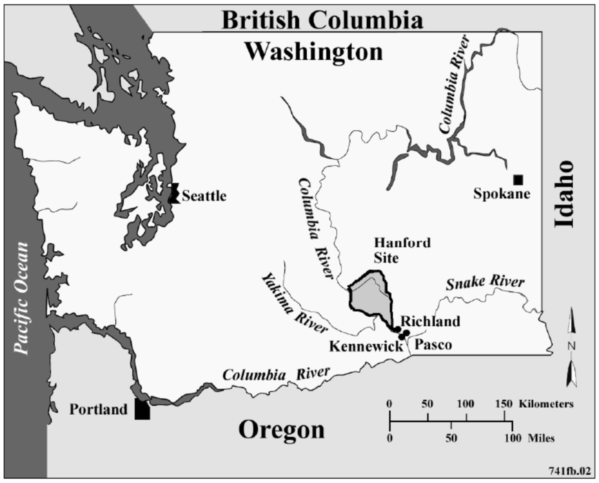


Figure 39. Location of the Hanford site. Reproduced from Ref. 391 with permission from the Pacific Northwest National Laboratory.

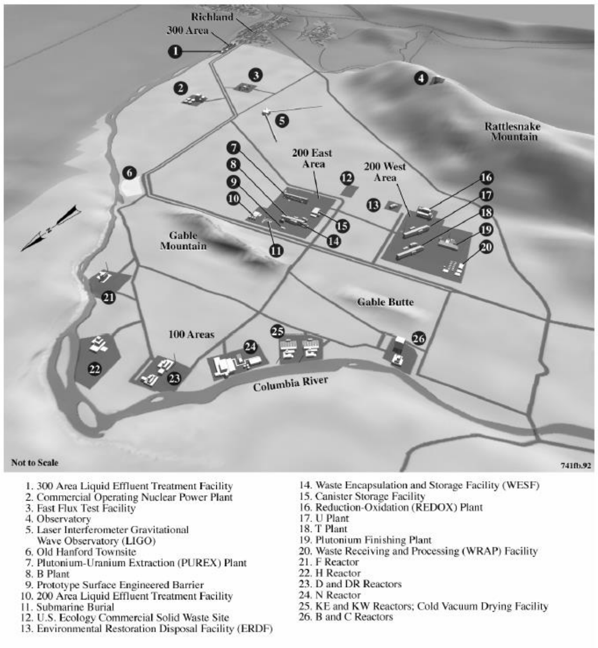


Figure 40. Location of major facilities at the Hanford site. Reproduced from Ref. 391 with permission from the Pacific Northwest National Laboratory.

Separating the plutonium produced from the reactors and reprocessing the waste resulted in the discharge of large quantities of plutonium and other actinides to the shallow subsurface.[393] The chemical composition of the waste was highly variable, with extremes in pH, salinity, and radionuclide composition and concentration. It is estimated that 400 TBq (174 kg) of ^{239}Pu, 1000 TBq of ^{241}Am, and 2 TBq of ^{237}Np were released as liquid waste into the environment. The majority of this contamination occurred in the vicinity of the Plutonium Finishing Plant in the 200 West Area. A comprehensive review of the contamination from the various locations at Hanford can be found in Cantrell.[394]

Significant quantities of these transuranic elements have not yet reached the groundwater. This is because of the relatively thick vadose zone, the low rainfall, and the strong sorption behavior of the radionuclides (particularly plutonium and americium). However, because of the complex and varied nature of transuranic contamination at Hanford, the exact condition of plutonium in the subsurface at Hanford is uncertain. The results of two recent studies of plutonium migration at Hanford are described below.

Dai et al. used low-flow pumping techniques to examine the potential for plutonium transport in several shallow groundwater wells near known plutonium releases in the 100K Area.[79] The pH of the groundwater ranged between 7 and 8. They detected only very low levels of plutonium (4×10^{-6} Bq/kg) in several of the groundwater wells, concluding that the known plutonium inventory previously released to the vadose zone nearby has yet to reach the groundwater in appreciable quantities. In this study, only 7 to 29 % of the plutonium detected in the shallow groundwater was associated with the colloidal fraction.

Felmy et al. evaluated plutonium migration at the Z-9 Trench associated with the Plutonium Finishing Plant.[393] An estimated 4×10^{6} L of acidic (pH ~2) reprocessed waste was deposited in the Z-9 trench between 1955 and 1962; this waste contained approximately 1 TBq (1.8 g) of ^{238}Pu, 70 TBq (30 kg) of ^{239}Pu, 10 TBq (1.3 kg) of ^{240}Pu, and 40 TBq (10 g) of ^{241}Pu. Core samples collected below the Z-9 trench showed that large quantities of plutonium and americium have migrated vertically within the vadose zone to a depth of ~36 m.[393, 394] In addition to the actinides, trace tributyl phosphate was detected in some of the deep soil samples, suggesting that the original organic waste solutions have also migrated and possibly facilitated the migration of actinides. In the 1970s, crystalline PuO_2 was detected in the trench sediments, and analysis of the shallow cores showed that the acidic waste caused extended chemical dissolution.[395] More-recent analysis of the sediments using X-ray absorption fine structure (XAFS) analysis reconfirmed the presence of intrinsic PuO_2.[393] In addition, PuO_{2+x} particles with phosphorus incorporated in the oxide crystal have been reported in Hanford crib Z-9.[148]

5.2.13 United States: Los Alamos National Laboratory.

The world’s first atomic bomb was developed in 1943 in Los Alamos, New Mexico. The site, designated as Los Alamos National Laboratory, became part of the US nuclear weapons complex and, like other such sites in the United States, harbors a legacy of radioactive waste and environmental contamination (Figure 41). In recent years, Los Alamos National Laboratory has actively worked on remediation and monitoring programs to address their legacy waste issues.[396]

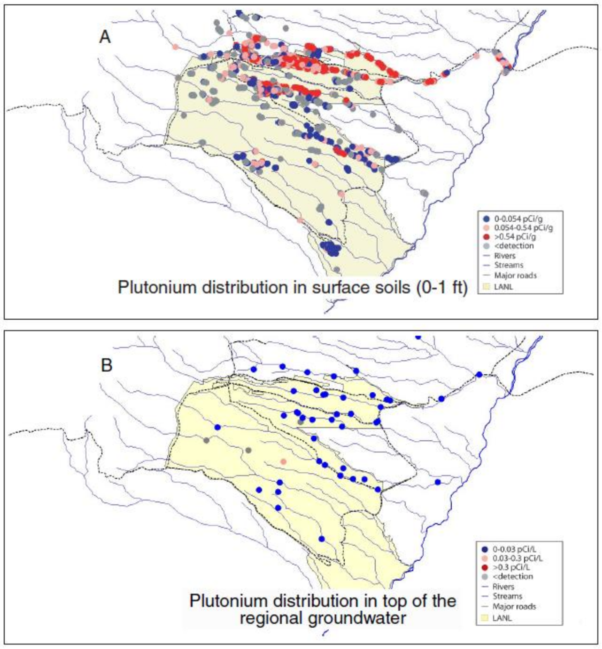


Figure 41. Plutonium distribution in (A) surface soils and (B) regional groundwater at Los Alamos National Laboratory (LANL). Reproduced from Ref. 396.

Over the years, on-site disposal of radioactive waste included the discharge of liquid effluent into canyons and the emplacement of solid/liquid wastes into unlined pits, filtration beds, or shafts. The most significant liquid discharge point was Mortandad Canyon, into which 0.01 TBq (3 g) of ^{239,240}Pu and 0.004 TBq (6 mg) of ^{238}Pu were discharged. In the 1990s, significant effort was undertaken to control radiological releases at Mortandad Canyon, and radiological releases are now considered to be minimal. Plutonium contamination of the underlying aquifers has been detected.[397-400]

The composition and state of solid waste emplacement sites at Los Alamos National Laboratory have not been fully characterized.[396] The study of radionuclide transport from these sites is more limited because it was assumed that the solid waste had a much lower potential to migrate to groundwater than the liquid discharges. Nevertheless, vertical migration distances as large as tens of meters were demonstrated at one filtration bed used for liquid waste disposal.[401] Nine of the 25 material disposal areas contained[396] a total amount of 1,600 TBq of plutonium, of which at least 800 TBq (0.2 kg) was ^{241}Pu. The total inventory of plutonium by mass is uncertain but is known to be greater than 43 kg. At the TA-21 waste disposal site, particulate plutonium was observed in association with iron or as isolated PuO_{2+x} particles in waste buried in soils.[148] Extensive efforts are under way to characterize all solid waste sites and implement a variety of environmental management strategies (in situ stabilization, isolation, excavation and disposal, etc.).[396, 402-409]

The most studied plutonium contamination plume at Los Alamos National Laboratory is associated with the Mortandad Canyon liquid waste discharge. Migration of plutonium and other radionuclides to distances significantly larger than those predicted by theoretical calculations was confirmed experimentally by Penrose et al.[400] The authors detected plutonium and americium contamination in groundwater more than 3.3 km from the liquid discharge point. The main form of migration of both elements was identified as colloidal particles. In spite of this evidence, the question about the nature of colloids controlling the transport and differences in the behavior of americium and plutonium remained open. In 1997, Marty et al. determined that both plutonium and americium likely migrated downgradient through a combination of surface water runoff in Mortandad Canyon and vertical migration along the poorly sealed borehole.[399] Thus, although colloid-facilitated transport was the mechanism by which plutonium was transported downgradient, a significant fraction of that transport occurred as surface water runoff.

5.2.14 United States: Savannah River National Laboratory.

Operating since 1954, the Savannah River Site (SRS) produced plutonium and tritium for national defense and government programs, and a detailed review of the releases of plutonium from activities at the SRS is available.[410] Over a 35-year period from 1954 to 1989, approximately 0.14 TBq of plutonium was released to the atmosphere and 0.023 TBq of plutonium was released to surface waters.[410, 411] Most releases were small and routine, resulting in relatively low concentrations of plutonium in the environment compared with other legacy weapons sites. Because of the relatively low levels of plutonium released across a large area at the SRS, distinguishing between global atmospheric fallout and site-released isotopes requires careful and sensitive measurements. The isotope ratios of samples from the site are typically enriched in ^{238}Pu and ^{242}Pu because of production at the site, and the $^{240}Pu/^{239}Pu$ ratio is lower than that of typical fallout measurements because of the admixture with weapons-grade plutonium.[412]

Almost all releases occurred at the chemical separations areas (Figure 42), known as H and F Canyons, although trace levels of plutonium can also be found in PaR Pond, a manmade pond receiving cooling water from the P and R

Reactors. In 1957, failure of an experimental fuel element in R Reactor resulted in the release of 0.011 TBq (5 g) of ^{239}Pu into the 100-R seepage basin, which led to PaR Pond.[410] Other releases were relatively small and were on the order of 10^4 Bq. Because of the low release rates and levels of radioactivity, specific radiochemical analysis was not performed until the 1970s (except in specific cases in which a known isotope was released). The total α-activity releases from site reactor and separations facility operations are listed in Table 17. In addition to these releases, plutonium that was unrecoverable from PUREX separations or plutonium from other unusable sources is currently within underground waste tanks or disposed of in engineered subsurface disposal facilities (formerly referred to as the Burial Grounds). The total activity of plutonium within the waste tanks and subsurface disposal units is shown in Table 18. The amounts shown in Table 18 represent a much larger mass/activity of plutonium isotopes than the amount that has been released to site surface waters, seepage basins, and the atmosphere.

