6. POTENTIAL FOR HUMAN EXPOSURE

6.1 OVERVIEW

Plutonium has been identified in at least 16 of the 1,689 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2007). However, the number of sites evaluated for plutonium is not known. The frequency of these sites can be seen in Figure 6-1. Of these sites, all are located within the United States.

Trace amounts of plutonium are found worldwide, mostly due to fallout from atmospheric nuclear testing, which ended in 1980, and released several isotopes of plutonium, including ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Pu (Clark et al. 2006; DOE 2005a; Eisenbud and Gesell 1997). Plutonium is not naturally occurring; however, trace amounts of ^{239}Pu are found in naturally occurring uranium ores, but the amounts are in such small amounts that extraction is not practical (Clark et al. 2006; Lide 2005). Small amounts of ^{244}Pu exist in nature from remnants of primordial stellar nucleosynthesis (Clark et al. 2006). Small amounts of plutonium were produced in natural reactors, such as the Oklo natural reactor in the African nation of Gabon, which existed about 2 billion years ago (DOE 2005a). The most common form of plutonium found in the environment is ^{239}Pu, followed by ^{240}Pu (DOE 1999a).

Large quantities of plutonium were first produced during the 1940s as part of the Manhattan Project in order to produce the atomic bomb. Production continued throughout the years of the Cold War (DOE 2005a). The United States built and operated 14 plutonium-production reactors at the Hanford, Washington and Savannah River, South Carolina sites starting in 1944 and ending in 1988 with the shutdown of the last reactor. A total of approximately 100 metric tons of plutonium was produced during this time (DOE 1996b).

The principal plutonium isotopes used in military and nonmilitary applications are ^{238}Pu and ^{239}Pu. These two isotopes are used because of their ease of production and their relatively long half-lives. ^{238}Pu is used as a heat source in nuclear batteries to produce electricity in devices such as unmanned spacecraft, and interplanetary probes (DOE 2005a; Koch 2005). ^{239}Pu and ^{240}Pu are produced in nuclear power plants as a product of nuclear fission as well as in production facilities for use in nuclear weapons.

Possible sources of plutonium to the environment include: past atmospheric weapons testing, accidents involving weapons transport, accidents involving failed space launches of satellites, operating nuclear reactors and radioisotope generators, fuel processing and reprocessing activities, and fuel transport

6. POTENTIAL FOR HUMAN EXPOSURE

Figure 6-1. Frequency of NPL Sites with Plutonium and Selected Isotopes Contamination

Frequency of
NPL Sites

☒ 1
▨ 2
◩ 3
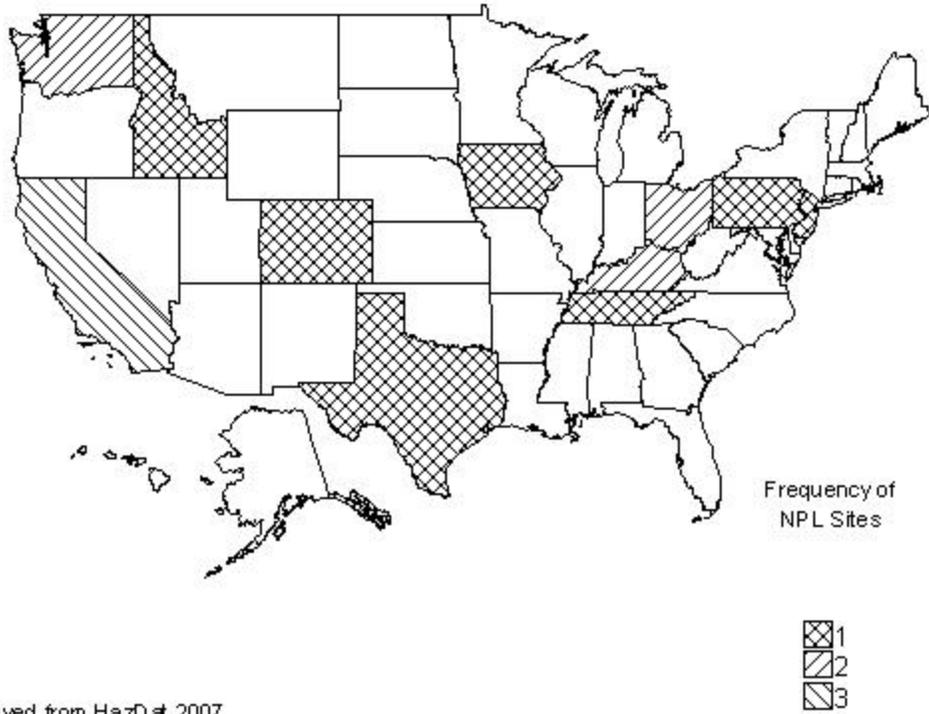
Derived from HazDat 2007

(NEA/OECD 1981). Plutonium is a byproduct of nuclear energy generation. It is produced in uranium-fueled reactors through neutron capture by uranium-238 (^{238}U) (Clark et al. 2006; Koch 2005).

Approximately 1,855 metric tons of plutonium were estimated to exist worldwide at the end of 2003, with 1,370 metric tons found within used fuel from nuclear power plants. A plutonium production rate of 70–75 metric tons/year was estimated for reactors worldwide at the end of 2003 (Albright and Kramer 2004; Clark et al. 2006).

The main sources of plutonium in the environment are releases from research facilities, past atmospheric nuclear weapons testing, waste disposal, nuclear weapons production facilities, and accidents (DOE 1999a). Atmospheric testing of nuclear weapons, which ended in 1980, is the source of most of the plutonium in the environment worldwide, which released approximately 10,000 kg of plutonium (DOE 2005a). Nuclear reactor accidents (e.g., the Chernobyl reactor in 1986) and other accidents involving non-U.S. nuclear-powered submarines or nuclear weapons have also released plutonium into the environment. The total amount of plutonium released during these accidents is small on a global scale as compared to the amount of plutonium released during atmospheric nuclear weapons testing. Plutonium released to the atmosphere reaches the earth's surface through wet and dry deposition to the soil and surface water. Once in these media, plutonium can sorb to soil and sediment particles or bioaccumulate in terrestrial and aquatic food chains.

6.2   RELEASES TO THE ENVIRONMENT

Concentrations of plutonium are generally expressed in terms of activity, either in the curie (Ci) or the SI unit, the becquerel (Bq), where 1 Ci=3.7x10^{10} Bq=0.037 TBq or 1 Bq=2.7x10^{-11} Ci=27 pCi. Activities may be converted into mass units using the specific activities for each plutonium isotope. Specific activities for various plutonium isotopes are provided in Table 4-3. Throughout this chapter, the units used to express concentration or intake of plutonium are generally the same units reported by the authors, which are followed by converted units in parenthesis. However, in some cases, the units originally reported by the authors may be converted (e.g., from Bq to mBq or from nCi to pCi) for ease of comparison of concentrations within a section. Common metric prefixes are provided in Table 6-1.

Possible sources of plutonium to the environment include: atmospheric weapons testing, accidents involving weapons transport, operating nuclear reactors and radioisotope generators, fuel processing and reprocessing activities, and fuel transport (NEA/OECD 1981). However, plutonium or plutonium

Table 6-1. Common Metric Prefixes

Factor	Prefix	Symbol	Factor	Prefix	Symbol
10^{-18}	atto	a	10^2	hecto	h
10^{-15}	femto	f	10^3	kilo	k
10^{-12}	pico	p	10^6	mega	M
10^{-9}	nano	n	10^9	giga	G
10^{-6}	micro	μ	10^{12}	tera	T
10^{-3}	milli	m	10^{15}	peta	P
10^{-2}	centi	c	10^{18}	exa	E

compounds are listed on the Superfund Amendments and Reauthorization Act (SARA) Section 313 toxic chemical list and, therefore, are not included in the Toxics Release Inventory (TRI).

6.2.1   Air

The main sources of plutonium in the environment are releases from research facilities, nuclear weapons testing, waste disposal, nuclear weapons production facilities, and accidents (DOE 1999a). Areas contaminated with plutonium, such as the Nevada Test Site or other national facilities, could release plutonium if the contaminated soils are re-suspended during windy or fire conditions (e.g., Cerro Grande fire in New Mexico), surface cleanup, construction, vehicular travel, or other disturbances to the contaminated soil (DOE 2005b).

Atmospheric testing of nuclear weapons, which ended in 1980, is the source of most of the plutonium in the environment worldwide, which released approximately 10,000 kg of plutonium (DOE 2005a). Approximately 320 kCi (1.2×10^4 TBq) of ^{239,240}Pu and 9 kCi (300 TBq) of ^{238}Pu have been released to the atmosphere by nuclear tests and distributed worldwide (Eisenbud and Gesell 1997). Concentrations of transuranics introduced into the environment through underground test venting, accidents involving U.S. nuclear weapons, and releases during weapon production operations have been negligible in comparison with those released during atmospheric testing of nuclear explosives in the 1960s (DOE 1980g).

In April, 1964, a Transit Navigational Satellite was launched in California with a payload that included a Satellite for a Nuclear Auxiliary Power Generator (SNAP-9A) containing 17 kCi (630 TBq) of ^{238}Pu. The rocket system failed and the satellite reentered the atmosphere in the Southern Hemisphere and burned over the Indian Ocean at an altitude of about 50 km (Harley 1980). The destruction of the SNAP-9A resulted in the largest single release of ^{238}Pu to the atmosphere, primarily in the form of very small oxide particles (Harley 1980). An estimated 37 TBq (1 kCi) of ^{239,240}Pu was released during the Chernobyl accident, April 26, 1986 (Clark et al. 2006). The only area around Chernobyl after the April 1986 accident with plutonium levels exceeding 4 kBq/m^2 was located within the 30-km zone. ^{239,240}Pu deposition densities ranged from 0.07 to 0.7 kBq/m^2 in the Gomel-Mogilev-Bryansk area, 200 km north-northeast of the reactor, and from 0.07 to 0.3 kBq m^2 in the Kaluga-Tula-Orel area, 500 km northeast of the reactor. At Korosten, located about 115 km southwest of the Chernobyl power plant, the ^{239,240}Pu deposition density due to the Chernobyl accident was about 0.06 kBq/m^2, 4–8 times lower than the ^{239,240}Pu deposition density from global fallout (UNSCEAR 2000b). Garger et al. (2006) reported that the

total flow of activity through the gaps of the shelter of the Chernobyl reactor measured during 1996–1999 was 8.64×10^9 Bq/year (0.234 Ci/year); 0.4% of this was due to ^{239,240}Pu.