Plutonium is generally immobile in the SRS environment because of strong sorption to soil minerals and lake sediments. For example, the 2014 SRS Environmental Report notes maximum concentrations of 0.001 Bq/L of ^{238}Pu in Z-Area stormwater basins.[413] In 17 of 18 soil samples taken from across the site, ^{239}Pu had a maximum concentration of 0.003 Bq/g, compared with a background concentration of 0.0001 Bq/g.[413] Maximum concentrations of ^{238}Pu and ^{239}Pu in lake sediments were 0.024 and 0.032 Bq/g, respectively, from samples retrieved from Four Mile Creek and Pond 400.[413] The relatively low mobility of plutonium in the SRS environment has been verified in laboratory testing as well as in a series of field lysimeter experiments.[91, 414-417] Reactive transport models developed to describe these field lysimeter experiments have indicated that plant uptake could be a potential pathway for mobilization of small amounts of plutonium.[106, 417, 418] This has also been experimentally verified, although the contribution to off-site dose is expected to be minimal.[107, 411, 419]

The primary mechanisms of plutonium mobilization in the SRS environment include enhanced transport due to ingrowth of ^{240}Pu following ^{244}Cm subsurface transport.and redox-coupled cycling of plutonium in lake sediments and It is noteworthy that colloid-facilitated transport of plutonium, which has been observed at numerous other legacy weapons sites, has not been observed at the SRS. Kaplan et al. performed a detailed study of enhanced actinide migration within an acidic groundwater plume emanating from the F-Area seepage basin.[420] Plutonium and thorium were effectively retained by the subsurface matrix, and filtration did not decrease the aqueous concentrations. The relatively high mobility of americium and curium within this plume is related to enhanced plutonium mobility due to ingrowth of ^{240}Pu progeny from ^{244}Cm.[160] Elevated ^{240}Pu/^{239}Pu ratios have been observed downstream of the F-Area seepage basin as a result of ingrowth of ^{240}Pu from the decay of relatively mobile ^{244}Cm.[159, 160, 421] The production of ^{240}Pu via decay of ^{244}Cm produces pentavalent PuO_2^+, which is relatively mobile compared to Pu(III) and Pu(IV). Therefore, the ^{244}Cm progeny ^{240}Pu is inherently more mobile than plutonium released directly from the seepage basin, which exhibits expected trends with respect to pH and redox conditions (i.e., increasing pH and decreasing redox potentials leading to decreased aqueous concentrations of plutonium).[159]

Table 17. α-Activity Releases from Savannah River Site Reactor and Separations Facility Operations between 1954 to 1989 (Ref. 410)

Source	Operational timeframe	Total α-activity released into surface waters	Total α-activity released into the atmosphere
C Reactor	1955–1985	3.6×10^5 Bq to Fourmile Branch; 1.4×10^5 Bq to seepage basins	1.4×10^6 Bq
K Reactor	1954–1988	3.6×10^5 Bq to Pen Branch; 8.1×10^5 Bq to seepage basins	1.8×10^6 Bq
L Reactor	1965–1968, 1985–1988	7.4×10^4 Bq to Steel Creek and L Lake; 8.5×10^4 Bq to seepage basins	3.7×10^5 Bq
P Reactor	1954–1988	6.3×10^5 Bq to Steel Creek/PaR Pond; 3.7×10^5 Bq to seepage basins	1.1×10^6 Bq
R Reactor	1953–1964	Only measured release was 1.1×10^{10} Bq (specifically ^{239}Pu) to 100-R seepage basin as a result of the failure of an experimental fuel element in 1957	NA
H-Area separations	1955–	8.9×10^{10} Bq of ^{238}Pu and 7.3×10^{10} Bq of ^{239}Pu to seepage basins	2.5×10^{10} Bq of ^{238}Pu and 2.2×10^{10} Bq of ^{239}Pu; maximum release of 2.3×10^{10} Bq in 1969 due to collapse of a sand filter
F-Area separations	1954–	2.1×10^{11} Bq of ^{239}Pu and 5.7×10^{10} Bq of ^{238}Pu to F-Area seepage basins	9.1×10^{10} Bq; maximum release of 8.1×10^{10} Bq in 1955 due to startup problems with filtration system
Note: Relatively small releases from the Savannah River Technology Center (now the Savannah River National			

Laboratory), the Heavy Water Rework Facility, the Heat Exchange Repair Center in Central Shops, experimental reactors, and other site facilities are not included. NA = not applicable.

The rich redox chemistry of plutonium is demonstrated by the cycling of plutonium within lake sediments within manmade cooling water basins at the SRS. Concentrations of plutonium in lake waters change with depth and increase until reaching a maximum concentration in the early spring when lake stratification occurs. In the early summer, the stratified lake reaches anoxic conditions and the concentrations of aqueous plutonium decrease.[422-424] Thus, aqueous concentrations of plutonium increase during the time of year when waters are oxic and decrease (returning to low concentrations) at the onset of stratification that leads to anoxic conditions. Isotopic analysis verified that the increased plutonium concentrations are not the result of inputs from atmospheric deposition,[424] although the lack of direct correlation between plutonium and iron/manganese suggested that increased concentrations were due to downward transport of plutonium in the overlying water column.[422]

Table 18. Subsurface Sources of Plutonium in Engineered Systems at the Savannah River Site.[410]

Location	Isotope	Inventory	
		Bq	kg
Waste storage tanks	^{238}Pu	5.9×10^{16}	93
	^{239}Pu	8.1×10^{14}	350
	^{240}Pu	3.8×10^{14}	45
	^{241}Pu	5.3×10^{16}	14
	^{242}Pu	6.3×10^{11}	4.3
Solid waste disposal facility	^{238}Pu	1.7×10^{16}	27
	^{239}Pu	3.4×10^{14}	150
	^{242}Pu (<60%)	7.2×10^{14}	4900
	^{242}Pu (>60%)	1.9×10^{10}	0.1

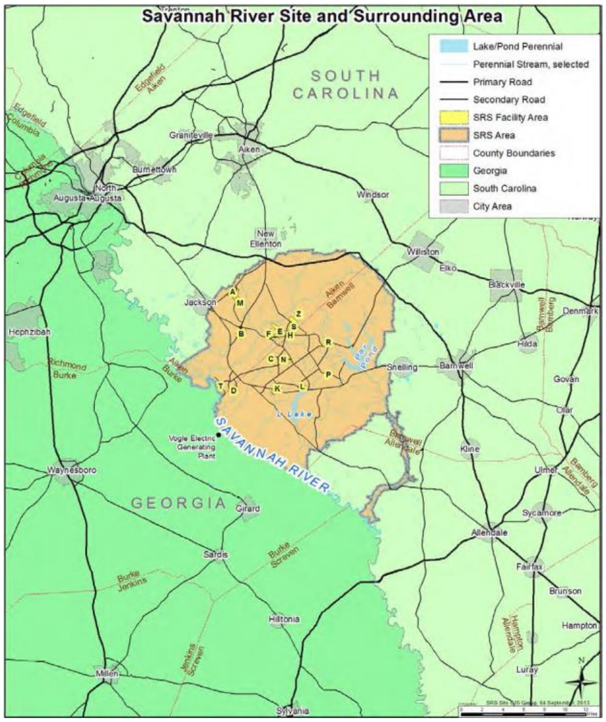


Figure 42. Savannah River Site and surrounding area, showing the Savannah River as the southwestern site boundary and processing areas by letter. Reproduced from Ref. 413.

5.2.15 United States: Idaho National Laboratory.

The primary disposal site of transuranic elements at INL is the Radioactive Waste Management Complex (RWMC), which consists of the Subsurface Disposal Area (SDA), the Transuranic Storage Area (TSA), and the Administrative Area. The SDA is a 39-hectare storage facility consisting of pits, trenches, and soil vaults. The TSA is an aboveground storage facility for remote and contact-handled transuranic waste that is destined for final disposition at the Waste Isolation Pilot Plant (WIPP). Between 1954 and 1970, about 65,000 m^3 of transuranic solid waste was buried in the SDA.[425] Approximately 4,000 m^3 of this is calcined solid waste stored in seven stainless steel tanks in massive underground concrete enclosures. A total of 21 TBq (0.03 kg) of ^{238}Pu and 780 TBq (340 kg) of ^{239}Pu was buried in the SDA along with 1,800 TBq [14 kg] of ^{241}Am. Detailed records of the waste disposed at the SDA from 1952 to 2003, including a discussion of the ^{238}Pu and ^{239}Pu content in the waste, have been reported.[426, 427]

Two flooding events coupled with wind-facilitated dispersal resulted in the release of radionuclides, including plutonium, into the environment at INL. Relevant to this chapter are the releases and environmental transport of plutonium that have occurred at the RWMC. The SDA is located in a shallow valley. Snowmelt in 1962 and 1969 was significant enough to cause flooding and surface water runoff, which carried mobile radionuclides off-site. In addition, approximately 25 % of the SDA consists of open transuranic burial pits, allowing for wind-facilitated transport. As a result, plutonium concentrations in surface soils are above background levels up to 2 km away from the RWMC.[425] The influence of wind transport can be clearly seen by the higher concentrations of plutonium in soils to the northeast of the SDA, which is the preferential wind direction.[425] Depth-discrete sampling of plutonium from 0 to 8 cm indicated relatively little downward transport of plutonium.[425] This is consistent with the relatively strong sorption of plutonium to soils from the RWMC, with K_d values ranging from 50 to 5000 L/kg.[428, 429] Thus, subsurface migration of plutonium appears to be relatively low at this site.

5.2.16 United States: Waste Isolation Pilot Plant.

The WIPP, located east of Carlsbad, New Mexico, is the only deep geologic waste repository that has been licensed to operate in the United States (operating since 1980). The WIPP is mined out of a thick bed of salt 655 m below ground surface and is used for the disposal of defense transuranic waste generated primarily from the cleanup of Department of Energy sites (Figure 43). It is authorized to dispose of 176,000 m^3 of defense-related transuranic waste. Disposal operations began in 1999 and are expected to continue for 35 years. Approximately 5,500 kg of plutonium is projected to be disposed of at the WIPP.[430-432]

On February 14, 2014, a high-radiation alarm was received at the WIPP. At the time, there were no employees working in the repository and only 11 employees working on the surface. In response, the underground ventilation system automatically switched to a high-efficiency particulate air (HEPA) filtration mode. Unfortunately, poorly functioning dampers in the HEPA filtration/ventilation system led to the release of radionuclides into the atmosphere. On February 19, the Carlsbad Environmental Monitoring and Research Center reported radiological levels above background levels in air samples 1 km northwest of the WIPP. Analyses indicated slightly elevated levels of ^{239,240}Pu and ^{241}Am. The direct cause of the accident was an exothermic reaction of incompatible materials in a Los Alamos National Laboratory waste drum (drum #68660) within Panel 7 of the WIPP facility.[433, 434] This incident, as well as a separate truck fire incident that occurred on February 5, 2014, triggered an intense investigation into all aspects of the WIPP operation. Ongoing forensic investigations are attempting to understand the potential for additional exothermic releases of radionuclides.[431, 432,434]

The radiological composition of drum #68660 included uranium, neptunium, plutonium, and americium (0.2 TBq). The plutonium activity was dominated by ^{241}Pu (0.07 TBq), whereas the total plutonium mass (~8 g) was dominated by ^{239}Pu. Based on filter analyses, approximately 7.4×10^9 Bq of radioactivity was released underground and only 4×10^7 Bq was released into the environment. The total amount of plutonium released into the environment was estimated to be 1 mg.[435]

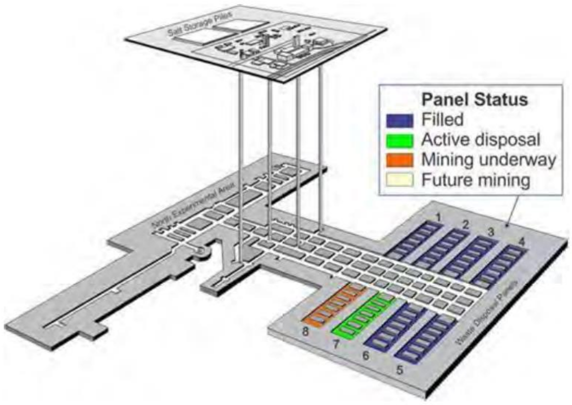


Figure 43. State of repository mining and waste disposal at the time of the Waste Isolation Pilot Project incident. Reproduced from Ref. 431 with permission from the US Department of Energy.

5.3 Airplane, Submarine, and Weapons Accidents

Numerous accidents involving nuclear weapons are known to have occurred. It is believed that at least 230 accidents involving the nuclear weapons of the United States, the former Soviet Union, and the United Kingdom occurred between 1950 and 1980.[436] The US Department of Defense has confirmed the occurrence of 32 serious accidents between 1950 and 1980. In a number of these events, high explosives in the nuclear weapons caught fire or even detonated conventionally, causing contaminations with fissile material.[437] Information about accidents in the former Soviet Union is more difficult to obtain. However, at least 25 serious nuclear weapon accidents have been mentioned in the literature,[438] although no inadvertent nuclear weapon detonation (fission) is known to have occurred.[439] Only 4 nuclear weapon accidents releasing plutonium have been described in the open literature: McGuire Air Force Base, New Jersey, Johnston Atoll, Palomares, Spain, and Thule Air Base, Greenland. In all four cases, the nuclear weapons were conventionally detonated and fragmented, and the environment was contaminated mainly by radioactive particles. In addition, a series of accidents have occurred with other nuclear driven vehicles such as nuclear submarines, also carrying nuclear weapons, and nuclear powered satellites. So far, leakage from sunken submarines have not been reported, while disintegration especially of the SNAP satellite increased the global ^{238}Pu fallout signal by a factor of 3, particularly in the southern hemisphere. Of relevance for this chapter, only events where plutonium has been released or where a potential future release is of concern are summarized.

5.3.1 United States: Johnston Atoll and McGuire Air Force Base.

Johnston Atoll: The Johnston Atoll in the Pacific Ocean.was operating as a launch site for atmospheric nuclear weapons tests from the late 1958 to early 1975. In 1962, three nuclear warhead–carrying Thor missiles were aborted and destroyed; one on the launch pad and two at altitudes of 9 and 33 km, resulting in contamination with plutonium- and uranium-containing particles throughout the atoll. The particles containing >99 % of the total activity exhibited widely varying U/Pu ratios, with a higher concentration of activity near the launch pad.[174]

McGuire Air Force Base: On June 7, 1960, a fire occurred in a shelter at McGuire Air Force Base in New Jersey. The shelter contained missiles loaded with warheads. A Boeing Michigan Aeronautical Research Center (BOMARC) missile caught fire inside the shelter. The warhead did not explode but partially melted down. Fire suppression activities and weather conditions during the fire led to the release of plutonium particles across a 28,000 m^2 area in front of the shelter. The plutonium concentration in the 75–147-µm soil particle size fraction (6.34 Bq/g) was 4 orders of magnitude higher than global fallout levels. Plutonium isotope ratio measurements identified the plutonium at the site as weapons-grade plutonium.[440] Characterization of isolated plutonium- and uranium-containing particles showed that they exhibited a smooth and crystalline structure different from particles reported from Palomares and Thule. Apparently, the Pu/U ratio on BOMARC particle surfaces was higher than that observed for Palomares and Thule particles.[173] Microbeam EXAFS and XRD analyses demonstrated the presence of $Pu(U)O_{2+x}$ and UO_{2+x} in two particles from the McGuire Air Force Base accident.[148] In the same study, one particle was described as a conglomerate of a plutonium-rich and a uranium-rich particle in which uranium and plutonium were not significantly mixed and in which small iron and gallium spots were also present. In a second particle, plutonium and uranium were mixed. This is more in line with previous observations for a range of particles originating from nuclear weapon materials.[150, 170, 439]

5.3.2 Spain: Palomares.

In January 1966, a B-52 bomber and KC-135 refueling tanker collided during high-altitude refueling above the Mediterranean Sea near the village of Palomares, Spain. Both planes were destroyed and four weapons were released: two were recovered intact (one successfully deployed a parachute and one was recovered from the seabed) and two impacted the ground, detonating high explosives and dispersing plutonium and uranium over an area of approximately 2 km^2.[441] Considerable amounts of dispersed plutonium particles contaminated 2.30 km^2 of the urban areas and farmlands surrounding Palomares (Figure 44). The decontamination of the area consisted of removing layers of soil and vegetation (~1400 tons) and storing them in drums. Most of the waste was shipped to the United States for disposal,[442] and some was dumped in trenches. However, it was estimated that 0.1 TBq (0.04 kg) of ^{239,240}Pu was not recovered.[441] Detailed characterization of the contamination indicated that the radioactive particles contained aged weapons-grade plutonium and enriched uranium (Figure 45).[443] Submicrometer- to millimeter-sized particles and even fragments have been identified in soils.[114, 442, 443] Uranium and plutonium coexist in the particles as mixed oxides with varying elemental and isotopic compositions. Uranium and plutonium were also inhomogeneously distributed within individual particles. Based on XANES analysis, plutonium was present as Pu(III)/Pu(IV), Pu(IV)/Pu(V), or a mixture of the three oxidation states.[170] Despite remediation, residual plutonium particles are still present in the affected area. Recent investigations have also demonstrated that Pu particles are taken up by free-living organisms such as snails and hare within the affected areas.[115] In 2015, the United States signed an agreement to perform additional cleanup.

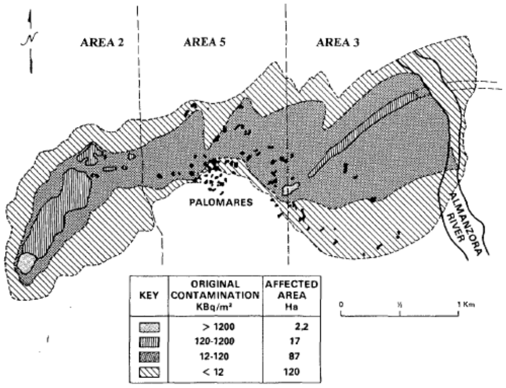


Figure 44. Contamination resulting from the Palomares accident.[442]

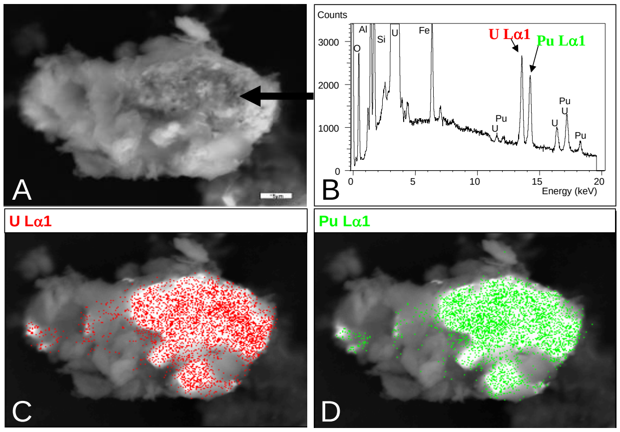


Figure 45. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) analysis of radioactive particles isolated from Palomares soils. (A) SEM used in secondary electron imaging mode showing particle morphology. (B) EDX spectrum showing the elemental composition of the particle (analysis spot marked with arrow). (C) X-ray mapping of uranium superimposed on an image recorded in backscattered electron imaging (BEI) mode. (D) X-ray mapping of plutonium superimposed on an image recorded in BEI mode. Bar 5 µm.[170]

5.3.3 Greenland/Denmark: Thule Air Base.

On January 21, 1968, a US B-52G Stratofortress bomber ‘HOBO 28’ carrying four plutonium-containing bombs caught fire and crashed on ice-covered sea 11 km away from Thule Air Base in Greenland (Figure 46). As a result of weapon rupture, ~6 kg of plutonium (~10^{13} Bq) was dispersed over a distance of several kilometers in the snow pack, ocean water, and underlying seabed sediments.[169] The major fraction of the plutonium was removed by mechanical collection of the munitions debris (7000 m^3). The debris was sent to the United States for disposal. The residual contamination has been estimated to be about 1.4–6 TBq (~0.53 – 2.3 kg) of ^{239}Pu, mainly in the form of plutonium particles.[444] Measurable levels of plutonium were found primarily in a 6-km radius around the crash point at sea and on land.[169] The plutonium inventory was, however, underestimated until early 2000, as Pu particles were not fully dissolved by the presently used analytical procedure.

The Thule source term is dominated by a single source having a ^{240}Pu/^{239}Pu atomic ratio of 0.055 and a U/Pu atom ratio of about 1,[215] with a second less abundant source with a ^{240}Pu/^{239}Pu atomic ratio of about 0.025.[445] The composition of plutonium-containing particles and the partitioning and speciation of plutonium in seawater have been studied by several authors. Small particles (about 2 µm) occur most frequently, while submicrometer- to 1000-µm-sized particles have been identified in sediments (up to 1500 Bq of ^{239}Pu/particle) and soils (up to 150 Bq of ^{239}Pu/particle).[170, 444] Similar to the Palomares particles, uranium and plutonium coexist in the particles as mixed oxides with varying elemental and isotopic compositions. Heterogeneous distributions of uranium and plutonium within individual particles were also observed. Based on XANES, plutonium was present as Pu(III)/Pu(IV), Pu(IV)/Pu(V), or a mixture of the three oxidation states.[170, 446] Unlike the sedimentary particles, plutonium in seawater around Thule appeared to be primarily in the dissolved and oxidized Pu(V)/Pu(VI) form.[447] Plutonium isotopic ratios in seawater near the Thule site were consistent with global fallout. Thus, a signature of weapons-grade plutonium from the Thule accident is not evident in Arctic waters.[447] As in Palomares, residual Pu particles are still present on land, and plutonium in feces reflects uptake in muskoxen.[115]

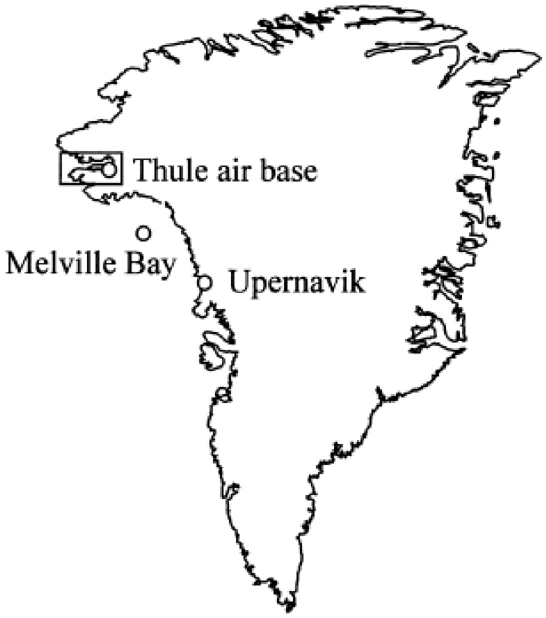


Figure 46. Location of the Thule Air Base in Greenland. Reproduced from Ref. 447.

5.3.4 Former Soviet Union/Russia: Submarine Komsomolets K-278.

On April 7, 1989, the Russian nuclear submarine *Komsomolets* experienced an engine fire and sank in the Norwegian Sea at a depth of 1655 m.[448] The submarine was powered by a single pressurized water reactor and included two nuclear torpedoes. The nuclear reactor was shut down before the submarine was abandoned. It was estimated that 13 TBq (5.7 kg) of ^{239}Pu and 3.0 TBq (0.36 kg) of ^{240}Pu were associated with the weapons-grade plutonium of the 2 nuclear torpedoes and an additional 2.2 kg of plutonium was associated with the nuclear fuel.[448] Based on monitoring programs in Norway, no significant leakage of radionuclides such as ^{137}Cs from the sunken submarine has been detected so far. It is unclear when the nuclear torpedoes or the reactor core will corrode and cause the potential release of plutonium into the Norwegian Sea. However, given the plutonium load that is present as a result of global fallout and the Sellafield operations, it is expected that the additional plutonium flux from the *Komsomolets* will not appreciably increase the plutonium inventory of the Norwegian Sea.[448]

5.3.5 Former Soviet Union/Russia: Submarine **K-159**.

At the Kola Peninsula, a series of nuclear-powered submarines have been taken out of operation. Many have been decommissioned, and spent nuclear fuel is stored at the Andreeva Bay and in Gremikha sites at the Kola Peninsula.

Several submarines, still fueled, have been waiting for decommissioning for many years. As part of the decommissioning program, the submarine *K-159*, carrying two nuclear reactors was transported from Gremikha to the Nerpa shipyard at Murmansk in 2003. On its way from Gremikha, the *K-159* sank at 246 m depth north of Murmansk because of a heavy storm. The total radioactive inventory of K-159 at the time of sinking has been estimated to 6.5 - 7.4 PBq).[449] A joint Norwegian–Russian expedition to K-159 in 2014 reported that no leakages have been observed so far.[450] Most of the stored submarines in Gremikha have been decommissioned during recent years due to international collaborations.

5.4 Satellite Accidents

The most prevalent civil application for ^{238}Pu as fuel for heat and power sources for space exploration.[451] The ^{238}Pu isotope provides 99.9 % of the thermal power in heat source fuel. Radioisotope thermoelectric generators (RTGs) have been used in the United States to provide electrical power for spacecraft since 1961. Early ^{238}Pu-fueled power sources used Space Nuclear Auxiliary Power (SNAP) units to power satellites and remote instrument packages. SNAP units served as power sources for instrument packages on the five Apollo missions to the Moon, the *Viking* unmanned Mars lander, and the Pioneer and Voyager probes to the outer planets. RTGs were also flown on the *Galileo, Ulysses, Cassini,* and *New Horizons* spacecraft.[451]

Both the United States and former Soviet Union space programs had accidents with their nuclear-powered satellite systems. On April 21, 1964, a navigational satellite carrying 630 TBq (1 kg) of ^{238}Pu failed to stabilize in the Earth's orbit and reentered the atmosphere over the Indian Ocean within the Southern Hemisphere. The plutonium release was first detected 4 months later at an altitude of 30 km, with particles ranging in size from 5 to 58 µm. The released ^{238}Pu activity led to a nearly 3-fold increase in the global fallout of ^{238}Pu, especially in the Southern Hemisphere. At the end of 1970, it was estimated that only 37 TBq of the ^{238}Pu remained in the >12 km atmosphere; the majority had been deposited as particulate matter in the ocean and on land. By mid-1970, 95 % of the plutonium had been deposited on earth, predominantly in the Southern Hemisphere. Analyses of samples from Madagascar could, however, not reflect any significant local fallout of plutonium originating from the satellite failure.[452]

Satellite accidents in the former Soviet Union were associated with uranium power/heat sources. In 1978, the former Soviet Union *Cosmos-954* satellite, containing kilogram quantities of highly enriched uranium, reentered the earth's atmosphere and disintegrated in large radioactive fragments over Canada. The total amount of radioactivity released was estimated to be 1,700 TBq.[329] Only parts of the nuclear materials have been retrieved. In 1983, the Soviet RORSAT *Cosmos-1402* satellite reentered over the Indian Ocean and the core reentered several days later over the Atlantic Ocean. The fuel containing highly enriched uranium disintegrated at high altitudes. Although no radioactive residues were found, the radioactivity released was estimated to be less than 560 TBq.[329]

6. NUCLEAR WASTE DISPOSAL

As described in detail in Section 2, radioactive waste disposal in the early nuclear era was haphazard, and the long-term repercussions of poor waste management practices were ignored. To some extent, this has to be regarded in the historical context of the World War II and the subsequent Cold War, a time in which military requirements were prioritized over safe waste management aspects. In contrast to the "concentrate and contain" concept, disposal according to the "dilution and dispersal" principle was for quite some time a generally accepted waste management concept. Therefore, at the beginning of the nuclear era, liquid wastes were often discharged directly into rivers or the sea. Other concepts relied on a waste management solution to be developed in the future. Thus, waste has been stored temporarily at sites either in temperature-controlled tanks, underground, or in surface ponds or even lakes. Examples of improperly stored spent nuclear fuel in ships or in submarines taken out of service and of dumping reactor assemblies or submarines with fuel into the sea are well known. The behavior of plutonium in some of these cases will be described in more detail in Section 3.3, and many of these cases necessitate severe efforts and measures to mitigate the potential environmental impact of these "nuclear legacies". Billions of dollars are being spent and will have to be spent in the future to remediate contaminated sites in the United States, Russia, and worldwide. Large G8, regional, bilateral, and national remediation programs have been initiated to recover improperly stored spent nuclear fuel in northwest Russia.