Research facilities and plants have also released plutonium to the atmosphere. For example, the Department of Energy (DOE) Mound Plant in Miamisburg, Ohio, released about 30 Ci (1×10^{12} Bq) to the atmosphere from the beginning of its operation through 1976 (NEA/OECD 1981). The vast majority of these releases occurred in the 1960s. By 1972, total ^{238}Pu air releases were about 0.1% of the quantity released in 1967, and they have been much lower than that in the years since 1972 (Agency for Toxic Substances and Disease Registry 1998). A commercially operated reprocessing plant in West Valley, New York, has reportedly released 5×10^{-3} Ci (2×10^{-8} Bq) of plutonium to the atmosphere over the course of 6 years (NEA/OECD 1981). The Savannah River Site, which produced plutonium and tritium as well as other nuclear materials, released 1.4×10^{11} Bq (3.8 Ci) of plutonium to air during the period of 1954–1989 (Carlton et al. 1996). An estimated total air emissions from the Nevada Test Site (NTS) of 0.29 Ci (1.1×10^{10} Bq) ^{239,240}Pu was reported for calendar year 2004 (DOE 2005b). Air samplers in two areas of the NTS showed that ^{239,240}Pu is routinely detected due to blowing contaminated soil; however, concentrations are only slightly above minimum detectable concentrations. Air sampling in the past has shown that ^{238}Pu is not detected in air at the NTS (DOE 2005b).

Small amounts of various long-lived radionuclides, including ^{238}Pu, ^{239,240}Pu, and ^{241}Pu, are still released to the environment through state and federally permitted release points at the Hanford Site. Generally, the radionuclide emissions in these releases are near concentrations that are indistinguishable from background radionuclide concentrations that occur naturally or are from fallout (DOE 2005c). From 1994 to 2004, releases of ^{239,240}Pu to air from the Hanford Site ranged from 6×10^{-4} Ci (2×10^7 Bq) in 1998 to 1×10^{-4} Ci (4×10^6 Bq) during 2002–2004. During 2004, releases of ^{238}Pu to air ranged from 1.1×10^{-8} to 2.7×10^{-6} Ci (407–1.0×10^5 Bq) in three areas at the Hanford Site. Releases of ^{241}Pu to air were 1.5×10^{-4} and 5.3×10^{-4} Ci (5.6×10^6 and 2.0×10^7 Bq) at two areas, and not detected at two other areas. Releases of ^{239,240}Pu, which included gross alpha data, ranged from 1.4×10^{-7} to 6.7×10^{-5} Ci (5.2×10^3–2.5×10^6 Bq) at five areas at the Hanford Site during 2004 (DOE 2005c).

Plutonium has been identified in 9 air sample collected from 1,689 current or former NPL hazardous waste sites where it was detected in some environmental media (HazDat 2007).

6.2.2   Water

Fallout from atmospheric weapons testing, accidents involving nuclear weapons, planned as well as accidental reactor effluent releases, and disposal of radioactive wastes are all means by which plutonium can be introduced into water systems (Harley 1980; NEA/OECD 1981). In a typical 1,000 megawatt electric (MWe) light water reactor in a nuclear power plant, about 200 kg of plutonium [equivalent to 1.3×10^4 Ci (4.8×10^{14} Bq), one curie of ^{239}Pu=16 g] are generated per year of operation (DOE 1980g; NEA/OECD 1981). Contaminated cooling water containing plutonium from nuclear production facilities may have been discharged into oceans or rivers. If release occurs from waste containers, buried radioactive wastes may migrate or seep into groundwater (NEA/OECD 1981). As an example of plant emissions, the Mound Plant in Miamisburg, Ohio, discharged a total of about 0.5 Ci (2×10^{10} Bq) ^{238}Pu into a river near the site from the beginning of its operation through 1976 (NEA/OECD 1981). The Savannah River Site, South Carolina, which produced plutonium and tritium as well as other nuclear materials from 1954 to 1988, released 2.3×10^{10} Bq (0.62 Ci) of plutonium to site streams and ponds during the period of 1954–1989 (Carlton et al. 1996). From 1954 to 1988, the plutonium and uranium extraction (PUREX) process was used in the F-area of the Savannah River Site to recover ^{239}Pu, as well as other radionuclides, from irradiated ^{238}U. During this time, the total reported release of ^{239}Pu to the seepage basin at the F-area was 2.09×10^{11} Bq (5.65 Ci) (Dai et al. 2002).

Liquid effluent containing various radionuclides is discharged from some of the facilities at the Hanford Site. During 2004, 5.5×10^{-6} Ci (2.0×10^5 Bq) of ^{239,240}Pu were released to the Columbia River from the 100 areas at the Hanford Site (DOE 2005c).

In January, 1968, while attempting to make an emergency landing, a U.S. military aircraft with four nuclear weapons on board crashed in Thule, Greenland. The impact resulted in detonation of the high explosives in all four nuclear weapons aboard. The oxidized plutonium was dispersed by both the explosion and the fire involving the fuel in the jet (Harley 1980). Amounts of plutonium released to the air in this accident have been estimated at 24 Ci (8.9×10^{11} Bq) of insoluble plutonium (NEA/OECD 1981). The maximum concentration of plutonium in ocean sediments was found 1 km from the point of impact. The sediment-bound plutonium was found to migrate both downward in the sediment column and horizontally from the point of impact. The concentrations decreased with distance from the point of impact.

Sediments can act as both a repository for and a source of waterborne plutonium. Atmospheric fallout reaching surface water can settle in the sediments. The plutonium in the ocean sediments at Bikini Atoll, for example, was found to be resuspended and released to the bottom waters (DOE 1980b). In a freshwater waste pond at the Hanford reactor, plutonium was found to be bound to the sediments and was not available for uptake by plants or animals in the pond (DOE 1980f). The difference between the observations in the two ecosystems may be due to the dynamic nature of the ocean water near Bikini Atoll versus the relatively static nature of a waste water pond.

On May 4, 2000, a prescribed burn grew out of control in Cerro Grande, New Mexico near the Los Alamos National Laboratory (LANL), which burned about 7,400 acres of forest on the LANL site (DOE 2004). The burned landscapes resulted in increased storm runoff and transport of various contaminants, which included plutonium and other radionuclides by runoff and erosion in the canyons traversing LANL. Compared with amounts measured in the 5 years before the fire, the yearly average amount of radioactivity carried by storm runoff flows beyond LANL downstream boundary in the two to three years following the fire increased about 55 times for ^{239,240}Pu. The increases were due mostly to erosion of LANL contaminated sediments. Annually, the estimated postfire transport of ^{239,240}Pu downstream ranged from 2 millicuries (mCi) in the first year after the fire to 28 mCi in year 1 and a total of about 64 mCi of ^{239,240}Pu was transported downstream in storm runoff through the 4-year period from 2000 through 2003 (DOE 2004).

Plutonium has been identified in 6 groundwater and 7 surface water samples collected from 1,689 NPL hazardous waste sites, where it was detected in some environmental media (HazDat 2007).

6.2.3   Soil

Plutonium has been detected in extremely small amounts as a naturally occurring constituent of some minerals and ores. Uranium and thorium ores in Canadian pitchblende, Belgium Congo pitchblende, Colorado pitchblende, Brazilian monazite, and North Carolina monazite have been found to contain ^{244}Pu at a weight ratio of up to 9.1×10^{-12} kg plutonium/kg ore (Leonard 1980).

Soils may become contaminated from fallout associated with nuclear weapons tests, such as those conducted at the Trinity Site in southern New Mexico, the Pacific Proving Ground at the Enewetak Atoll, and the Nevada Test Site or with accidental, nonnuclear detonation of nuclear weapons, such as occurred at Palomares, Spain. Research facilities, such as the Los Alamos National Laboratory, Los Alamos, New

Mexico, may release treated radioactive wastes under controlled conditions. Production facilities, such as the Hanford and Savannah River Plants, and experimental reactor stations, for example, the Idaho National Engineering Laboratory, Idaho Falls, Idaho, also released treated plutonium-bearing radioactive wastes under controlled conditions to soils (Hanson 1975).

Atmospheric weapons testing fallout has been a global source of transuranics, including plutonium, in soils (Agency for Toxic Substances and Disease Registry 1999; Harley 1980; NEA/OECD 1981). The Centers for Disease Control and Prevention (CDC) has estimated that the total deposition of plutonium from weapons tests at the Nevada Test Site was 1.8×10^4 Ci (6.7×10^{14} Bq) (CDC 2005).

During 2004, only facilities in the 200 Areas of the Hanford Site discharged radioactive liquid effluents to the ground at a State-Approved Land Disposal Site. Releases of ^{238}Pu and ^{239,240}Pu were 6.9×10^{-6} and 7.5×10^{-6} Ci (2.5×10^5 and 2.8×10^5 Bq), respectively (DOE 2005c).

Several of the major nuclear facilities in the United States use plutonium and some of these have released plutonium to the environment. These releases have taken place at remote sites and generally have not been measurable outside the plant property. Approximately 2 Ci (7×10^{10} Bq) of plutonium have been disposed in the Los Alamos National Laboratory canyon waste disposal sites (Harley 1980). The Savannah River Plant, Aiken, South Carolina, has released a total of 5 Ci (2×10^{11} Bq) of plutonium to local soil (Harley 1980). Leakage of stored waste released between 10–100 Ci (3.7×10^{11}–3.7×10^{12} Bq) of plutonium to the soil over a period of several years at the Rocky Flats facility, Golden, Colorado (DOE 1980g). A break in a waste transfer line caused the release of about 300 Ci (1×10^{13} Bq) of ^{238}Pu at the Mound Plant, Miamisburg, Ohio, in 1969 (DOE 1980g).

A fire on May 11, 1969, occurred at the plutonium processing facility at Rocky Flats, which caused concerns about possible contamination of the surrounding areas (Agency for Toxic Substances and Disease Registry 2005). Studies showed that while trace amounts of plutonium were present in soil, the distribution was not consistent with the wind direction at the time of the fire. It was determined that the major source of plutonium contamination was leakage from drums of machine oil containing plutonium that were being stored in an outdoor area (Eisenbud and Gesell 1997).

Another source of soil contamination at Rocky Flats was the leakage of plutonium-contaminated oil. Plutonium was present as the dioxide when it was released. The dioxide was then adsorbed to the soil. Fugitive dust emissions caused plutonium-contaminated soil to be distributed away from the spill. Most

of the plutonium remained on the surface, although some was released and migrated downward through the soil column (Little and Whicker 1978).

A U.S. military aircraft carrying four nuclear bombs collided with a tanker aircraft during refueling in Palomares, Spain, in January, 1966. The bombs broke free of the airplane and the high explosive in two of the weapons detonated when the bombs hit the ground. Initial surveys showed plutonium concentrations of $3x10^{-5}$ Ci/m^2 ($1x10^6$ Bq/m^2), in the form of a finely powdered dioxide, were spread over 2 hectares (20,000 m^2) (Harley 1980). A large amount of the contaminated soil was brought back to the Savannah River facility in the United States for decontamination and the soil with low-level contamination was plowed to a depth of 30 cm (Harley 1980).

Plutonium has been identified in 6 soil and 9 sediment samples collected from 1,689 NPL hazardous waste sites, where it was detected in some environmental media (HazDat 2007).

6.3   ENVIRONMENTAL FATE

6.3.1   Transport and Partitioning

Plutonium enters the environment primarily through releases to the atmosphere or direct discharge to ponds, streams, or oceans. Emissions to the atmosphere will result in plutonium fallout. In the case of weapons testing, approximately one-fifth of the plutonium released falls on the test site (Harley 1980). The rest is carried in the atmosphere, adsorbed to particulate matter and is transported back to earth via dry or wet deposition. Once plutonium is deposited either on the land or surface water, sorption to soils or sediments is the primary environmental fate of plutonium. A small fraction of plutonium reaching the soil will become solubilized either through chemical or biological processes, depending upon its chemical form. In soluble form, plutonium can either migrate in groundwater or surface water or be available for uptake into plants; colloidal forms of plutonium are not as available for uptake as soluble forms.