At the end of the 1960s and the beginning of the 1970s, the philosophy for dealing with hazardous residues and waste changed significantly. The OSPAR London Convention regulating waste dumping into the sea was developed and implemented. Dumping of all kinds of radioactive waste into the open sea was finally banned only as recently as 1993.[453] Today, accepted radioactive waste concepts require the isolation of the waste from the biosphere.[454]

Different plutonium-containing waste streams and waste forms are generated depending on the nuclear energy policy of individual states (either a "closed" nuclear fuel cycle involving recycling plutonium or a direct disposal strategy) (Table 19). As of 2014, about 2113 metric tons of civil reactor plutonium worldwide exist in irradiated nuclear fuel and 275 metric tons have been separated by reprocessing (see chapter 5: Plutonium Inventories). Using a direct disposal strategy, comparatively large amounts of plutonium have to be disposed of in a repository in the form of spent nuclear fuel—either irradiated UO_2 (UOX) or U/PuO_2 (MOX) fuel. This is presently the case for Sweden, Finland, Switzerland, and Germany, among others. Other countries, such as France, the United Kingdom, and Japan, pursue nuclear fuel reprocessing so that plutonium is recycled to produce MOX fuel. Estimations predict until 2020 a cumulative spent fuel inventory of 445,000 metric tons,[455] containing about 1 % plutonium. The rate of spent nuclear fuel reprocessing was less than one third in 2010. Presently, the increasing buildup of heavier isotopes, such as ^{240}Pu, in irradiated fuel prevents plutonium multirecycling from being used in light-water reactors. Multirecycling requires the establishment of a Generation IV reactor fleet utilizing fast neutrons (e.g., sodium-cooled reactors). In reprocessing, only trace plutonium amounts end up as waste, and they are typically immobilized (vitrified) in borosilicate waste forms (high-level waste [HLW] or intermediate-level waste ILW) or in cemented or bituminized waste forms (low-level waste [LLW] and ILW). Various investigations and strategies also consider the separate immobilization of civil and military plutonium by proposing dedicated waste forms. In the latter case, ceramic matrices (e.g., those based on pyrochlore, phosphates, or zircon) and tailored glass matrices are regarded as appropriate.

Table 19. Plutonium in Different Solid Waste Forms

Waste form	Content	Chemical plutonium form
Irradiated uranium oxide fuel	ca. 1 wt % HM	Mainly PuO_2
Nonirradiated MOX fuel	ca. 1.5–30 wt % HM[456,457]	Mainly PuO_2
Irradiated MOX fuel	Up to 6 wt %	Mainly PuO_2; minor fractions of $PuO_{1.61}$ and $PuO_{1.5}$

	HM[458,370]	(Ref. 459)
Borosilicate glass	<1 wt %[460]	Pu(IV), PuO_2 (Ref. 461)
Tailored borosilicate glass for plutonium immobilization	>4 wt % (reducing conditions)[462]	Pu(III, IV) under reducing conditions[462]; Pu(IV), PuO_2, and britholite under oxidizing conditions[463]
Ceramic waste forms	Up to 35 wt %	Mainly Pu(IV) in mixed phases[460]
Cemented waste	Variable, generally low content	Variable chemical forms
Bituminized waste	Variable, generally low content	Variable chemical forms

Note: HM = heavy metal; MOX = mixed oxide.

Different concepts of isolating nuclear waste from the biosphere have been discussed and assessed. Disposal in a mined repository constructed in a stable, deep geological formation, such as crystalline rock, clay rock, and rock salt, is considered the safest strategy for confining highly radioactive heat-generating waste. In the case of LLW and ILW, a number of countries have decided to store the waste for a period of some centuries in a protected site close to or at the surface. In any case, all disposal concepts necessitate appropriate waste conditioning in order to obtain a "low-release" waste form. To limit the potential release to the biosphere, repositories are designed as multibarrier systems containing technical, engineered, and geological barriers aimed at maximizing protection against water access to the waste and minimizing radionuclide propagation from the source.

The behavior of plutonium related to mobilization and retention in a repository system strongly depends on the waste form considered; the disposal concept, such as the host rock type and the backfill and container material; and the prevailing chemical and geochemical boundary conditions. The challenge of isolating plutonium from the biosphere is its long half-life. Isolation must be maintained on a time scale of 100,000–1,000,000 years, which challenges traditional model predictions and the associated uncertainty quantification and leads to complex philosophical and political debates.

6.1. Release from High-Level Waste Forms

HLW forms are characterized by a high specific activity whereby radiation induces damage in solid-phase structures and thus has an impact on the chemical nature and environment of plutonium in the waste matrix. Furthermore, the high radiation dose induces radiolysis at the waste matrix–aqueous solution interface, which influences redox conditions in solution by generating oxidizing radiolysis products ($OH^{\cdot}$, H_2O_2, OCl^-, etc.).[464] Plutonium releases from HLW and chemical reactions in the near field of a repository are determined by the chemical milieu, which is determined by the complex interplay of container corrosion, radiolysis, dissolution of waste matrices, secondary phase formation, and reactions with engineered barriers and construction material (cement).

6.1.1 Spent Nuclear Fuel.

Plutonium isotopes form in UOX fuel in a reactor from neutron capture by various pathways (Figure 47). Light-water reactors operating with low-enriched UOX represent the majority of nuclear power plants worldwide. Spent fuel from these reactors contains approximately 1 wt % plutonium relative to the heavy metal content.[23] Depending on flux, irradiation, and cooling time, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu mainly contribute to the mass composition. In UOX fuel with 4.25% ^{235}U at a burnup of 50 GWd/t, the isotopic composition of plutonium immediately after discharge is as follows: ^{238}Pu (2.5 wt %), ^{239}Pu (51 wt %), ^{240}Pu (21.6 wt %), ^{241}Pu (18.9 wt %), and ^{242}Pu (6 wt %).[465]

Plutonium release from spent fuel in a geological repository upon water access depends on various parameters:

- The chemical form of plutonium in the waste form
- The chemical/geochemical conditions in the repository near field
- The retention properties of the technical, geotechnical, and geological barriers

Because of the redox potential of the irradiated fuel matrix, plutonium mainly forms thermodynamically stable double dioxides with U(IV) and thus appears to stay as a tetravalent cation at the position where it has been generated.[466] However, minor fractions of $Cs_2(U_{0.97}Pu_{0.03})_4O_{12}$, Pu_2O_2Te, and (U, Pu, Zr, Mo, RE)O_3 phases may form (RE: rare earth elements).[467] XAS investigations of both nonirradiated and irradiated MOX fuel (4.7 wt % plutonium) showed plutonium predominantly in the oxidation state Pu(IV); Pu(III) contributions were less than 10

% in the center of the irradiated pellet and no oxidized species (Pu(V) or Pu(VI)) were visible, presumably because of redox buffering by the $UO_{2(+x)}$ matrix.[186, 459]

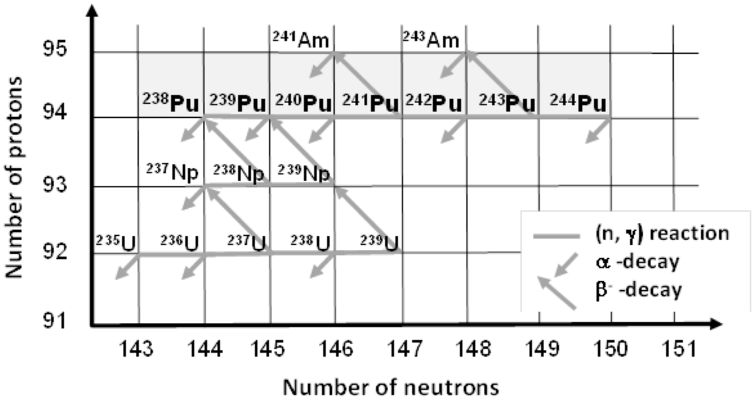


Figure 47. Major pathways for the generation of plutonium isotopes by neutron capture reactions in a nuclear fission reactor.

Plutonium in the fuel pellet is not homogeneously distributed, and it is well known that plutonium can be significantly enriched in the rim zone, where neutron flux is high. Using micro-Raman spectrometry, Jegou et al.[468] investigated the oxidation resistance of those high-burnup structures in UOX and MOX fuel by heating and exposing to air. The surface crystal structure as analyzed by Raman spectrometry does not vary significantly, indicating high stability against oxidation.

Plutonium examined by transmission electron microscopy–electron energy loss spectroscopy[469] in an irradiated UOX sample corroded under water vapor was determined to be Pu(V) because of radiolytically driven oxidation. There were indications that Pu(V) is stabilized in a U_3O_8-like secondary phase matrix.[469]

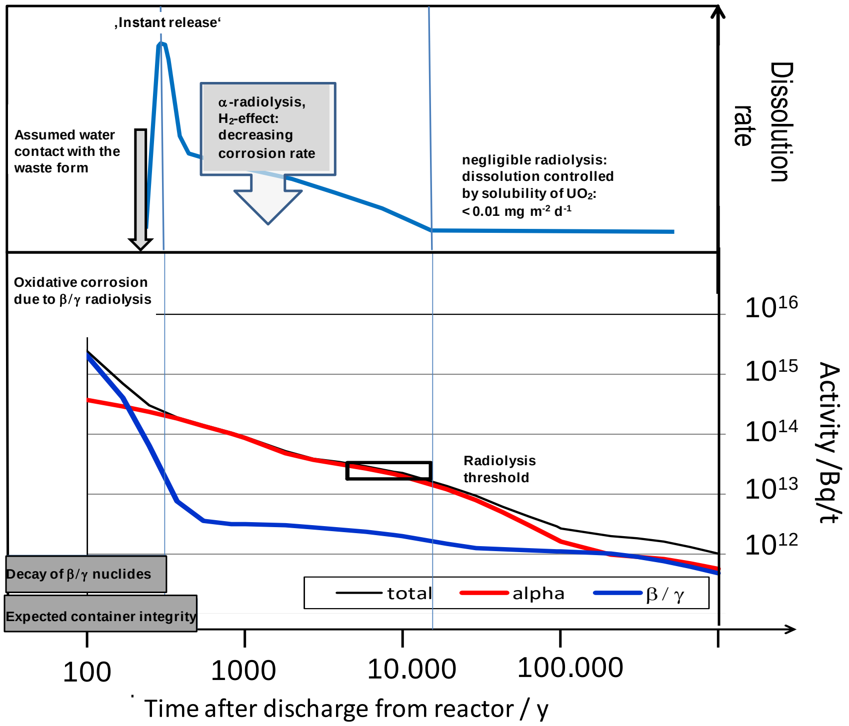


Figure 48. Corrosion and dissolution behavior of irradiated uranium oxide fuel as a function of radiolysis evolution over time. The instant-release fraction relates to radionuclides located in gaps and grain boundaries of spent fuel assemblies. In the case of water access to spent fuel pellets, fractions of ^{135}Cs, ^{129}I, ^{36}Cl, ^{79}Se, and others can be released relatively rapidly. Below a certain radiation threshold of the spent fuel, radiolysis becomes negligible, and radiolytically driven oxidative dissolution of the UO_2 matrix stops. Plutonium release is clearly driven by UO_2 matrix dissolution (Reprinted after modification from Ref. 470, Copyright (2012), with permission from Elsevier).

Kropf and Fortner et al.[471, 472] performed XAFS analysis on a piece of irradiated UOX corroded under aerobic conditions. Plutonium was found to exist as Pu(IV), most likely in the form of a solid solution in $U(Pu)O_2$ in the unaltered fuel. Alteration layers consisting of U(VI) silicate phases still contained plutonium and neptunium, mostly in the tetravalent state and very much depleted compared to the Pu(Np)/U ratio in the unaltered fuel.

Numerous experiments have been performed to study the corrosion of spent nuclear fuel under variable geochemical conditions in different groundwater types and to quantify the release of radionuclides (e.g., see Refs. 473-477). In general, release “mechanisms” for different radionuclide groups can be distinguished by given boundary conditions

(Figure 48). Fission and activation products, such as isotopes of cesium, iodine, and chlorine, are enriched in gaps and grain boundaries of irradiated nuclear fuel pellets, so they can be easily accessed by groundwater and rapidly released (the so-called instant-release fraction). As discussed previously, plutonium exists as Pu(IV) in a solid solution with UO_2. Oxidizing conditions caused by either oxygen access under aerobic atmosphere or the presence of oxidizing radiolysis products (H_2O_2, $^{\cdot}OH$, OCl^-, etc.) induce oxidative dissolution of UO_2 and thus the release of matrix-associated radionuclides. For plutonium, low concentrations have usually been measured in leachates. Dynamic leaching of spent fuel samples at pH = 7 and oxidizing conditions (Eh standard hydrogen electrode [SHE] = 400 mV) revealed slow plutonium dissolution compared to that of the UO_2 matrix (fraction of inventory in the aqueous phase [FIAP]: $FIAP_{Pu}/FIAP_U = 0.07 \pm 0.02$). Plutonium concentrations of 5×10^{-10} M are considered steady-state levels rather than driven by solubility constraints.[478] Concentrations of 10^{-9} to 10^{-7} M of plutonium were found in spent nuclear fuel leachates over a wide pH range in 5 M NaCl solutions, simulating brines in a rock salt repository and Eh SHE values ranging from 400 to 480 mV.[479] In leaching experiments with deionized and granitic groundwater under oxic conditions, plutonium concentrations were ~10^{-8} M and lower.[480] These low plutonium concentrations are usually attributed to the predominance of Pu(IV) oxyhydroxide solid phases controlling the solubility of plutonium. However, it has also been noted that significant fractions of dissolved plutonium could be colloidal.[481, 482]

As already shown in Figure 3, plutonium oxidation state prevalence in an aquatic environment depends on Eh and pH. Pu(IV) is predominant in a broad range of Eh/pH conditions and likely controls the solubility and mobility of plutonium under the geochemical conditions of a repository. However, various studies correctly claim that very reducing conditions must be expected in a “real” repository because of the anoxic corrosion of container material (e.g., $Fe + H_2O \rightarrow H_2 + Fe(OH)_2$). In this case, geochemical redox conditions will be located at the lower boundary of the water stability field and in the predominance field of Pu(III). Solubilities of Pu(III) oxyhydroxide phases under circumneutral conditions are orders of magnitude higher than those of the corresponding Pu(IV) phases. However, such large increases in plutonium release under reducing conditions (e.g., in the presence of corroding iron or under an H_2 atmosphere) have not been noticed. This is mainly because (1) under elevated H_2 partial pressures, oxidative UO_2 corrosion becomes strongly inhibited and thus matrix dissolution constrains plutonium release; and (2) Pu(III) strongly sorbs to iron corrosion products, such as magnetite (Figure 49).[99, 483] Investigations of plutonium that was produced in the natural Oklo reactor and subsequently decayed to ^{235}U revealed that it was incorporated in apatite and adsorbed to iron-containing clay minerals (chlorite).[89] Even though these findings cannot be directly translated to predictions for a repository for spent nuclear fuel in a given host rock, they provide valuable insight into the long-term geochemical reactions of plutonium at a natural analogue site: strong retention by formation of solid mineral phases and surface sorption in a reducing environment.

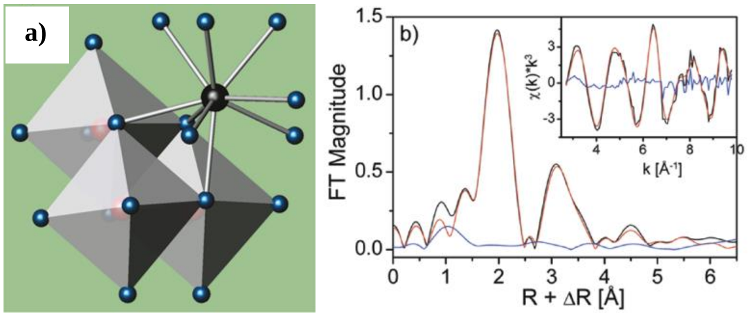


Figure 49. (A) Structure of a Pu(III) surface complex at the octahedrally terminated magnetite (111) plane. (B) Fourier transformed (FT) Pu L_3-edge extended X-ray absorption fine structure (EXAFS) data.[99] Pu_{tot} added to magnetite as Pu(V) or Pu(III): $1.3\ 10^{-5}$ M; magnetite: 5.55 g/L; pE = −5 and pH = 8 (Reprinted (adapted) with permission from Ref. 99. Copyright (2011) American Chemical Society).

6.1.2 Vitrified Waste.

High activity waste (HAW) generated by reprocessing activities (i.e., after uranium and plutonium separation) is usually conditioned by vitrification in a borosilicate matrix. Phosphate glasses and other glass types have also been used less frequently.[460, 484] Plutonium content is low (<0.12% of the originally present plutonium in spent nuclear fuel, according to Ref. 485), and speciation in such matrices is governed by Pu(IV), as identified by recent XAFS investigations in real highly radioactive HAW glass.[461] The solubility of plutonium in a borosilicate glass melt is about 4.5 wt %.[460, 486] The plutonium L_3-XANES spectrum shows the characteristic position of the white line (WL) for Pu(IV) and multiple scattering features visible as a shoulder above the WL typical of trans-dioxo (plutonyl) structures of Pu(V) and Pu(VI) are absent. Plutonium thus mainly exists as Pu(IV) dissolved in the borosilicate network; however, plutonium has also been observed to be associated with separated CeO_2 phases.[460] Vitrification has occasionally been proposed as an appropriate immobilization matrix for excess plutonium, such as that from weapon production.[487] Specific lanthanide borosilicate types can host higher plutonium loading in the glass matrix but with minor crystalline PuO_2 and/or PuO_2–HfO_2 solid solution components.[488]

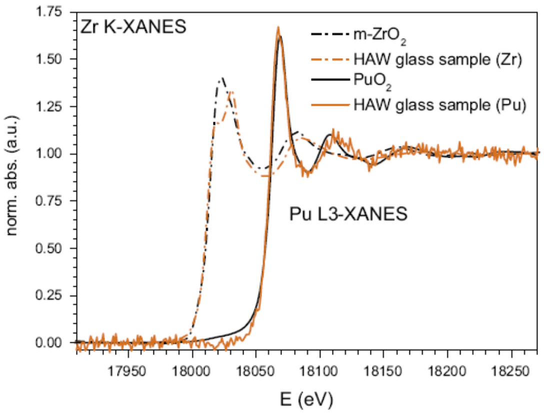


Figure 50. Normalized Zr K–X-ray absorption near-edge spectroscopy (XANES) (dash-dotted lines) and Pu L_3-XANES spectra (solid lines) of a real HAW borosilicate glass fragment and corresponding reference spectra obtained for monoclinic Zr(IV)O_2 and Pu(IV)O_2 (Reprinted from Ref. 461, Copyright (2015), with permission from Elsevier).

Investigations related to waste glass corrosion upon contact with groundwater have been carried out for more than 30 years[485] and can be summarized as follows. Individual glass corrosion phases consist of

1. rapid initial dissolution of reactive sites at the glass surface and exchange of alkali cations;
2. water diffusion into the surface glass layer, proton exchange with alkali ions, and formation of a hydrated silica-like gel layer; and
3. generation of secondary solid-phase precipitates, such as oxyhydrates, clay minerals, zeolites, and molybdates, and ongoing slow corrosion, probably governed by further water diffusion through the gel layer.

In principle, such processes can also be observed for natural glasses, such as basaltic glasses, over hundreds of thousands of years.[489] Radionuclide release is determined by the corrosion behavior of the glass matrix, the specific radionuclide chemistry properties, and the environmental chemical conditions. A comprehensive summary of existing knowledge and open questions was prepared by the European Community.[485] Estimates for radionuclide release from glass in a clay barrier environment in the water-filled void volume of a canister in terms of element fractions are 10^{-14}/y for americium, 10^{-10}/y for plutonium, and 5×10^{-6}/y for cesium and iodine.[490] Analyzing plutonium concentrations in glass leachates demonstrates a strong dependence on redox conditions (Figure 51).[491] Under oxidizing conditions, solution concentrations can be described by an equilibrium between PuO_2(am) or $PuO_{2.5}$(s) with PuO_2^+ in solution. Under reducing conditions, solution concentrations appear to be controlled by reductive PuO_2(am) dissolution and Pu^{3+} in solution. Furthermore, various studies imply that at least a portion of actinides may also be retained in secondary solid phases, such as clay minerals,[492] or molybdates, such as powellite.[493, 494]

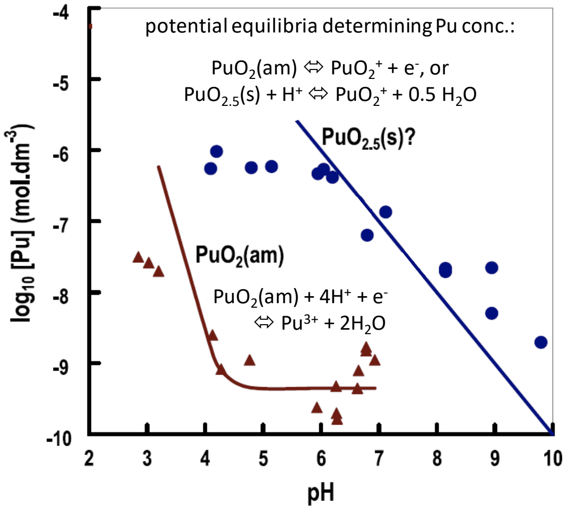


Figure 51. Plutonium concentrations found in plutonium-doped borosilicate leachates. Solid circles: glass equilibrated with 0.1 mol/L $NaNO_3$ in air; solid triangles: glass equilibrated with 0.0015 mol/L $CaCl_2$ containing hydrochinone buffer; solid lines: calculated solubilities based on indicated solid/solution equilibria (modified from Ref. 491 with permission of Springer).

6.2. Low- and Intermediate-Level Waste Forms

6.2.1. Ceramic Waste.

Various ceramic waste forms have been proposed for plutonium immobilization.[457, 460, 484, 495, 496] These were originally developed as alternatives to borosilicate glass forms, and the primary aim was to find an appropriate disposal strategy for decommissioned nuclear weapon plutonium. Table 20 describes some of the discussed mineral phases.

Table 20. Properties of Potential Ceramic Waste Forms for Plutonium Immobilization (reprint with permission from Ref. 495)

	Aqueous durability	Chemical flexibility	Waste loading	Radiation tolerance	Volume swelling	Natural analogues
Perovskite $(Ca,Sr)TiO_3$	Low	Medium	Low	Medium	High	Yes
Pyrochlore $Gd_2(Ti,Hf)_2O_7$	High	High	High	Low-high	Medium	Yes
Zirconolite $CaZrTi_2O_7$	High	High	Medium	Low-medium	Medium	Yes
Zircon $ZrSiO_4$	High	Medium	Low(?)	Low	High	Yes
Monazite $LnPO_4$	High	Medium	High	High	Low	Yes
Zirconia $(Zr,Ln,Act)O_{2-x}$	High	Medium	Medium	High	Low	No

All host matrices can incorporate relatively high plutonium fractions (up to 35%) by forming solid solutions without segregation of pure plutonium solids. Initially proposed synthetic rock materials consist of titanates and are reported to exhibit much higher leaching resistance properties than those reported for borosilicate waste forms.[497, 498] They are designed as host matrices for the whole range of elements in nuclear waste, including fission products. Radiation stability has been set as a main criterion in order to prevent enhanced solubilities due to amorphization due to recoil damage. Pyrochlore and phosphates are reported to have high radiation-damage resistance specifically designed for actinide (notably plutonium) incorporation; they keep their crystallinity even at high dose exposure. Experimental studies related to radiation stability using irradiation with ion sources are complemented by examining the respective naturally occurring minerals. These minerals mostly contain primordial or radiogenic radionuclides, are stable over millions of years, and conserve radiation damage so that the long-term radiation stability over time can be studied.

Leaching rates for crystalline ceramic waste forms are usually significantly lower than those for borosilicate glasses. But plutonium concentrations found in leachates appear to be as well controlled by redox conditions and are usually very low, suggesting that solubility-controlling Pu(IV) solid phases are present (e.g., see Refs. 499, 500).