Atmospheric releases of plutonium occurred as a result of former atmospheric nuclear weapons testing or routine or nonroutine nuclear reactor operations and fuel reprocessing. The rate at which plutonium is removed from the atmosphere depends on the chemical and physical properties of the particles, as well as the meteorological conditions. The larger the particles, the faster fallout will occur. The particle size expected to be released from either of the above mentioned sources ranges from 0.3 to 1.1 µm. At the highest altitudes, aerosols in the atmosphere descend by gravity; at lower levels, they are transported with the general air movement (UNSCEAR 2000a). In the lower stratosphere, the mean residence time of

aerosols range from 3–12 and 8–24 months in the polar and equatorial regions, respectively. Removal half-times from the upper atmosphere to the next lower region range from 6 to 9 months and removal half-times from the high atmosphere were found to be 24 months (UNSCEAR 2000a). The global fallout rate of ^{238}Pu, predominantly from the SNAP-9 accident, as determined by Harley (1980), was 0.002 pCi/m^2/day (7.4x10^{-5} Bq/m^2/day) based on plutonium levels measured in surface soils. The global deposition rate of ^{239,240}Pu was equal to 0.03 pCi/m^2/day (1x10^3 Bq/m^2/day) (Corey et al. 1982).

Plutonium deposited on soil surfaces may be resuspended in the atmosphere especially in areas that have low soil moisture levels, such as the Nevada Test Site. In drier areas, the levels of ambient airborne dust are expected to be higher than in areas with normal rainfall (Harley 1980). The highest concentrations of plutonium are likely to be found in the fine silt-clay particle size range. Particles of this size tend to be transported the farthest distance by wind and water (WHO 1983).

The transport and partitioning of plutonium in soils depends on the form of the compound. The solubility of plutonium depends on the properties of the soil, the presence of organic and inorganic complexing agents, the form of plutonium that enters the soil environment, and the presence of soil microorganisms (Bell and Bates 1988; DOE 1980c; Kabata-Pendias and Pendias 1984; WHO 1983). Plutonium fallout from the atmosphere, for example, tends to be deposited primarily as the insoluble dioxide (DOE 1987b; Harley 1980). The majority of plutonium remains within the top few centimeters of the soil surface as the dioxide form (WHO 1983). Microorganisms can change the oxidation state of plutonium, thereby either increasing or decreasing its solubility.

The types of organic and inorganic materials disposed of in waste streams can also affect the mobility of plutonium. For example, in some waste streams, such as the Hanford location, the chelating agent ethylenediaminetetraacetate (EDTA) was used during the production and processing of plutonium and was widely present in the mixed wastes at the site (Smith and Amonette 2006). EDTA forms complexes with plutonium, which will increase its mobility in soils and also possesses the ability to adsorb onto soil itself, thus reducing the number of available surface sites at which plutonium can adsorb to.

Plutonium will migrate in soils as the hydrolyzed ion or as a complex, formed with organic or inorganic acids. Mewhinney et al. (1987) found that particles subjected to wetting and drying, such as those found on the soil surface, released more plutonium than soils continually immersed in a solvent, such as that found in lakes. This phenomenon is attributed to the formation of a soluble dioxide layer on the particle's surface during the drying phase. Soil organisms have also been found to enhance the solubility of

plutonium (DOE 1987b). Once plutonium enters the soluble phase, it then becomes available for uptake by plants. The plutonium(IV) oxidation state is found in plants due to the ability of the environment to hydrolyze it (DOE 1987c; Garland et al. 1981). Cataldo et al. (1987) postulate that reduction of the higher oxidation states, such as plutonium(VI), occurs prior to absorption/transport across the root membrane.

In aqueous solution, plutonium typically exists in one of four common oxidation states and the environmental fate of plutonium in surface waters is dependent upon both the oxidation state and the nature of the suspended solids and sediments contained in the water column. Under reducing conditions, plutonium(III) and plutonium(IV) are the most stable oxidation states, with plutonium(III) dominating at pH values <8.5 and plutonium(IV) dominating at pH values >8.5 (Smith and Amonette 2006). Under oxidizing conditions, plutonium(IV), plutonium(V), and plutonium (VI) oxidation states tend to form at pH values >4. The plutonium(V) and plutonium(VI) oxidation states typically form more soluble complexes and possess greater mobility than the plutonium(III) and plutonium(IV) complexes. Humic materials (naturally occurring organic acids) were found to reduce plutonium(V) to plutonium(IV) in seawater. This was followed by adsorption of plutonium(IV) onto iron dioxides and deposition into the sediments (DOE 1987h).

The partitioning of plutonium from surface water to sediments in freshwater and marine environments depends on the equilibrium between plutonium(IV) and plutonium(V), and the interaction between plutonium(IV) in solution and plutonium sorbed onto sediment particle surfaces (NCRP 1984). Sorption onto marine clays was found to be largely irreversible (Higgo and Rees 1986). Higgo and Rees (1986) also found that the initial sorption of plutonium onto clays was effective in removing most of the plutonium species that would be able to sorb onto the clay. When sorption to carbonate marine sediments was investigated, it was found that some desorption from the surface would also occur. This behavior was due to the presence of plutonium carbonate complexes on the sediment surfaces which were sorbed less strongly than plutonium dioxide complexes (Higgo and Rees 1986). In fact, the formation of plutonium complexes with organic carbon causes plutonium to remain in solution as a complex (NCRP 1984). Plutonium can become adsorbed onto colloids, small (micrometer) particles that are often found in groundwater. Adsorption to colloidal particles can enhance the mobility of plutonium in groundwater (DOE 1999a).

Carroll et al. (1999) reported distribution coefficients (K_d) ranging from $3x10^4$ to $8x10^4$ for plutonium in bottom sediments from the Kara Sea. The International Atomic Energy Agency (IAEA)-recommended K_d value for sediments is $1x10^5$ for plutonium (Carroll et al. 1999; IAEA 2004).

Plutonium can be taken up from various environmental media into plants and animals. The primary factor that governs whether plutonium in soil can be taken up by plants roots is the presence of soluble forms of plutonium in adjacent subsurface soils. The highest concentrations of plutonium in plants are generally found in the roots where plutonium is present as a surface-absorbed plutonium complex, a stabilized complex, or a soluble plutonium complex (Garland et al. 1981). Concentration ratios (concentration of plutonium per gram of dry plant tissue divided by concentration in the soil) of $1x10^{-6}$–$2.5x10^{-4}$ were calculated based on radioisotope experiments in soybean plants grown in controlled environments. The stems and leaves were found to possess lower overall concentrations of plutonium than the roots, but higher concentrations of soluble plutonium (Cataldo et al. 1987).

In studies on orange trees, Pinder et al. (1987) found that ^{238}Pu was deposited on the leaf or soil surface, remained there, and that no measurable quantities were transferred to the fruits. Grain crops grown near the Savannah River Plant, Aiken, South Carolina, were found to contain higher concentrations of plutonium the closer to the facility they were grown. During harvesting, plutonium from soils or straw was resuspended and mixed with the crop. Plutonium in vegetable crops grown at Oak Ridge National Laboratory, Oak Ridge, Tennessee, contained higher plutonium concentrations in the foliage biomass than in the fruit. Peeling of potatoes and beets removed 99% of the residual plutonium (DOE 1980d).

The Mayak Production Association (PA), which processed weapons-grade plutonium from 1949 to 1952, discharged radioactive wastes into the Techa River, which belongs to the Kara Sea basin of the Arctic Ocean. Akleyev et al. (2000) reported plutonium accumulation coefficients ranged widely from $2x10^{-4}$ to 0.8 for vegetation samples the area of the Techa River. The authors noted that plutonium accumulation is highly species-dependent.

Plutonium uptake by grazing herbivores was predominantly located within the animal's pelt and gastrointestinal tract (DOE 1980i). Rodents studied near the Los Alamos and Trinity sites in New Mexico support this claim. DOE (1980i) found no evidence of bioconcentration through the food chain from soil to plants to rodents. They concluded that soil was the source of plutonium in rodents. In contrast, a study by Sullivan et al. (1980) showed that rodents absorbed more ^{238}Pu when it was incorporated into alfalfa (by growing it in soil containing plutonium) than when it was administered in the

inorganic form (Sullivan et al. 1980). This study suggests that plutonium bound to organic compounds may have increased availability.

Plutonium was found to bioaccumulate in aquatic organisms, primarily at the lower end of the food chain. The bioconcentration factors (i.e., the amount of the chemical found in the organism divided by the concentration in the surrounding water over the same time period) were 1,000 for mollusks and algae, 100 for crustacea, and 10 for fish (WHO 1983). Plutonium is concentrated in the bones of fish rather than in muscle tissues, as seen by whole fish to muscle tissue ratios of 40:1 (NCRP 1984). Swift (1992) reported that whole-body concentration factors for juvenile lobsters did not exceed 250 over an exposure period of 49 days in seawater containing ^{237}Pu. ^{237}Pu was found to accumulate mostly in the gills and exoskeleton.

6.3.2   Transformation and Degradation

Plutonium isotopes are transformed by radioactive decay to either uranium or americium based on the isotope, but as an element, plutonium cannot degrade. The most common isotopes of plutonium are ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Pu with respective half-lives of 87.7, 2.410×10^4, 6.56×10^3, and 14.4 years (Lide 2005). The half-lives for ^{239}Pu and ^{240}Pu are very long, and only a small amount of transformation would occur over a human lifetime. ^{241}Pu has a much shorter half-life and would undergo transformation over a human lifetime. ^{241}Pu decays into ^{241}Am, which has a half-life of 432.7 years and is also an alpha particle emitter (Baum et al. 2002). Information on the radioactive transformation of various plutonium isotopes can be found in Table 4-3.

6.3.2.1   Air

Plutonium does not undergo transformation processes in the air beyond those related to radioactive decay. Radioactive decay in air is not significant for those plutonium isotopes with long half-lives compared with residence times in the atmosphere. For plutonium injected into the atmosphere from a weapon detonation, the residence half-time of particulate debris in the troposphere of approximately 30 days (Bennett 1979; Nero 1979).

6.3.2.2   Water

The solution chemistry of plutonium is complex due to the ease with which it can undergo oxidation-reduction reactions and its extreme oxophilicity (tendency to bind oxygen) of plutonium cations (Clark et

al. 2006). Oxidation states (III)–(VII) can be prepared and stabilized in solution under appropriate conditions. The lower oxidation states (III and IV) are more stable under acid conditions; the higher oxidation states (VI and VII) are more stable under alkaline conditions. Pu(IV) is the most stable and most studied oxidation state, followed by (III) and (VI). Pu(V) and Pu(VI) cations are strong Lewis acids and hydrolyze in solution to form trans dioxo cations, PuO_2^+ and PuO_2^{2+}, which are commonly referred to as plutonyl ions. The reduction potentials that couple the four most common oxidation states of plutonium (III, IV, V, VI) in acidic solution are very close in magnitude and are close to 1 volt vs. the standard hydrogen electrode. In addition the kinetics oxidation-reduction reactions between these oxidation states are such that multiple oxidation states of plutonium can exist in aqueous solution under appropriate conditions (Clark et al. 2006; EPA 2006b).

The important chemical transformation process in surface water is the oxidation or reduction of plutonium. In waters with low suspended solids, plutonium is generally found in oxidized forms, dissolved in the water. In waters with high suspended solids, plutonium is generally reduced and sorbed onto either suspended solids or sediments (DOE 1987a, 1987h; Higgo and Rees 1986).

Plutonium behaves differently than many other inorganic elements in that it can exist simultaneously in four oxidation states over a range of pH values. Under acidic conditions, the nature of the complexing ligands present in solution will influence the oxidation state of plutonium. The presence of fulvic acid (a naturally occurring organic acid) facilitates the reduction of plutonium(IV) to plutonium(III), especially below pH 3.1. The reduction of the higher oxidation states appears to be even less dependent on pH, especially below pH 6 (IAEA 1976d).

6.3.2.3 Sediment and Soil

Plutonium found in soils may undergo the same oxidation/reduction reactions described for surface waters in places where soil contacts water. In addition to oxidation/reduction reactions, plutonium can react with other ions in soil to form complexes. These complexes may then be absorbed by roots and move within plants; however, the relative uptake by plants is low. In plants, the complex can be degraded but the elemental plutonium will remain.

6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to plutonium depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of

plutonium in unpolluted atmospheres and in pristine surface waters are often so low as to be near the limits of current analytical methods. In reviewing data on plutonium levels monitored or estimated in the environment, it should also be noted that the amount of chemical identified analytically is not necessarily equivalent to the amount that is bioavailable. The analytical methods available for monitoring plutonium in a variety of environmental media are detailed in Chapter 7.

Monitoring studies typically report combined ^{239,240}Pu concentrations because ^{239}Pu and ^{240}Pu are not readily distinguishable by alpha spectroscopy (Eisenbud and Gesell 1997).

6.4.1   Air

Atmosphere nuclear weapons testing, which ended in 1980, is the major source of plutonium contamination. Since this time, essentially all fallout ^{239}Pu has been removed from the atmosphere, allowing for measurement of baseline measurement of plutonium in air.

Air concentrations of ^{239}Pu at the Pacific Northwest National Laboratory near Richland, Washington averaged 1.3×10^{-7} Bq/m^3 (3.5×10^{-6} pCi/m^3). During 2004, a network of 85 continuously operating air samplers were used to monitor radioactive material in air near the Hanford Site (DOE 2005c). In 2004, ^{238}Pu was detected in 4 of 40 site-wide composite air samples, with average and maximum concentrations of 5×10^{-7} and 1.3×10^{-5} pCi/m^3 (2×10^{-8} and 4.8×10^{-7} Bq/m^3), respectively. From 1999 to 2003, ^{238}Pu was detected in 10 site-wide air samples, with a maximum concentration of 5.3×10^{-6} pCi/m^3 (2.0×10^{-7} Bq/m^3). Only 7 of the 40 site-wide air samples had detectable amounts of ^{239,240}Pu in 2004 with an average concentration of 1.5×10^{-6} pCi/m^3 (5.6×10^{-8} Bq/m^3). One of the 28 perimeter samples had a detectable amount of ^{239,240}Pu at a concentration of 2.5×10^{-6} pCi/m^3 (9.3×10^{-8} Bq/m^3). In 2004, none of the nearby or distant communities site air samples contained detectable amounts of ^{238}Pu or ^{239,240}Pu. From 1999 to 2003, ^{238}Pu was found in one air sample each from perimeter site and nearby communities sites; ^{239,240}Pu was detected in seven, four, and one of the perimeter, nearby, and distant communities air samples, respectively (DOE 2005c).

Concentrations measured at the Argonne National Laboratory-East near Chicago, Illinois ranged from 6×10^{-8} to 1.4×10^{-7} Bq/m^3 (1.6×10^{-6}–3.8×10^{-6} pCi/m^3) (DOE 1999a).

^{239,240}Pu concentrations in airborne particulate matter collected during 2005 from five locations at the site boundary of the Rocky Flats Environmental Technology Site (RFETS), Colorado, a former nuclear

weapons plant, were all <$1x10^{-5}$ pCi/m^3 (<$4x10^{-7}$ Bq/m^3) (DOE 2005d, 2005e, 2005f, 2006a). ^{239,240}Pu concentrations in airborne particulate matter collected during the first and second quarters of 2005 at RFETS from an industrial area were $8.3x10^{-5}$ and $1.2x10^{-4}$ pCi/m^3 ($3.1 x10^{-6}$ and $4.4 x10^{-6}$ Bq/m^3), respectively.

Aerosol particulate samples were collected at three sites (On Site, Near Field, and Cactus Field) near the Waste Isolation Pilot Plant (WIPP), a deep underground nuclear waste-storage facility near Carlsbad, New Mexico (Arimoto et al. 2005). The On Site sampling location was 0.1 km downwind of the WIPP exhaust shaft. The Near Field station was 1 km downwind of WIPP. The Cactus Field station was 19 km upwind of the WIPP, and served as a reference background site. Concentrations of ^{241}Pu were below the minimum detection limit ($1.2x10^{-6}$ Bq/m^3 [$3.2x10^{-5}$ pCi/m^3]) for all 204 samples collected. ^{238}Pu was detected above the minimum detection limit ($3.9x10^{-9}$ Bq/m^3 [$1.1x10^{-7}$ pCi/m^3]) in 6 of the 204 samples. ^{239,240}Pu was detected above the minimum detection limit ($2.6x10^{-9}$ Bq/m^3 [$7x10^{-8}$ pCi/m^3]) in 203 of the 204 samples. Mean concentrations of ^{239,240}Pu in the 10 µm particulate matter fraction were $1.1x10^{-8}$ and $8.1x10^{-9}$ Bq/m^3 ($3.0x10^{-7}$ and $2.2x10^{-7}$ pCi/m^3) at the Cactus Flats and Near Field stations, respectively. Mean concentrations of ^{239,240}Pu in the total suspended particulate were $1.8x10^{-8}$, $1.3x10^{-8}$, and $1.4x10^{-8}$ Bq/m^3 ($4.9x10^{-7}$, $3.5x10^{-7}$, and $3.8x10^{-7}$ pCi/m^3) at the Cactus Flats, Near Field, and On Site stations, respectively (Arimoto et al. 2005).

Lehto et al. (2006) determined radionuclide concentrations from air sampler filters collected in the town of Kurchatov and the city of Astana in Kazakhstan. Kurchatov is near the former Semipalatinsk nuclear test site, which is highly contaminated from nuclear explosions carried out from 1949 to 1989. Astana is about 500 km west of Kurchatov. Median concentration of $1x10^{-7}$ and $3.4x10^{-8}$ Bq/m^3 ($2.7x10^{-6}$ and $9.2x10^{-7}$ pCi/m^3) for ^{239,240}Pu and ^{238}Pu, respectively, were reported in weekly air samples (25,000 m^3 volume) collected during 2000–2001 in Kuchatov. Median concentrations of $2.9x10^{-8}$ and $9x10^{-9}$ Bq/m^3 ($7.8x10^{-7}$ and $2.4x10^{-7}$ pCi/m^3) for ^{239,240}Pu and ^{238}Pu, respectively, were reported in air samples collected during a 3-month period in 2001 in Astana; ^{238}Pu activity was below the detection limit in half of the filters (Lehto et al. 2006).

Hölgye (2008) reported ^{239,240}Pu and ^{238}Pu concentrations in air collected from 1997 to 2006 in Prague, Czechoslovakia of 0.53–5.06 and <0.16–1.10 nBq/m^3($1.4x10^{-8}$–$1.7x10^{-7}$ and <$4.3x10^{-9}$–$3.0x10^{-8}$ pCi/m^3), respectively. ^{239,240}Pu concentrations in Prague post-Chernobyl air samples taken in April 29–May 5, 1986 were 10–28Bq/m^3 ($2.7x10^{-4}$–$7.6x10^{-4}$ pCi/m^3).

6.4.2   Water

Hirose and Aoyama (2003) used the HAM database, a comprehensive data set of various anthropogenic radionuclides, to calculate background levels of ^{239,240}Pu concentrations surface waters of the Pacific Ocean. In this study, the authors divided the Pacific Ocean basin into 12 "boxes", which take into account the analyses of latitudinal and longitudinal distributions of anthropogenic radionuclides. Based on their analysis, ^{239,240}Pu concentrations ranged from 6×10^{-7} to 2.7×10^{-6} Bq/L (2×10^{-5}–7.3×10^{-5} pCi/L) within the 12 "boxes".

Seawater samples collected in 1999 in various regions of the southern Baltic Sea were analyzed for plutonium (Struminska and Skwarzec 2004). The highest concentrations of plutonium were generally found in the dissolved fractions of seawater, and ranged from 1.5×10^{-6} to 1.45×10^{-4} Bq/L (4.1×10^{-5}–3.92×10^{-3} pCi/L) for ^{238}Pu in samples from Gdansk Bay seaport and ^{239,240}Pu in samples from Pomeranian Bay, respectively. The lowest plutonium concentrations were found in the colloidal fractions. ^{238}Pu and ^{239,240}Pu concentrations in the colloidal fractions were generally $\leq 1\times10^{-6}$ Bq/L (2.7×10^{-5} pCi/L) (Struminska and Skwarzec 2004). Hirose and Aoyama (2002) reported that the ^{239,240}Pu particulate concentrations in surface waters of the western North Pacific Ocean ranged from 3×10^{-8} to 3×10^{-7} Bq/L (8×10^{-7}–8×10^{-6} pCi/L) during 1987–1997. Ahier and Tracy (1995) reported ^{239,240}Pu water concentrations in Lake Michigan, Huron, Erie, and Ontario of 4.4×10^{-7}, 4.8×10^{-7}, 1.8×10^{-7}, and 1.7×10^{-7} Bq/L (1.1×10^{-5}, 1.3×10^{-5}, 4.8×10^{-6}, and 4.6×10^{-6} pCi/L), respectively.

Hirose et al. (2007) reported ^{239,240}Pu concentrations in surface waters collected during 2003–2004 from the South Pacific Ocean mid-latitude region (32.5°S) ranging from 0.5 to 4.1 mBq/m^3 (0.01–1.1 pCi/m^3). Yamada and Zheng (2008) reported ^{239,240}Pu surface water concentrations in samples taken in the vicinity of the nuclear fuel reprocessing plant at Rokkasho, Japan of 7.6 and 7.8 mBq/m^3 (0.20 and 0.21 pCi/m^3) on sampling dates September, 1991 and June 1993, respectively. ^{239,240}Pu concentrations in surface water collected at sites along the Japan Sea coast sampled in June, 2003 were 4.9 and 5.9 mBq/m^3 (0.13 and 0.16 pCi/m^3) at Sado Island and at Ajigasawa, respectively. Yamada et al. (2007) reported ^{239,240}Pu concentrations of 13.4, 20.7, 37.2, 26.8, 39.6, 20.6, and 19.2 mBq/m^3 (0.362, 0.559, 1.01, 0.724, 1.07, 0.557, and 0.519 pCi/m^3) at depths of 0, 150, 250, 600, 900, 1,200, and 1,490 m, respectively, in samples from Sagami Bay, Japan, western Northwest Pacific Ocean collected on March 23, 1992.