6.2.2. Cemented Waste.

LLW and ILW with comparably low plutonium content are characterized by complex compositions. Instead of disposing of high-level and long-lived radioactive waste in deep geological formations, many countries consider disposal of this type of waste near or at the surface. Besides the abundance of mostly old bituminized waste, by far the highest volumes of residues from nuclear activities have been and will continue to be waste mixed with cement materials. The potential for creating a positive geochemical environment for radionuclide immobilization is also the reason for the "supercontainer concept" pursued by Belgium, in which encapsulation of even spent fuel in a concrete hull is considered a reference container concept.[501]

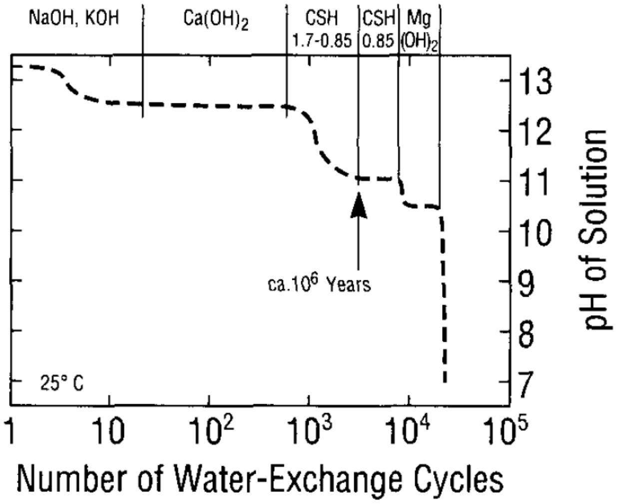


Figure 52. Simplified scheme representing the variation of the geochemical milieu upon cement corrosion (according to Ref. 502). CSH = calcium silicate hydrate.

Because of its high porosity and permeability, cement does not provide sealing against water access but does provide shielding against radiation and, to some extent, mechanical protection. Cementitious systems, cementitious matrices, and encapsulants, however, provide high pH (>10) for long time periods (about 10^6 years) in the vicinity of the waste.[503, 504] In addition, cement phases that are originally present or that form during degradation offer large surfaces and reactive sites for radionuclide retention (Figure 52) (e.g., see Ref. 505).

In general, there is strong retention of plutonium at cementitious phases,[506,507,508] and measured K_d values range from 10^3 to 10^6 mL/g. The Eh/pH diagram in Figure 3 shows that under hyperalkaline conditions, the plutonium redox state is not necessarily determined by the tetravalent species. As has been recently demonstrated, neptunium might be stabilized even as Np(VI) if oxygen is present and the redox potential is oxidizing in an early stage of the repository or in the presence of oxidizing agents, such as NO_3^-.[509] Sorption of Np(IV), Np(V), and Np(VI) to cementitious phases appears to be similarly strong.[510] For plutonium, such systematic investigations have not been performed, but through analogy we can assume similar behavior. Under reducing conditions, the predominance of Pu(III) is likely. For other trivalent actinide ions, such as Am(III) and Cm(III), sorption to cement phases is determined by incorporation into calcium silicate hydrate phases by replacing Ca^{2+}.[511, 512] Again, by analogy, such strong retention can also be expected for Pu(III) but has not yet been proven.

Special conditions can be established in a repository in rock salt if $MgCl_2$-rich brines come into contact with cement and Mg^{2+} is exchanged for Ca^{2+}. As a consequence, Ca^{2+}-rich solutions may be prevalent and the solubility of tetravalent plutonium can be significantly increased by the formation of ternary complexes, such as $Ca_4[Pu(OH)_8]^{4+}$ (Figure 53).[513] Formation of calcium-stabilized hydroxo complexes is observed for plutonium and other tetravalent and trivalent actinides; however, strong sorption to cement phases appears to some extent to counterbalance solubility increase.[514, 515]

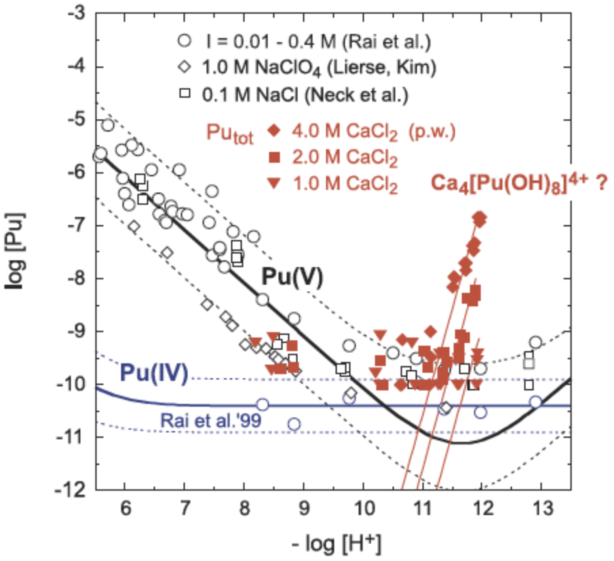


Figure 53. Solubility of PuO_{2+x} (am,hyd) in alkaline $CaCl_2$ solutions under argon atmosphere (taken from Ref. 513 with permission).

A specific problem of LLW/ILW disposal is the heterogeneity of waste components. One such issue is the impact of cellulose degradation products (mainly isosaccharinic acid [ISA] and gluconate [GLU]) on radionuclide sorption and retention.[516-518] In the presence of 10^{-4}–10^{-3} M ISA, the K_d value for the sorption of Pu(IV) to cement and mortar can decrease by 3–5 orders of magnitude because of formation of ISA complexes.[518] Pu(IV) forms $Pu(IV)(OH)_x(ISA/GLU)_y$-type ternary complexes in the absence of Ca^{2+}. For Th(IV), a similar $CaTh(OH)_4(ISA/GLU)_2(aq)$ species is found.[517] Complex stability constants for Pu(IV) have been derived by applying experimental data and linear free-energy relationship estimates.

Additional issues relate to the potential impact of organic superplasticizers, such as polycarboxylated comb and polyether comb–type materials, found in modern cement materials on plutonium remobilization from cement. Only a moderate decrease in sorption of various radionuclides in the presence of relevant typical organic plasticizer materials has been found.[519] Some mobilization under specific conditions is reported in Ref. 520. No data currently exist for plutonium.

6.3. Plutonium Behavior in the Bentonite Barrier and the Far Field of a Deep Geological Repository.

Plutonium is considered immobile under the reducing conditions below the water table and at low (stagnant) groundwater flow conditions of a deep geological repository. In most safety analysis studies, plutonium is considered to decay within the disposal zone.[521,522] This result is based on the assumption that permanent reducing conditions lead to the presence of only the reduced species Pu(III) and Pu(IV). As discussed previously, these are generally poorly soluble, strongly sorbing to mineral surfaces, and thus are only slowly transported in diffusion-controlled regimes.

In many repository designs, compacted swelling bentonite is viewed as a geotechnical barrier, providing a barrier against water access, strong sorption capacity to prevent radionuclide migration, and a geochemical buffer controlling chemical boundary conditions. A number of investigations of plutonium sorption and diffusion in bentonite systems have been reported. Spent UOX leaching studies in the presence of bentonite showed a significant decrease in plutonium concentrations in solution due to strong sorption to clay minerals.[523, 524] When contacting bentonite with the UOX pellet, diffusive migration of plutonium was less than 1 mm during an experimental observation period of 6 years.[525] Similar investigations using waste glass revealed similar results. Although the glass corrosion rate increases (potentially because of a pump effect where the silicate dissolution rate is enhanced and quartz precipitates in the clay plug), plutonium concentration and mobility remain low.[526]

Results of diffusion experiments are to some extent contradictory. Diffusion coefficients are found to vary (10^{-12}–10^{-15} m^2/s) depending on bentonite type, compaction density, redox conditions, and so forth.[527-530] Those values, however, must be considered with care. In some cases redox conditions were not controlled. Furthermore, it is well known that experimental diffusion studies with strongly sorbing tracers are often hampered by experimental artifacts, such as sorption to tubing, filters, and the impact of disturbed zones at the boundaries of clay plugs used for the studies (e.g., see Refs. 531, 532). Such effects can have a significant impact on diffusion coefficients. The presence of carbonate and HA in general appears to enhance the diffusivity of a small plutonium fraction in compacted bentonite.[527] Investigations with cement leachate solutions rich in calcium and bentonite aimed to simulate the situation in a repository where concrete contacts the geotechnical barrier.[533] In those experiments, no movement of americium and plutonium was observed over periods of 2.5 to 5 years. Similar results were obtained in experiments using compacted sand/bentonite mixtures. Very little diffusive plutonium transport was observed, and the result was explained by the physical filtration of colloidal plutonium species.[534]

The available data are in agreement with the general finding of strong plutonium sorption to clay minerals and thus immobilization.[85, 88, 90, 92, 535, 536] As discussed in Section 1.1, redox reactions play an important role in plutonium sorption and are also not independent from the presence of mineral phases inducing surface redox reactions. The presence of organic complexants, such as HA, and microbial exudates, such as desferrioxamine, may alter the interaction mechanism and lead to either enhanced retention or mobilization.[52] Whereas mobilization is facilitated by dissolved low molecular mass organic ligands, plutonium sorption is significantly enhanced as soon as desferrioxamine, for example, gets trapped in clay interlayers.

Plutonium mobilization by clay particles eroding from bentonite barriers has also been investigated. Inorganic clay colloid release from bentonite barriers in repository concepts in crystalline rock is discussed in the context of far future scenarios where low-mineralized glacial melt water intrusion may lead to erosion.[537] Plutonium could in principle be mobilized in the case of defective containers and water contact to the spent fuel. Laboratory and field experiments related to the clay colloid–facilitated plutonium migration in granitic fractures have demonstrated the strong binding of Pu(III/IV) to colloidal clay particles and the mobility of colloid-borne plutonium (notably in low-ionic-strength groundwater) for at least some meters at migration times of several days.[83, 84, 538, 539] However, slow plutonium desorption from clay colloids and colloid attachment to granite surfaces are also found and contribute to the retention of a part of the plutonium. Experimentally determined desorption rates of plutonium fractions from different synthetic and natural clay colloids range from 2.7×10^{-4} to 1×10^{-3} h^{-1}.[540] Consequently, plutonium recoveries decrease with increasing residence times in a water-conducting fracture. However, the fact that small plutonium fractions could remain stably bound to colloids for long time scales cannot be excluded.

The repository concept in Yucca Mountain, the previous reference concept for the disposal of spent nuclear fuel in the United States, envisaged waste emplacement above the water table in an arid zone so that oxygen access could not be disregarded. Formation of oxidized species may increase actinide solubility and release.[24] Therefore, several studies examined the interaction of Pu(V) and Pu(VI) with mineral surfaces typical of the tuff rock at the site and found significant retention. Duff et al.[541] found Pu(V) sorption to tuff samples, primarily to ranceite ((Ca,Mn)Mn_4O_9 x $3H_2O$), where apparently partial oxidization to Pu(VI) by mineral-bound Mn(III) took place. In a later study of plutonium interaction with tuff and synthetic pyrolusite (β-MnO_2), time-dependent redox reactions were discovered: oxidation to Pu(V/VI) was observed initially, followed by reduction to Pu(IV) within days and months.[542] The latter finding is consistent with the general geochemical considerations discussed in Section 1.1.

Colloid-mediated transport is considered to enhance plutonium mobility.[76, 77] Safety analyses for disposal concepts in plastic and consolidated clay rock emphasize the efficient colloid filtration properties of the nanoporous sediment layers (e.g., Ref. 521). In the organic-rich Boom clay formation considered as a repository host rock formation in Belgium, plutonium associated with colloidal humic/fulvic matter can be regarded as mobile to some extent, if the molecular mass of colloids remains below 20 kDa.[59] Complexation of tri- and tetravalent radionuclides to colloidal organic matter in the pore water is quite well known.[57] However, during diffusive transport of humic-borne colloid-borne radionuclides, dissociation is also observed, leading to the sorptive retention of radionuclides at clay mineral surfaces and thus to retention in the long term.[57] Experiments on the humic colloid–mediated actinide transport in porous sandy aquifer layers overlying the previously proposed German site for final disposal in rock salt, Gorleben, resulted in similar findings[58] and pointed to the limited mobility of humic-/fulvic-borne plutonium. Whether reactions, such as conformation changes, or formation of inorganic/organic colloid assemblages is responsible for the observed kinetics (and may even lead to the irreversible binding of a residual actinide fraction to colloids) remains an open question.[42]

6.4. Plutonium Behavior in Existing Disposal Sites

6.4.1 Deep-Well Injection of Liquid Radioactive Waste.

As discussed above, liquid radioactive waste from reprocessing is usually immobilized by vitrification before disposal. But direct disposal of liquid hazardous waste by injection into geological reservoir horizons has been practiced worldwide.[543] Since 1963, the former Soviet Union/Russia has disposed of LLW and ILW from reprocessing activities at three sites at depths ranging from 180–500 to 1130–1550 m (Figure 54).[544, 545] Storage horizons with porous rock layers, such as sandy, clayey or limestone formations, confined by impermeable sedimentary clay deposits were selected. The decision to use deep-well injection disposal for liquid radioactive waste was made because of accidental environmental contamination problems arising from surface-disposed liquid waste in regions with large nuclear facilities (see previous sections). More than 50 million m^3 of liquid radioactive waste, containing about 3.3 10^7 TBq, was injected at the three sites.[504] Waste streams differed in their composition but were rich in nitrate, acetic acid, and corrosion products (aluminum, iron, chromium, manganese). Radionuclide activity concentrations were dominated by fission products like ^{137}Cs, ^{90}Sr, and ^{99}Tc. Activities for transuranium elements are orders of magnitude lower and plutonium is not believed to be a significant component of this waste.[329] Some typical components of liquid wastes are given in Table 21.