During 2004, water samples from the Columbia River were collected at Priest Rapids Dam, the most upstream dam from the Hanford Site, and from Richland, Washington, on the Hanford Site. Average

^{239,240}Pu concentrations in water samples collected at the Priest Rapids Dam were 9.5×10^{-6} and 2.7×10^{-5} pCi/L (3.5×10^{-7} and 1×10^{-6} Bq/L) in the particulate and dissolved fractions, respectively, in samples collected in 2004, and were 3.2×10^{-5} and 2.4×10^{-5} pCi/L (1.2×10^{-6} and 8.9×10^{-7} Bq/L) in the particulate and dissolved fractions, respectively, collected in 1999–2003 (DOE 2005c, 2005g). Average ^{239,240}Pu concentrations in river water samples collected at Richland, Washington were 1.5×10^{-5} and 3.0×10^{-5} pCi/L (5.6×10^{-8} and 1.1×10^{-6} Bq/L) in the particulate and dissolved fractions, respectively, in samples collected in 2004, and were 2.5×10^{-5} and 3.0×10^{-5} pCi (9.3×10^{-7} and 1.1×10^{-6} Bq/L)in the particulate and dissolved fractions, respectively, collected in 1999–2003 (DOE 2005c, 2005g). Dai et al. (2005) reported ^{239}Pu concentrations ranging from $<3 \times 10^{-4}$ to 9.71×10^{-2} pCi/kg ($<1 \times 10^{-5}$–3.6×10^{-3} Bq/kg) in unfiltered water collected from the Hanford Site 100K-Area groundwater monitoring wells.

The Mayak nuclear fuel reprocessing plant in Russia PA, discharged radioactive wastes into the Techa River, which belongs to the Kara Sea basin of the Arctic Ocean. ^{239,240}Pu concentrations in water samples from the Techa River showed a decrease from approximately 3×10^{3} Bq/L down to 2 Bq/L, over a distance of 150 km starting from Dam 11, which is 30 km from the site of radioactive waste disposal (Akleyev et al. 2000). Børretzen et al. (2005) reported concentrations of 0.31 and 0.088 mBq/kg (8.4×10^{-3} and 2.4×10^{-3} pCi/kg) for ^{239}Pu and ^{240}Pu, respectively, in water samples collected on June 26, 1994 from Reservoir 11 at Mayak, which received radioactive wastes,. Levels in samples from the Asanov Swamp, downstream from the Mayak PA, were 0.12 and 0.13 mBq/kg (3.2×10^{-3} and 3.5×10^{-3} pCi/kg) for ^{239}Pu and ^{240}Pu, respectively.

Skipperud et al. (2009) reported average ^{239,240}Pu concentrations of 40.6, 29.0, and 6.4 Bq/m^3 (1,100, 780, and 170 pCi/m^3), respectively, in water samples collected in 1996 from the Ob Estuary, Yenisey Estuary (both of which have weapons-grade plutonium sources in their catchment areas), and Kara Sea, Russia. Surface water samples upstream and downstream from the Savannah River Site are analyzed quarterly or on a bi-annual basis for ^{238}Pu and ^{239}Pu (Agency for Toxic Substances and Disease Registry 2007). From 1993 to 2004, there were no detectable levels of ^{238}Pu or ^{239}Pu upstream or downstream from the facility (Agency for Toxic Substances and Disease Registry 2007).

Groundwater samples were collected in May 1998 from four of the F-area wells at the Savannah River Site (Dai et al. 2002). Well 1 is upgradient from the F-area seepage basins, and wells 2–4 define a transect along the contamination plume. ^{239}Pu concentrations were lowest in well 1, at approximately 1×10^{6} and 1×10^{5} atoms/kg (approximately 2×10^{-5} and 2×10^{-6} pCi/kg [7×10^{-7} and 7×10^{-8} Bq/kg]) in unfiltered and filtered fractions, respectively. ^{239}Pu concentrations were highest in well 2, which is

closest to the seepage basins, and were approximately $1x10^8$ and $1.5x10^8$ atoms/kg (approximately $2x10^{-3}$ and $3.7x10^{-3}$ pCi/kg [$7.4x10^{-5}$ and $1.4x10^{-4}$ Bq/kg]) in the unfiltered and filtered fractions, respectively (Dai et al. 2002).

^{238}Pu concentrations ranging from <0.01 to 0.078 pCi/L ($<3.7x10^{-4}$–$2.9x10^{-3}$ Bq/L) and from <0.01 to 0.059 pCi/L ($<3.7x10^{-4}$–$2.2x10^{-3}$ Bq/L) were reported in unfiltered and filtered (0.05 µm filtrate) groundwater, respectively, sampled near the disposal well at the Idaho Chemical Processing Plant, Idaho National Engineering Laboratory (Cleveland and Rees 1982). Mururoa and Fangataufa Atolls were used from 1975 to 1996 for underground testing of nuclear weapons (Mulsow et al. 1999). Of the nine sites at Mururoa sampled for underground water, only the site at Ceto, had a measurable concentration of ^{239,240}Pu at $2x10^{-5}$ Bq/L ($5x10^{-4}$ pCi/L). The remaining eight sites at Mururoa and the two sites at Fangataufa had ^{239,240}Pu concentrations ranging from $<5x10^{-5}$ to $<4x10^{-6}$ Bq/L ($<1x10^{-3}$–$<1x10^{-4}$ pCi/L). ^{238}Pu concentrations at both of these sites ranged from $<2x10^{-6}$ to $<5x10^{-5}$ Bq/L ($5x10^{-5}$–$<1x10^{-3}$ pCi/L) (Mulsow et al. 1999).

Gordeev et al. (2007) reported ^{239,240}Pu concentrations in groundwater samples obtained in 2005 from the Sary-Uzen nuclear excavation explosion site of the Semipalatinsk test area, Russia, ranging from $4x10^{-3}$ to $6.0x10^{-2}$ Bq/L (0.1–1.6 pCi/L). Concentrations of ^{239,240}Pu in water samples from the Tobol-Irtysh area of the Techa-Iset-Tobol-Irtysh-Ob river system, through which Mayak PA radioactive wastes are transported, were studied using samples collected from September 11 to 28, 2004 (Nikitin et al. 2007). ^{239,240}Pu concentrations ranged from 4.1 mBq/m^3 (0.11 pCi/m^3) at the left-bank confluence of the Iset-Tobol Rivers to 7.5 mBq/m^3 (0.20 pCi/m^3) at the left bank confluence of the Tobol-Irtysh Rivers; a value of 13.0 mBq/m^3 (0.35 pCi/m^3) was reported at midstream samples of the Ob River (Nikitin et al. 2007).

6.4.3   Sediment and Soil

Average plutonium concentrations in surface soil from fallout range from about 0.01 to 0.1 pCi/g ($4x10^{-4}$–$4x10^{-3}$ Bq/g) (DOE 2005a). Essentially all of the plutonium found in the surface of the Earth's crust is a product of human activity occurring over the past 60 years (Ketterer and Szechenyi 2008).

The Rocky Flats Plant in Colorado processed weapons-grade plutonium from 1952 to 1989 (Ibrahim et al. 1997). Contamination from plutonium production is composed mostly of ^{239,240}Pu and a small amount (~3%) of ^{238}Pu. Other releases of plutonium to this site, now called the RFETS, include global fallout, low-level releases during normal plant operations, accidental releases during fires between 1957 and

1969, and leakage of drums of plutonium contaminated cutting oil to soil onsite. Resuspension of contaminated soils during remediation activities resulted in most of the releases of plutonium at the RFETS. Soil samples collected at the RFETS during 1992–1994 were reported to range from 1.1 Bq/kg (30 pCi/kg) offsite to 57 Bq/kg (1,500 pCi/kg) onsite. Isotopic ratios of ^{240}Pu:^{239}Pu increased from 0.055 onsite to 0.123 at 19 km east of the RFETS boundary. An isotopic ratio of 0.06 is associated with contamination from activities at the RFETS, whereas the world mean isotopic ratio due to fallout was estimated at 0.176 (Ibrahim et al. 1997). ATSDR examined surface-soil contamination from an industrial portion of RFETS known as the "903 Pad Area", because multiple site reports indicate that off-site surface-soil contamination largely originated from this location (Agency for Toxic Substances and Disease Registry 2005). Surface soils in the 903 Pad Area were originally contaminated when industrial oils containing trace amounts of plutonium leaked from steel drums stored at the site between 1958 and 1968. Although DOE contractors remediated many of the highest priority waste sites to levels meant to be protective of workers and rural residents near the site, soil sampling activities in this area found ^{239,240}Pu levels as high as 457,000 pCi/kg (16,909 Bq/kg), which is nearly 10 times greater than the action level of 50,000 pCi/kg (Agency for Toxic Substances and Disease Registry 2005). The highest off-site concentration of ^{239,240}Pu observed during a remedial investigation was 6,500 pCi/kg (240 Bq/kg). A separate sampling study conducted in the 1990s at 42 locations adjacent to RFETS measured ^{239,240}Pu concentrations in soil ranging from 0.22 to 14.80 Bq/kg (5.9–400 pCi/kg) (Litaor 1999).

In 1960 at the McGuire Air Force Base in New Jersey, a missile caught fire at the Boeing Michigan Aeronautical Research Center and the warhead partially burned and melted, releasing weapons-grade plutonium (WGP) to the local environment (Lee and Clark 2005). The WGP at this site consisted of mostly ^{239,240}Pu, with a small amount of ^{241}Pu and a negligible amount of ^{241}Am (Amercium-241) at the time of its manufacture. Soil samples (0–2 inches) were collected from this site in June 2000 and analyzed for various plutonium isotopes. Concentrations were 0.42–6.34 Bq/g (11–171 pCi/g) for ^{239,240}Pu, 0.010–0.110 Bq/g (0.3–3.0 pCi/g) for ^{238}Pu, and 0.33–8.17 Bq/g (8.9–220 pCi/g) for ^{241}Pu in soil samples with various particle size fractions. The soil fraction with the smallest particle size (75–147 µm) contained the highest concentrations of plutonium, which were about 4 orders of magnitude higher than fallout levels. Based on the activity ratios of ^{241}Pu/^{239,240}Pu and ^{241}Am/^{239,240}Pu in the samples, the origin of the plutonium isotopes was identified as WGP (Lee and Clark 2005).

Soil samples were collected in 2004 on and around the Hanford Site (DOE 2005c). Average ^{239,240}Pu concentrations in surface soil collected on the 100-N Area, near facilities and operations in the 200 and 600 areas, and near facilities and operations in the 300 and 400 Areas were 0.004, 0.35, and 0.03 pCi/g (1×10^{-4}, 1.3×10^{-2}, and 1×10^{-3} Bq/g) dry weight, respectively. With the exception of the concentration from the 200 and 600 Areas, the soil concentrations in 2004 were similar to levels determined from 1999 to 2003. Average ^{239,240}Pu concentrations in surface soil collected near Hanford Site facilities and operations in the 200 and 600 Areas from 1999 to 2003 were reported as 0.08, 0.29, 0.10, 0.12, and 0.09 pCi/g (3×10^{-3}, 1.1×10^{-2}, 4×10^{-3}, 4×10^{-3}, and 3×10^{-3} Bq/g) dry weight, respectively. An average ^{239,240}Pu concentration of 0.0033 pCi/g (1.2×10^{-4} Bq/g) dry weight was reported in surface soil collected from a distant community in 2004 (DOE 2005c). Radionuclides, including ^{239,240}Pu, were detected in river sediment adjacent to and downstream from the Hanford Site during 2004. Maximum ^{239,240}Pu concentrations in Columbia River sediment collected from four sites near the Hanford Site ranged from 7.8×10^{-4} to 0.011 pCi/g (2.9×10^{-5}–4.1×10^{-4} Bq/g) dry weight (DOE 2005c, 2005g). Median ^{239,240}Pu concentrations from two of these sites, where more than one sample was collected, were 0.0084 and 0.0078 pCi/g (3.1×10^{-4} and 2.9×10^{-4} Bq/g) dry weight. Median ^{239,240}Pu concentrations in sediment collected from 1999 to 2003 from six sites in the Columbia River near the Hanford Site ranged from 0.0016 to 0.0098 pCi/g (5.9×10^{-5}–3.6×10^{-4} Bq/g) (DOE 2005c).

Concentrations of ^{239,240}Pu ranged from 0.006 to 0.80 pCi/g (2×10^{-4}–3×10^{-2} Bq/g) dry weight in soil collected from communities surrounding the Nevada Test Site in southern Nevada and southern Utah during the summer 1996 and spring 1997. The activity ratios of radiocesium to plutonium in the soil samples suggest that the Nevada Test Site had a significant contribution to plutonium levels in this area as compared to global fallout (Cizdziel et al. 1998).

A study on radionuclide levels in west Cumbrian soils contaminated by low-level discharges from Sellafield reported ^{238}Pu levels detected at a range of 200–18,000 pCi/kg (8–670 Bq/kg) and ^{239,240}Pu levels detected at a range of 800–83,000 pCi/kg (30–3,100 Bq/kg) (Livens and Baxter 1988). Core samples of surface soil at the Maxey Flats facility, Kentucky, where radioactive wastes were buried, were reported to contain a mean concentration of 1.9×10^{5} pCi/kg (7,000 Bq/kg) of ^{238}Pu and 2.2×10^{4} pCi/kg (810 Bq/kg) of ^{239,240}Pu (NEA/OECD 1981).

Maximum ^{239,240}Pu concentrations of 488 and 27,900 Bq/kg (1.31×10^{4} and 7.54×10^{5} pCi/kg) have been reported in composite (0–20 cm) and surface (0–5 cm) soil samples, respectively, collected in the vicinity of ground zero of the first thermonuclear explosions at the Semipalatinsk Test Site (STS) (Carlsen et al.

2001). Maximum ^{239,240}Pu concentrations of 192 and 8,850 Bq/kg (5.19×10^3 and 2.39×10^5 pCi/kg) have been reported in composite (0–20 cm) and surface (0–5 cm) soil samples, respectively, collected at a crater created by an underground nuclear explosions in 1965 along the Shagan River at the STS. Maximum ^{239,240}Pu concentration of 2.8 and 3.98 Bq/kg (76 and 108 pCi/kg) have been reported in composite (0–20 cm) and surface (0–5 cm) soil samples, respectively, from villages near the STS. The activities in soil from the villages are typical of levels associated with global fallout (Carlsen et al. 2001).

Michel et al. (2002) reported mean concentrations 101 and 4.5 Bq/m^2 (2.8×10^3 and 120 pCi/m^2), for ^{239,240}Pu and ^{238}Pu, respectively, for soil cores collected at seven sites adjacent to the catchment of Blelham Tarn, a small lake in Cumbria, United Kingdom. Sediment cores were collected from 14 locations in the lake during March 1997 and mean concentrations of ^{239,240}Pu and ^{238}Pu were 183 and 4.5 Bq/m^2 (4.95×10^3 and 120 pCi/m^2), respectively. Isotopic ratios indicated that the source of these plutonium isotopes was fallout from atmospheric weapons testing (Michel et al. 2002). ^{239,240}Pu concentrations in 96 surface soil samples (0–5 cm) collected from 32 areas in Iran ranged from 0.080 to 0.360 Bq/kg (2.2–9.7 pCi/kg) (Aliabadi et al. 2005). Luksiene et al. (2006) reported ^{239,240}Pu concentrations in beach and forest surface soils (0–5 cm) collected in 1996–2001 from the Baltic coastline in Lithuania ranging from 0.06 to 0.80 and from 0.09 to 0.4 Bq/kg (1.6–22 and 2.4–11 pCi/kg), respectively. Ivanova et al. (1995) reported concentration ranging from 0.05 to 2.73 Bq/kg (1– 73.8 pCi/kg) for ^{238}Pu and from 0.37 to 5.04 Bq/kg (10–136 pCi/kg) for ^{239,240}Pu in surface soils (0–2 cm) collected in the Bryansk, Orel, and Tula regions of Russia in 1992.

^{239,240}Pu concentrations in surface (0–5 cm) soil samples collected in 1996 in the Gomel region of Belarus, near the Chernobyl nuclear plant, were reported as 3.7 and 0.8 Bq/kg (100 and 20 pCi/kg) dry weight from Chiepietovitach and Pecki, respectively (Michel et al. 1999). Concentrations of ^{239,240}Pu in soil samples from the 5–10 and 10–15 cm depths at Pecki were 0.52 and 0.45 Bq/kg (14 and 12 pCi/kg) dry weight, respectively. Soil concentrations of ^{238}Pu were 2.2 and 0.39 Bq/kg (59 and 11 pCi/kg) dry weight from Chiepietovitach and Pecki, respectively. ^{238}Pu concentrations in soil samples from the 5–10 and 10– 15 cm depths at Pecki were 0.04 and 0.06 Bq/kg (1 and 2 pCi/kg) dry weight, respectively (Michel et al. 1999).

The Mayak PA, which processed weapons-grade plutonium from 1949 to 1952, discharged radioactive wastes into the Techa River. Contamination densities of ^{239,240}Pu in floodplain soil on the Techa River showed a decrease from approximately 2 to 4×10^{-2} kBq/m^2 (50–1 nCi/m^2) over a distance of 200 km starting from Dam 11, which is 30 km from the site of radioactive waste disposal. ^{239,240}Pu concentrations

in bottom soil along the river course decreased from approximately 5×10^{-2} to 2×10^{-2} Bq/kg (1.4–
0.5 nCi/m^2) over the same distance (Akleyev et al. 2000). Børretzen et al. (2005) reported concentrations
of 1.81×10^6–2.0×10^6 and 1.22×10^5–1.35×10^5 mBq/kg (48.9–54.1 and 3.30–3.65 nCi/kg) dry weight for
^{239}Pu and ^{240}Pu, respectively in surface soil samples from the Asanov Swamp at Mayak PA, collected on
June 26, 1994.

In 1966, two nuclear weapons were accidentally detonated during a collision of two aircraft in the area of
the village of Palomares, Spain. ^{239,240}Pu inventories in surface soil ranging from 8 to 57,900 Bq/m^2 (0.2–
1,560 nCi/m^2) were reported in samples collected in the vicinity of the village of Palomares in October
2001 (Jimenez-Ramos et al. 2006). Concentrations in soil samples from Tabernas, 200 km away from
Palomares, were reported as 0.36 Bq/kg (9.7 pCi/kg) for ^{239,240}Pu Bq/kg dry weight and <0.48 Bq/kg
(<13 pCi/kg) dry weight for ^{238}Pu (Rubio Montero and Sanchez 2001).

Concentrations of ^{239,240}Pu in peat bog samples from the area of the Tomsk-Seversk nuclear facility
(Siberia, Russia) were reported as 0.5, 0.6, and 10.5 Bq/kg (13, 16, and 284 pCi/kg) at depths of surface-
5, 11–13, and 20 cm, respectively; reported concentrations for ^{238}Pu were 0.06, 0.01, and 0.34 Bq/kg (1.6,
0.3, and 9.2 pCi/kg), respectively. Concentrations of ^{239,240}Pu in forest soil samples from this area were
reported as 0.052, 0.055, and 0.054 Bq/kg (1.4, 1.5, and 1.5 pCi/kg) at depths of surface, 3-6, and 32–
40 cm, respectively, while concentrations in samples from an area river bank were 0.050, 0.049, and
0.050 Bq/kg (1.5, 1.4, and 1.5 pCi/kg) at depths of 0–3, 9–12, and 18–21 cm, respectively (Gauthier-
Lafaye et al. 2008).

Yamamoto et al. (2008b) reported ^{239,240}Pu concentrations ranging from 0.16 to 51.87 Bq/kg (4.3–
1,401 pCi/kg) in 26 soil samples collected in October 2005 from Dolon located 60 km northeast of the
Semipalatinsk Nuclear Test Site in Kazakhstan, an area contaminated mainly by the first USSR nuclear
test on August 29, 1949.

Yoshida et al. (2007) reported a ^{239,240}Pu soil (0–5 cm) concentration of 59.9 Bq/kg (1,620 pCi/kg) dry
weight at 300 m west from the Nishiyama reservoir Nagasaki Japan. This concentration decreased with
increasing distance for the Nishiyama reservoir. The ^{239,240}Pu concentration in the surface soil at farther
sampling point was 1.82Bq/kg (49.2 pCi/kg) dry weight, a level within the range with global fallout
plutonium concentrations in surface soil of Japanese forests (0.15–4.31 Bq/kg (3.8–116 pCi/kg, dry
weight) (Yoshida et al. 2007).

Concentrations of ^{239,240}Pu in soils from counties throughout Hungary ranged from 0.020 to 0.61 Bq/kg (0.54–17 pCi/kg) and concentrations of ^{241}Pu in these same samples were reported to range from 0.043 to 1.70 Bq/kg (1.2–46 pCi/kg) (Varga and Tarján 2008). Isotopic ratio analysis indicated that the plutonium levels in Hungary arise from global fallout related to atmospheric testing of nuclear weapons.

^{239,240}Pu concentrations in sediment cores collected from Lake Michigan in 1972–1974 ranged from 0.003 to 0.401 pCi/g (1×10^{-4}–1.48×10^{-2} Bq/g) dry weight. It was estimated in this report that radioactivity in the sediments was confined to the upper 6 cm of the sediments, and in many of the core samples, no radioactivity was detected below a depth of 3 cm (IAEA 1976g).