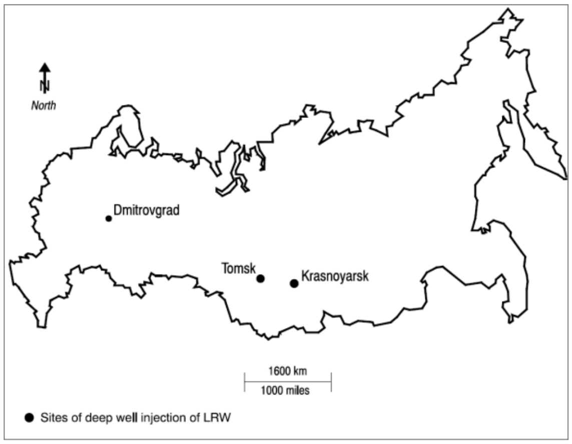
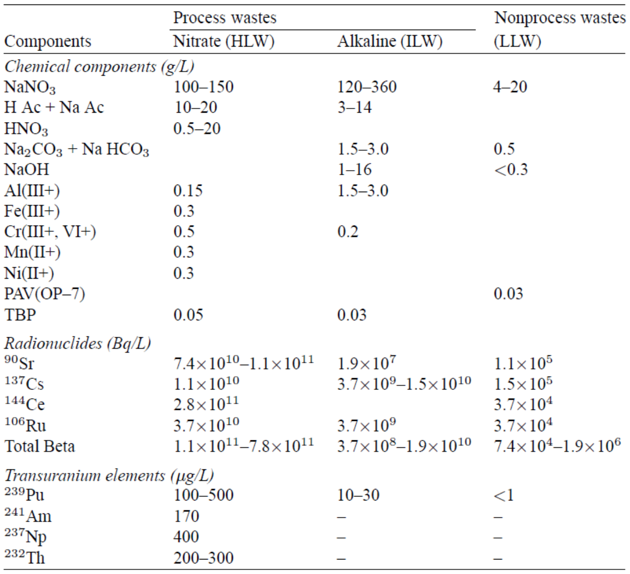


Figure 54. Sites of deep-well injection of low- and intermediate-level radioactive waste in the former Soviet Union.[546] (Reproduced with permission from the International Institute for Applied Systems Analysis (IIASA))

LRW = liquid radioactive waste.

Table 21. Radionuclide Composition in Different Waste Streams Injected at the deep injection disposal site "Severny" Krasnoyarsk Site[546] (Reproduced with permission from the International Institute for Applied Systems Analysis (IIASA))



	Process wastes		Nonprocess wastes
Components	Nitrate (HLW)	Alkaline (ILW)	(LLW)
Chemical components (g/L)			
$NaNO_3$	100–150	120–360	4–20
H Ac + Na Ac	10–20	3–14	
HNO_3	0.5–20		
Na_2CO_3 + Na HCO_3		1.5–3.0	0.5
NaOH		1–16	<0.3
Al(III+)	0.15	1.5–3.0	
Fe(III+)	0.3		
Cr(III+, VI+)	0.5	0.2	
Mn(II+)	0.3		
Ni(II+)	0.3		
PAV(OP–7)			0.03
TBP	0.05	0.03	
Radionuclides (Bq/L)			
^{90}Sr	7.4×10^{10}–1.1×10^{11}	1.9×10^{7}	1.1×10^{5}
^{137}Cs	1.1×10^{10}	3.7×10^{9}–1.5×10^{10}	1.5×10^{5}
^{144}Ce	2.8×10^{11}		3.7×10^{4}
^{106}Ru	3.7×10^{10}	3.7×10^{9}	3.7×10^{4}
Total Beta	1.1×10^{11}–7.8×10^{11}	3.7×10^{8}–1.9×10^{10}	7.4×10^{4}–1.9×10^{6}
Transuranium elements (µg/L)			
^{239}Pu	100–500	10–30	<1
^{241}Am	170	–	–
^{237}Np	400	–	–
^{232}Th	200–300	–	–

Safety analyses suggest that radionuclide plumes move slowly, so short-term risks of public radiation exposure and surface-water contamination are not expected.[547] Injected solutions can be quite acidic (pH ~2.5), and because of the high concentrations of fission products in HLW solutions, temperatures can reach about 150 °C. Experimental studies with simulated solutions suggest that under those conditions, corrosion products in solution form iron/chromium oxide-phase precipitates and surface coatings on sand grains. Sequential extraction and spectromicroscopy experiments reveal that under those conditions, plutonium is removed from solution and accumulates by sorption to and coprecipitation with mainly hematite and goethite.[548, 549]

At Oak Ridge in Tennessee, ILW injection of alkaline nitrate-rich (1–2 M $NaNO_3$) waste solutions containing 5,600 TBq of radionuclides (mainly ^{137}Cs and ^{90}Sr) took place from 1964 to 1984.[550] Waste also contained ^{3}H, ^{60}Co, ^{106}Ru, and isotopes of curium, uranium, americium, and plutonium. It was pressed as a slurry with cement and fly ash, with a total volume of about 2×10^{7} L of waste-bearing grout injected into porous formations at 240 m depth. After the end of operation in 1984, monitoring revealed that contaminated groundwater extended as far as 300 m around the injection well but remained confined to the host formation. Mainly ^{90}Sr was found to be mobile, along with traces of

^{3}H and ^{106}Ru. It was concluded that ^{137}Cs was retained by sorption to illite and illite/vermiculite minerals. As in the monitoring studies at the Russian sites, transuranium elements, including plutonium, apparently exhibit poor mobility under these conditions, and this mobility was not detectable.

6.4.2 Disposal of Radioactive Waste into the Deep Sea.

Dumping of liquid effluents from reprocessing and nuclear power plants (e.g., Sellafield, La Hague) directly into the sea was discussed in previous sections. Other examples of radioactive waste disposal in the sea include dumping of solid LLW and ILW from both military and civil sources as well as fueled submarines.

From 1946 until 1982, mostly packaged LLW was disposed of by many countries[551] in the deep sea at various places around the world.[552] Total activity in the waste contained in metal drums and embedded in cemented or bitumen matrices is estimated to be 63 PBq. In 1975, the London Convention entered into force, and open sea disposal of radioactive waste was completely abandoned in 1993. Most of the activity was disposed of at two main sites in the northeast Atlantic Ocean,[553] as well as in the Barents and Kara Seas and in the Far East (Figure 55).

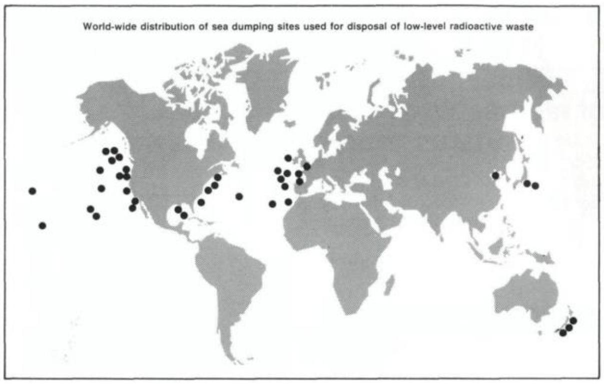


Figure 55. Sea dumping sites for low-level radioactive waste (taken from Ref. 552).

The concentration of ^{238}Pu was found to be 5–7 times higher in seawater at the disposal sites than at control areas.[553] The same is true for ^{239,240}Pu, ^{241}Am, ^{137}Cs, and ^{14}C. The ^{238}Pu/^{239,240}Pu activity ratio at those sites is significantly higher than that expected from global fallout in the Northern Hemisphere (0.029 ± 0.008). Still, ^{239,240}Pu activity concentrations are low (in the 20-μBq/L range) and thus radiologically negligible. However, the results show the mobility of a small fraction of waste-borne plutonium.

In the former Soviet Union, the Kara and Barents Seas and Far East seas were used for the disposal of liquid as well as solid radioactive waste from military and civil atomic fleets from 1960 to 1991.[554, 555] Significant amounts of radioactive waste were dumped in the Arctic region (Table 22), especially in the shallow fjords of Novaya Zemlya.[554]

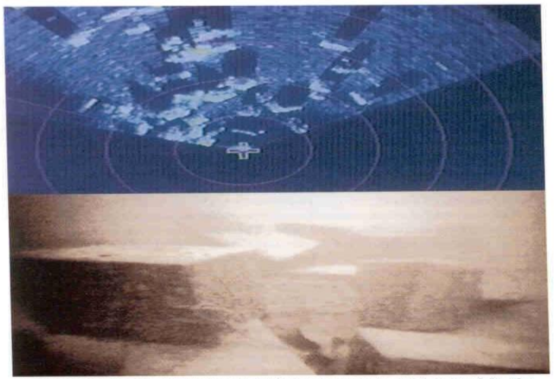
Table 22. Total Activity of Radioactive Wastes Dumped in the Arctic Region by the Former Soviet Union and Russia

Waste type	Total activity at time of dumping, TBq	Percent of total activity
Reactor units with spent nuclear fuel	21,781	56.1
Reactor units without spent nuclear fuel	14,802	38.1
Reactor components	20.8	0.1
Low-level solid waste	1,240.21	3.2
Low-level liquid waste	957.8	2.5
Total	38,801.81	100

Note: Data from the White Book 2000.[555]

In the Kara Sea and in the Abrosimov, Stepovogo and Tsivolki Fjords at Novaya Zemlya (Figure 56), 6 reactors with fuel (including K-27), 10 reactors without fuel, part of the fuel assembly from the icebreaker Lenis as well as more than 6000 containers, barges, and vessels containing radwaste were dumped at sea in the period 1960-1988. . The reactor vessels were partly filled with furfural-based polymers or with cement prior to dumping. Special focus has been put on the sunken November class submarine K-27, having two experimental reactors with lead-bismuth liquid metal coolants. The accident occurring in 1968 resulted in major contamination of the primary circuit and the reactor compartment, leading to radiation exposure and a number of fatalities amongst the crew. K-27 was dumped at a depth of 33 m in the Stepovogo fjord in 1981, containing about 1.7 PBq actinides at the time of dumping.[535]

The potential leaking from the dumped waste in the Kara Sea and associated fjords was inspected during the Joint Russian–Norwegian expeditions in 1992, 1993, 1994, and 2012. Based on in situ gamma measurements and collected seawater, sediment, and biota samples, no leakage from the K-27 reactor could be identified.[361, 551, 556] However, sediment samples in close vicinity of corroded waste containers showed enhanced levels of ^{60}Co, ^{90}Sr, ^{137}Cs, and ^{239,240}Pu, documenting that leakage had occurred.



Sonar screen and picture of dumped containers located in the inner part of the Stepovogo fjord.

Figure 56. Sonar screen (upper) and underwater photo (lower) of dumped waste containers in the Stepovogo Fjord.[557]

Plutonium concentrations ranged from a maximum of 3 Bq/kg in 1–2 cm depth to ~0.2 Bq/kg in 10–11.5 cm depth in sediment samples taken from the Stepovogo Fjord. In sediments samples from the Abrosimov Fjord, activity was about 2–5 Bq/kg regardless of the depth, down to 8 cm.[361] The plutonium concentration was inhomogeneously distributed, and the authors concluded that radionuclides were associated with particles. Crud particles containing ^{60}Co were also identified in the Stepovogo Fjord. Low radionuclide concentrations including plutonium in the open Kara Sea were attributed to other sources, such as global fallout, transport from the Ob and Yenisey Rivers, releases from European reprocessing plants, and the Chernobyl accident. Safety analyses suggested that in the future, radiological effects arising from waste disposed of in the Kara Sea may be important on a local scale only. On a global scale, other anthropogenic sources appear to be more relevant.[558]

At the Kola Peninsula in northwest Russia, large amounts of spent nuclear fuel (highly enriched uranium) from nuclear submarines are improperly stored at Andreeva Bay and Gremikha (Table 23). In addition, spent nuclear fuel is improperly stored onboard ships, such as the *Lepse*. A series of submarines taken out of service were stored without decommission at Gremikha (898 fuel assemblies). At Andreeva, about 21, 000 fuel assemblies were stored under unsafe and unacceptable conditions.