Rapiejko et al. (2001) reported ^{239,240}Pu median concentrations of 2.2 (59) (0.00–0.06 cm depth near sewage treatment plant), 1.3 (35) (0.06–0.15 cm depth), 1.1 (30) (0.15–0.24 cm depth), and 2.1 (57) (0.24–0.37 cm depth) Bq/kg (pCi/kg) in sediment samples collected in April 1999 from the Peconic River, downstream from the Brookhaven National Laboratory (BNL). Concentrations of ^{238}Pu in these same samples were 0.09, <0.07, <0.07, and <0.09 Bq/kg (2, <2, <2, and <2 pCi/kg), respectively. The median concentrations of ^{239,240}Pu in sediments from Donahues Pond and Forge Pond, further down stream from BNL, were 4.0 and 1.6 Bq/kg (108 and 43 pCi/kg), respectively; ^{238}Pu was not detected in these samples. Concentration ranges for ^{239,240}Pu in control samples from the Connetquot River were 1.7–3.7 Bq/kg (46–100 pCi/kg) at 0.0–0.06 cm depth and 0.13–0.48 Bq/kg (4–13 pCi/kg) at 0.06–0.15 cm depth; ^{238}Pu concentrations were reported as 0.15–0.26 Bq/kg (4–7 pCi/kg) at 0.0–0.06 cm depth and <0.07–0.074 Bq/kg (<2–2 pCi/kg) at 0.06–0.15 cm depth (Rapiejko et al. 2001).

Skipperud et al. (2009) reported average ^{239,240}Pu concentrations of 0.40, 0.24, and 0.55 Bq/kg (10, 6.5, and 15 pCi/kg), respectively, in sediments collected in 1996 from the Ob Estuary and Yenisey Estuary (both of which have weapons-grade plutonium sources in their catchment areas), and Kara Sea, Russia.

Surface sediment samples (0–1 cm) from the Rhone River collected in March 2001 at the input into the Gulf of Lions (Northwestern Mediterranean Sea) were reported to contain concentrations of ^{239,240}Pu and ^{238}Pu of 0.329–549 Bq/kg (8.89–41.86 pCi/kg) and 0.025–0.143 Bq/kg (0.68–3.86 pCi/kg), respectively (Lansard et al. 2007). Concentrations of ^{239,240}Pu in sediment cores collected in November 2001 ranged from 0.256 to 5.974 Bq/kg (6.92–161.5 pCi/kg) at 5–10 cm and 280–290 cm depth, respectively. Concentrations of ^{238}Pu in sediment cores collected in November 2001 ranged from 0.035 to 1.254 Bq/kg (0.95–33.89 pCi/kg) at 5–10 cm and 280–290 cm depth, respectively. Sources of plutonium isotopes in the Rhone River valley have been identified as weathering of the catchment basin contaminated by

atmospheric fallout and liquid effluents released from the Marcoule reprocessing plant (located upstream 120 km from the river mouth) since 1961 (Lansard et al. 2007).

Liao et al. (2008) reported ^{239}Pu concentrations in sediment from Lake Poyang, East China of 0.066, 0.395, and 0.062 mBq/g (1.8, 11, and 1.7 pCi/kg) at 0–1, 5–6, and 10–11 cm depth, respectively. ^{240}Pu concentrations of 0.046, 0.270, and 0.042 mBq/g (1.2, 7.3, and 1.1 pCi/kg) were reported at these same depths, respectively. The ^{240}Pu/^{239}Pu ratio (0.187) in sediment samples from Lake Poyang indicated that plutonium pollution was from global fallout.

6.4.4   Other Environmental Media

^{238,239,240}Pu was identified in imported food collected 2 weeks after the Chernobyl accident in an FDA/USDA-sponsored survey; however, concentrations were not provided. Generally, contamination levels for the radionuclides surveyed were below FDA's levels of concern (Cunningham et al. 1989). The FDA developed guidance levels for radionuclide activity concentration, called derived intervention levels (DILs), which help determine whether domestic food in interstate commerce or food offered for import into the United States present a safety concern (FDA 2005). The DIL for ^{238}Pu + ^{239}Pu + ^{241}Am is 2 Bq/Kg (FDA 2005). Various radionuclides were measured in 1996 on samples of mixed diet from regions throughout the United Kingdom (MAFF 1997b). Concentrations of all artificial radionuclides were reported to be low and of little significance. Concentrations of ^{238}Pu were generally <0.00030 Bq/kg (0.008 pCi/kg) and concentrations of ^{239,240}Pu ranged from 0.00011 to 0.00040 Bq/kg (3x10^{-3}–0.01 pCi/kg) (MAFF 1997b). Samples of milk, crops, bread, and meat collected from the United Kingdom in 1996 were analyzed for various natural and artificial radionuclides; concentrations of plutonium (^{238}Pu and ^{239,240}Pu) were generally <0.0002 Bq/L (<0.005 pCi/L) for milk and <0.0002 Bq/kg (<0.005 pCi/kg) for crops, bread, and meat (MAFF 1997b).

Seventy-two beverage brands available to the public in the United Kingdom were surveyed for natural and anthropogenic radionuclides. Beverages included in this survey were fruit juices, fruit juice drinks, fruit squashes, carbonated drinks, baby juices, flavored spring and mineral waters, ciders, wines, beers, and others beverages, such as powdered chocolate and malt drinks. Levels of all anthropogenic radionuclides surveyed, including ^{238}Pu and ^{239,240}Pu, were below the limits of detection (MAFF 1997a). Sanchez et al. (1999) studied doses of artificial radionuclides, including ^{239,240}Pu, in the diet of individuals living in Cumbria, United Kingdom. This investigation included three duplicate diet studies conducted in 1986, 1995, and 1996. In general, mean ^{239,240}Pu concentrations in diet samples from these surveys were

reported to range from $<1 \times 10^{-4}$ (the detection limit) to $<2.8 \times 10^{-3}$ Bq/kg ($<2.7 \times 10^{-3}$–$<7.6 \times 10^{-2}$ pCi/kg) fresh weight in both the control group from west Cumbria 1986 and the study group from Sellafield in 1995. The highest ^{239,240}Pu concentrations of 1.7×10^{4} and 1.2×10^{4} Bq/kg (0.46 and 0.32 pCi/kg) fresh weight were found in 1986 diet surveys, which contained crab (Sellafield) and cockles (west Cumbria) (Sanchez et al. 1999). Cooper et al. (1992) analyzed food and total diet samples for various radioactive isotopes that were collected from selected communities in areas of the former Union of the Soviet Socialist Republic (U.S.S.R.) that were contaminated with fallout from the accident at Chernobyl. Concentrations of ^{239,240}Pu in total diet samples ranged from 1.5×10^{-3} to 7.0×10^{-3} Bq/kg (4.1×10^{-3}–2×10^{-2} pCi/kg) dry weight (Cooper et al. 1992).

Twenty Emmental cheese samples were collected from 6 European regions (Allgäu, Germany; Bretagne, France; Savoie, France; Switzerland; Finland; and Vorarlberg, Austria,) and analyzed for various radionuclides. ^{238}Pu and ^{239,240}Pu concentrations were determined in one sample from each location, except Finland, and were found to be less than the detection limit (0.3 Bq/kg [8 pCi/kg]; Froidevaux et al. 2004).

Samples of bottom-feeding fish, white sucker (*Catostomus commersoni*), channel catfish (*Ictalurus punctatus*), and carp (*Cyprinus carpio*) were collected along the Rio Grande upstream and downstream of the Los Alamos National Laboratory (LANL) in September 1997 and analyzed for various radionuclides (Fresquez et al. 1999b). Mean concentration of ^{239,240}Pu in samples collected downstream of LANL ranged from 4.8×10^{-5} to 47.5×10^{-5} pCi/g (1.8×10^{-6} to 1.76×10^{-5} Bq/g) in muscle and bone, and from 27.5×10^{-5} to 135.0×10^{-5} pCi/g (1.02×10^{-5} to 5.00×10^{-5} Bq/g) in viscera. In samples collected upstream of LANL, ^{239,240}Pu concentrations ranged from 5.5×10^{-5} to 33.1×10^{-5} pCi/g (2.0×10^{-6} to 1.22×10^{-5} Bq/g) in muscle and bone, and a mean concentration of 85.1×10^{-5} pCi/g (3.15×10^{-5} Bq/g) was determined in viscera. For most of the radionuclides, concentrations in fish collected downstream of LANL were not significantly higher than those in fish collected upstream of LANL (Fresquez et al. 1999b).

Børretzen et al. (2005) reported ^{239}Pu concentrations of 1,010, 12, 95, and 119 mBq/kg (27.30, 0.32, 2.6, and 3.22 pCi/kg) wet weight and ^{240}Pu concentrations reported of 1,150, 4, 6, and 44 Bq/kg (31.1, 0.11, 0.16, and 1.2 pCi/kg) wet weight in mussels, pike bone, pike filet, and roach, respectively, collected on June 26, 1994 from a reservoir adjacent to the Asanov Swamp, downstream from the Mayak PA.

Oikawa and Yamamoto (2007) reported ^{239}Pu and ^{240}Pu concentrations livers of Surume squid caught during the fishery season from September–December 2002 in the coastal seawaters off Japan.

Concentrations of ^{239}Pu and ^{240}Pu of 1.5–28 mBq/kg (0.041–0.76 pCi/kg) and 1.1–24 mBq/kg (0.030–0.65 pCi/kg), respectively; these concentrations were several thousand times higher than levels found in seawater.

Various metals and radionuclides, including ^{238}Pu and ^{239,240}Pu, were measured in birds and eggs from Amchitka and Kiska Islands in the Bering Sea/Northern Pacific Ocean. ^{238}Pu was not detected over the minimum detectable activity (MDA) in any samples. ^{239,240}Pu was only detected above the MDA at 0.31 Bq/kg (8.4 pCi/kg) wet weight in a guillemot composite (Burger and Gochfeld 2007).

Concentrations of ^{239,240}Pu ranged from 12 to 680 pCi/kg (0.44 –25 Bq/kg) dry weight in attic dust collected from communities surrounding the Nevada Test Site in southern Nevada and southern Utah during the summer 1996 and spring 1997. The activity ratios of radiocesium to plutonium in the dust samples suggest that the Nevada Test Site had a significant contribution to plutonium levels in this area as compared to global fallout (Cizdziel et al. 1998).