Table 23. Solid and Liquid Radioactive Waste Stored at the Kola Peninsula[559]

Object/site	Solid, Bq	Liquid, Bq
Nuclear surface ships	2×10^{16}	
Andreeva	Up to 2×10^{16}	2×10^{15}
Gremikha	Up to 2×10^{15}	6×10^{10}
The enterprises	3×10^{16}	3×10^{14}
Nuclear maintenance ships	3×10^{15}	2×10^{14}
All	7.3×10^{16}	4.5×10^{15}

In Andreeva, most of the 21,000 spent nuclear fuel assemblies and about 21, 000 m^3 rad waste are still kept on site. Due to the severe degradation of the spent fuel at Andreeva, previous failure of containment barriers, leakages as well as and the overall poor conditions of the facility, this site has been of major concern for decades.

Comprehensive remediation initiatives have been undertaken nationally (Russia), bilaterally (e.g. Norway or France), regionally (Nordic countries), and internationally (e.g. G8 countries) to reduce the risk of nuclear legacies in the northwest of Russia. Activities include decommissioning submarines, retrieving improperly stored spent nuclear fuel and other radioactive waste materials, transporting spent nuclear fuel to Mayak PA, and cleaning up contaminated nuclear sites.[559] At Gremikha, decommission and shipment of the first fuel assemblies to Murmansk and then Mayak PA started in 2009. By 2012, all 898 fuel assemblies are reported to be shipped from the site. A clean-up program includes removal of radwaste and decommissioning of buildings has been initiated.[560] At Andreeva, the first shipment of fuel assemblies will take place in 2017.

6.4.3. Other Repositories and Dump Sites.

United States: Maxey Flats. The Maxey Flats site was an LLW disposal site in eastern Kentucky, United States (Figure 57). The 312-hectare site contains a disposal cell that was used from May 1963 to December 1977 for the disposal of LLW from research laboratories, hospitals, nuclear power stations, and commercial radioisotope users.[561] The cell contains 46 large unlined trenches that were up to 200 × 21 m in size and 9 m deep over an 11-hectare area. It also contains some "hot wells" that were used to dispose of smaller-volume wastes of higher activity. The volume of waste is estimated to be 125,000 m^3.[432] The waste contains 430 kg of special nuclear material, including ~180 TBq (80 kg) of ^{239}Pu as well as significant quantities of ^{238}Pu.

Natural stabilization was determined to be the most appropriate action for the restoration of this site. An interim cap has been placed on the site to minimize rainwater infiltration into the trenches. A permanent cap will be installed once the ground has stabilized.[562]

As early as the 1970s, leaching of radionuclides from the waste trenches into shallow groundwater was confirmed. High rainfall in the area led to the accumulation of water in the trenches and subsequent mobilization of radionuclides (referred to as the "bathtub effect"). To prevent overland flow, these water leachates are captured and treated. Filtration of the leachates indicated that the majority of plutonium was in the <50-nm fraction, was in the reduced tetravalent state, and was associated with organic ligands (including EDTA).[561]

A worker using a bulldozer filled one of the trenches at Maxey Flats, a nuclear-waste burial site, on Feb. 4, 1976. The state will continue to monitor Maxey Flats once a final cap is placed over the site next year. Photo by RON GARRISON — Herald-Leader

Figure 57. Shallow burial of waste at the Maxey Flats site. Reproduced from Ref. 563.

United States: Farallon Islands. Some 47,500 drums (55 gallons each), concrete blocks, and other containers were disposed of near the Farallon Islands near San Francisco Bay, United States. Excluding tritium, 540 TBq of thorium, uranium, transuranic elements, activation products, and fission products was deposited at this site. The plutonium inventory has not been determined. However, there are some indications of the presence of plutonium. Examination of the sediments and seawater at the site suggests that radiological releases from this site do not substantially increase radionuclide concentrations above those expected from global fallout.[564]

Australia: Little Forest Burial Ground. Between 1960 and 1968, radioactive waste containing small amounts of plutonium (~7 g) and americium was disposed of in shallow trenches at the Little Forest Burial Ground, located near the southern suburbs of Sydney, Australia. Water concentrations of 12 Bq/L of ^{239,240}Pu have been measured at this site, and plutonium contamination of surface soils extends tens of meters away from the trenches.[565] The migration of plutonium at this site has been attributed to the previously mentioned “bathtub effect”, in which higher porosity and permeability of the debris trenches leads to the focusing of water into the trenches. During periods of high rainfall, water levels can rise high enough to lead to overland flow of water and migration of radionuclides. Water sampling from the burial trenches indicated that plutonium is predominantly in the reduced Pu(IV) form and associated with the mineral and/or organic colloidal fraction.[566]

Other Burial Sites. A large number of plutonium-containing LLW sites exist globally, and it is beyond the scope of this chapter to describe the inventory and releases at each site.[567] Nevertheless, it is apparent that the mobilization of plutonium depends on the hydrologic conditions at the site, the composition of co-contaminants (e.g., organic complexants), and the presence of mineral colloids. Thus, the relative importance of each of the transport mechanisms cannot be determined without a careful evaluation of the specific conditions at each site.

6.5. Plutonium Behavior in the Natural Analogue Site of Oklo, Gabon, West Africa

As already mentioned in Section 2.1, about 2 metric tons of ^{239}Pu have been produced in natural reactor zones at the Oklo site in Gabon, West Africa. This site represents the only known place where criticality was reached in natural uranium mineralization pockets 2 billion years ago (Figure 58). A number of natural reactor zones have been identified at the Oklo site, at the adjacent Okélobondo site, and 30 km away in Bangombé.[89, 568] Although this plutonium has clearly been generated naturally, the site has been intensely examined as a “natural analogue site” for a nuclear waste repository and therefore is addressed here.

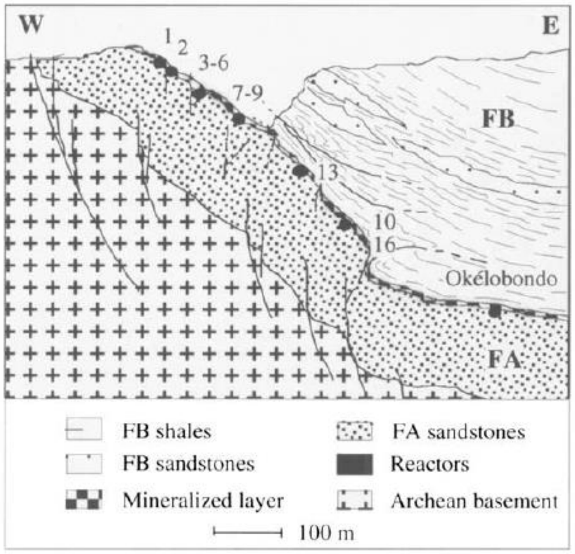


Figure 58. Cross section of the Oklo and Okélobondo deposit area with locations of natural reactor zones (taken from Ref. 569). Numbered black dots correspond to identified reactor zones.

The fission chain reaction running over 0.5 to 1 million years became apparent from the observation of significantly depleted uranium samples, with ^{235}U/^{238}U isotopic ratios as low as 0.0029.[570] In reaction zones, temperatures up to 500 °C with pressures up to 300 bar[571, 572] and thermal gradients of 100 °C/m were established. As a consequence of neutron capture reactions, ^{239}Pu was produced. Most of the ^{239}Pu was fissioned during the criticality period, and the residual part has decayed to ^{235}U. The site has thus been considered a unique natural analogue for radioactive waste disposal. Only here is it possible to investigate actinide (including plutonium) and fission product behavior under natural conditions over geological time scales. Conclusions on the fate of plutonium can be drawn by analyzing ^{235}U/^{238}U isotopic ratios in samples taken from the site. In most reactor zones, isotopic ratios indicate the immobility of plutonium and that ^{239}Pu has completely decayed within the core.[573] In some deeper-lying cores, enhanced ^{235}U/^{238}U isotopic ratios reaching values >0.00725 were found in some clay mineral and apatite samples.[89, 574, 575] The authors suggest that plutonium mobilization from the core took place by the impact of hydrothermal solutions followed by remineralization and plutonium incorporation into chlorite and fluoroapatite secondary phases, forming a hydrothermal alteration halo extending up some meters. Furthermore, the ^{235}U excess is interpreted as a consequence of ^{239}Pu dissolution or mineralization being preferential to that of uranium, leading to Pu/U fractionation. Recrystallization of secondary phases (apatite and chlorite) incorporating fissiogenic neodymium and samarium together with plutonium[574, 575] suggests the existence of plutonium in the trivalent oxidation state.

7. CONCLUSIONS

At the end of 2014, the global inventory of plutonium was estimated to be ~2630 metric tons, with expected yearly increased contributions of 70–90 metric tons from the nuclear fuel industry. In 2014, the global stockpile of separated plutonium was estimated to be ~500 metric tons, split nearly equally between the civil nuclear power industry and weapons-related activities. Some of this weapons plutonium has been declared excess to military needs and will be incorporated into the commercial nuclear power system. Production of plutonium for military use had greatly decreased by early in the 21st century, but the total plutonium inventory will continue to increase for the foreseeable future as a consequence of nuclear power production. The management of anthropogenic plutonium will continue to be a challenge in the decades to come, and accidental releases are inevitable. Indeed, these large inventories of plutonium must be prudently managed for many centuries. A complex blend of global political, socioeconomic, and technological challenges must be dealt with to manage these inventories efficiently and safely.[101, 197] We have observed that increased oversight and more-deliberate environmental management of nuclear reactor wastes and weapons production wastes have led to an overall decrease in annual plutonium release into the environment. Thus, experience in recent years indicates that responsible environmental management of radiological materials can be achieved.

The amount of plutonium released into the environment from a combination of atmospheric testing (~3000 kg), underground testing, and accidental and intentional releases is <1% of the global inventory of plutonium (Table 24). Disposal of spent nuclear fuel in deep geological repositories also contributes to the introduction of plutonium into the geosphere. However, the careful combination of geotechnical and geological barriers together with the low mobility of plutonium species under the reducing conditions in a repository is believed to restrict mobilization and to minimize potential access to the biosphere.

Following all severe nuclear events, a major fraction of refractory elements, such as plutonium, released into the environment is present as radioactive particles ranging in size from submicrometers to fragments. The particle characteristics depend on the source and release scenario. In particle-affected areas, sampling may not be representative because of uneven deposition, dissolution before analysis can be partial, and the plutonium inventory as well as the environmental impact and risk can be underestimated. Environmental plutonium chemistry remains a fascinating research field because of the multiple and complex interaction modes with environmental components. The fact that plutonium is clearly persistent in all environmental compartments (even though mostly at low concentrations), the long half-life of most plutonium isotopes, its radiological toxicity, the presence of plutonium-containing particles that transform into other plutonium species over time, the associated complex chemistry, and the perceived threat to the environment all contribute to a scientifically challenging problem. Further investigation of plutonium ecosystem behavior both in history and in the present day by extremely sensitive analytical tools can provide valuable progress for our knowledge of environmental behavior of plutonium and underlying processes and mechanisms. In addition, through the use of its unique isotope ratio signatures, plutonium may serve as an interesting tracer for the Anthropocene epoch and the general cycling of matter in environmental compartments.

Table 24. Summary of Plutonium Inventories in the Environment

Plutonium source	Mass, kg
Plutonium global inventory	~2,630,000
Natural plutonium	Several
Atmospheric testing	3400
Underground testing	2800 (NNSS only)
Weapons use	14
Reactor accidents	
Chernobyl	17
Chalk River Laboratories	Trace
Windscale fire	0.0087
Fukushima	0.001
Three Mile Island	0
Discharge from reactors and reprocessing plants	
Sellafield (sea)	276
Sellafield (airborne)	1.6
Dounreay	4.5
La Hague	1.5
Marcoule	0.2
Tokai	0.0002
Trombay/Bombay	Trace
Releases from large reactors/reprocessing facilities	
PA Mayak (formerly Chelyabinsk-65)	16,000[a]

Siberian Chemical Combine (formerly Tomsk-7)	850[a]
Mining and Chemical Combine (formerly Krasnoyarsk-26)	300[a]
Hanford	184
Rocky Flats	0.1
Los Alamos National Laboratory	43 (0.003)[b]
Idaho National Laboratory	340[c]
Savannah River Site	~0.01[d]
Waste repositories	
WIPP	0.000001 (5500)[e]
Maxey Flats	80
Farallon Islands	Trace
Little Forest Burial Ground	0.007
Beatty LLW site	21
Drigg site	5
Airplane, submarine, and weapons accidents	
McGuire Air Force Base	Trace
Johnston Atoll	Trace
Palomares	0.04
Thule	0.53–2.3
Komsomolets	8.3
K-159	Unknown
SNAP satellite	1 (^{238}Pu)
Ocean dump sites	Unknown

[a] Value is highly uncertain. [b] A total of 43 kg in various solid waste emplacements; 0.003 kg released to Mortandad Canyon. [c] Buried in the Subsurface Disposal Area and destined for final disposition at the Waste Isolation Pilot Plant (WIPP). [d] Much larger quantities remain stored in storage tanks and disposal facilities. [e] Only 1 mg has been released to the environment, although 5500 kg is planned for disposal at this site. LLW = low-level waste; NNSS = Nevada National Security Site; SNAP = Space Nuclear Auxiliary Power.

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