Plutonium concentrations in vegetation were monitored during 2004 on the Hanford Site. ^{239,240}Pu was not detected in vegetation samples collected on the Hanford Site in the 100-N Area and the 300 and 400 Areas (DOE 2005c). An average ^{239,240}Pu concentration of 0.003 pCi/g ($1x10^{-4}$ Bq/g) dry weight, was reported in vegetation samples collected from the 200 and 600 Areas. A ^{239,240}Pu concentration of 0.00033 pCi/g ($1.2x10^{-5}$ Bq/g) dry weight was reported in vegetation from distant communities. Average ^{239,240}Pu concentrations in vegetation samples collected in 1999–2002 in the 100-N Area and the 300 and 400 Areas ranged from 0.0004 to 0.024 and from 0.003 to 0.005 pCi/g ($1.5x10^{-5}$–$8.9x10^{-4}$ and $1x10^{-4}$–$2x10^{-4}$ Bq/g) dry weight and was not detected in the 2003 samples. Average ^{239,240}Pu concentrations in vegetation samples collected during 1999–2003 ranged from 0.003 to 0.033 pCi/g ($1x10^{-4}$–$1.2x10^{-3}$ Bq/g) dry weight (DOE 2005c). In 2004, mean ^{239,240}Pu concentrations of 0.0020, 0.0050, 0.0017, and 0.00022 pCi/g ($7x10^{-5}$, $2x10^{-4}$, $6.3x10^{-5}$, and $8.1x10^{-6}$ Bq/g) dry weight were reported in vegetation samples collected site-wide at the Hanford Site, at the perimeter, at the shoreline of the Hanford Reach of the Columbia River, and at a distant site, respectively. ^{238}Pu was only detected in one of five samples collected on-site at a concentration of $6.0x10^{-6}$ pCi/g ($2x10^{-7}$ Bq/g) dry weight. The results reported for the 2004 samples were similar to those reported in 1993, 1994, 1998, and 2001 (DOE 2005c).

Akleyev et al. (2000) reported that plutonium concentrations in grass samples from the Asanov Swamps and dams on the Techa River were estimated to be 7–80 Bq/kg (200–2,200 pCi/kg). Average values for plutonium concentrations in vegetation from the flood plain section from Dam 11 to the village of

Muslyumovo were reported as 7 Bq/kg (200 pCi/kg), and 1.1 Bq/kg (30 pCi/kg) in the section from Muslyumovo to Zarechnoye. These sites are in the area of the Mayak PA (Akleyev et al. 2000).

Børretzen et al. (2005) reported concentrations of 163 and 207 mBq/kg (4.41 and 5.59 pCi/kg) for ^{239}Pu and 23 and 24 mBq/kg (0.62 and 0.65 pCi/kg) for ^{240}Pu in two dried grass samples from the Asanov Swamp collected on June 26, 1994. ^{239}Pu and ^{240}Pu concentrations of 1,700 and 362 mBq/kg (46 and 9.78 pCi/kg) dry weight and 190 and 36 mBq/kg (5.1 and 0.97 pCi/kg) dry weight were also reported in two samples of water plants, respectively (Børretzen et al. 2005)

Plutonium concentrations in moss samples from counties in Hungary were reported as 1.06 and 0.007 Bq/kg (28.7 and 0.2 pCi/kg) for ^{239,240}Pu and 2.39 and 0.011 Bq/kg (64.6 and 0.30 pCi/kg) for ^{241}Pu in Komarom and Heves, respectively (Varga and Tarján 2008). ^{239,240}Pu concentrations in ashed fodder (Pest), hay (Bacs-Kiskun), and sedge (Tolna) were reported as 1.91, 0.004, and 0.038 Bq/kg (51.6, 0.1, and 1.03 pCi/kg), respectively. ^{241}Pu concentrations in these same samples were reported as 131, 0.22, and 0.69 Bq/kg (3540, 6.0, and 19 pCi/kg), respectively (Varga and Tarján 2008).

6.5   GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

The estimated 50-year dose commitment from plutonium for people in the north temperate zone due to atmospheric nuclear weapons tests conducted before 1973 is 0.2 mrad (0.002 mGy) to the bone lining cells (Eisenbud 1987). The average annual dose equivalent from all background radiation to an individual residing in the United States is estimated to be 360 mrem (3.6 mSv) (NCRP 1987).

Sanchez et al. (1999) reported that ^{239,240}Pu contributed the lowest dose of radionuclides studied in a survey of the diets of individuals living in Cumbria, United Kingdom; the average dose was <0.04 µSv (0.004 mrem). Concentrations of ^{239,240}Pu in total diet samples collected from areas of the former U.S.S.R. that were contaminated by fallout from Chernobyl ranged from 1.5×10^{-7} to 7×10^{-7} Bq/g (4.1×10^{-6}–2×10^{-5} pCi/g) dry weight; a worst-case calculated dose of 0.2 µSv (0.02 mrem) was reported for ^{239,240}Pu (Cooper et al. 1992). Pietrzak-Flis and Orzechowska (1993) studied the content of ^{239,240}Pu in daily diet samples collected from a hospital in Bialystok, Poland from March 1987 to May 1992. The estimated annual intake of plutonium was 0.774 Bq/year (20.9 pCi/year) in the first year after the accident at Chernobyl; after the sixth year, the daily intake was 0.088 Bq/year (2.4 pCi/year) (Pietrzak-Flis and Orzechowska 1993). Daily ingestion of ^{239,240}Pu in food in Japan between 1978 and 1980 due to atmospheric fallout was estimated to be 4.5×10^{-3} pCi/day (1.7×10^{-4} Bq/day) (Hisamatsu et al. 1987).

Filipy et al. (2003) reported plutonium concentrations in bone samples collect at autopsy from eight individuals for the United States Transuranium and Uranium Registries (USTUR). The USTUR documents levels and distribution of uranium and transuranium isotopes in human tissues for occupationally exposed workers who donate their bodies to science (USTUR 2003). Plutonium levels were measured in various bone samples: clavicle; patella; ribs (5–10); sternum; and vertebrae (T5–L3). ^{238}Pu concentrations ranged from 0.146 (clavicle) to 82.7 (sternum) Bq/kg (3.95–2,240 pCi/kg) dry weight. ^{239}Pu concentrations ranged from 0.441 (patella) to 398.0 (vertebrae) Bq/kg (11.9–10,800 pCi/kg) dry weight. ^{241}Pu concentrations ranged from 0.850 (sternum) to 25.2 (sternum) Bq/kg (23–681 pCi/kg) dry weight (Filipy et al. 2003). Ivanova et al. (1995) measured plutonium concentrations in lungs, tracheobronchial lymph nodes (TLN), liver, and bone in 59 individuals who lived in the areas of the Bryansk region of Russia that was contaminated by the Chernobyl accident. Average concentrations of ^{238,239,240}Pu in lung, TLN, liver, and bone tissue were 0.060, 0.530, 0.070, and 0.070 Bq/kg (1.6, 14, 1.9, and 1.9 pCi/kg) dry weight, respectively (Ivanova et al. 1995).

Total plutonium deposition in five Manhattan Project workers exposed to plutonium in 1944–1945 ranged from 98 to 3,300 Bq (2,600–89,000 pCi) according to autopsy data (Voelz et al. 1997). Mean concentrations of ^{239,240}Pu in human tissues from autopsy specimens in Japan ranged from 2.5×10^{-4} pCi/g (9.3×10^{-6} Bq/g) (cerebrum) to 1.5×10^{-3} pCi/g (5.6×10^{-5} Bq/g) (gonads) wet weight (Takizawa 1982). Wrenn and Cohen (1977) reported ^{239}Pu levels in tissues derived from 12 autopsy cases in New York City from 1973 to 1976. Average levels for lung, liver, vertebrae, and gonads were 2.4×10^{-4}, 7×10^{-4}, 1.7×10^{-4}, and 4×10^{-4} pCi/g (8.9×10^{-6}, 3×10^{-5}, 6.3×10^{-6}, and 1×10^{-5} Bq/g), respectively. Tissue samples from autopsy cases of nonoccupationally exposed individuals from Great Britain showed median ^{239,240}Pu concentrations for ribs, vertebrae, femur, liver, and lungs of 1.6×10^{-4}, 1.2×10^{-4}, 9.5×10^{-5}, 7×10^{-4}, and 4.9×10^{-5} pCi/g (5.9×10^{-6}, 4.4×10^{-6}, 3.5×10^{-6}, 2.6×10^{-5}, and 1.8×10^{-6} Bq/g), respectively. Comparable samples taken from autopsy cases from a region in Great Britain located near a plutonium processing plant had median concentrations of 2.2×10^{-4}, 1.9×10^{-4}, 1.5×10^{-4}, 1.4×10^{-4}, and 1.8×10^{-4} pCi/g (8.1×10^{-6}, 7.0×10^{-6}, 5.5×10^{-6}, 5.2×10^{-6}, and 6.7×10^{-6} Bq/g) for ribs, vertebrae, femur, liver, and lungs, respectively (Popplewell et al. 1988).

Ibrahim et al. (1999) studied the excretion of ^{239}Pu in urine of residents living near the Rocky Flats Environmental Technology Site (RFETS). The Rocky Flats group consisted of two groups of individuals living near RFETS, who were not occupationally exposed to plutonium. Urine was collected from the first group during 1992–1993 and samples were collected from the second group in 1995. Background

samples were also collected during two periods from individuals living in Colorado least 16 km from the RFETS. Mean ^{239}Pu excretion rates of 1.1×10^{-6} and 8.5×10^{-7} Bq/day (3.0×10^{-5} and 2.3×10^{-5} piCi/day) were reported for the entire Rocky Flats group and the background group, respectively. Analysis indicated that these data were not statistically significantly different. Measured levels of ^{239}Pu in urine from the Rocky Flats group were within the range reported for background levels (Ibrahim et al. 1999).

Bolotov et al. (2003) reported ^{239}Pu concentrations in human hair ranging from 0.90 to 3.0 Bq/kg (20–80 pCi/kg) in samples from the area of the heavily damaged Semipalatinsk nuclear bomb test site region in Russia. ^{239}Pu concentrations in human gall stones collected from three individuals from Minsk, Belarus were 0.28–0.53 Bq/kg (7.5–14 pCi/kg); gall stones from another individual in Krakow, Poland contained <0.05 Bq/kg (<1 pCi/kg) ^{239}Pu (Bolotov et al. 2003).

Yamamoto et al. (2008a) reported plutonium concentrations human tissue samples, including bone (vertebra), lungs, liver, and kidneys, collected during 2000–2002 at autopsy from nine residents who died in some settlements and in Semipalatinsk City around the Semipalatinsk Nuclear Test Site. ^{239,240}Pu concentrations in four bone (vertebra) samples ranged from 0.049 to 0.13 mBq/g ashed weight. ^{239}Pu concentrations in six kidney samples ranged from 0.023 to 0.25 mBq/g ashed weight; ^{240}Pu was not detected in these kidney samples. In the nine liver samples ^{239}Pu and ^{240}Pu concentrations were 0.39–4.83 and 0.2–2.74 mBq/g ashed weight, respectively. In the nine lung samples ^{239}Pu and ^{240}Pu concentrations ranged from 0.044 to 1.56 and from not detected to 1.83 mBq/g ashed weight, respectively. In addition, bone samples, mainly vertebral bone, were collected from 23 deceased residents of this area. ^{239,240}Pu activity in these bone samples ranged from 0.020 to 0.107 mBq/g ashed weight, with a mean of 0.46 mBq/g ash weight. Yamamoto et al. (2008a) reported that the ^{239,240}Pu levels in bone, lung, and liver samples in this study did not seem to be largely different from ranges found for human tissue samples for residents from other countries that were due solely to global fallout during the 1970s–1980s. Human tissue autopsy samples were obtained for the period of 1975–2003 from non-occupationally exposed residents of Ozyorsk, Russia in the vicinity of the Mayak nuclear facility. Since the early 1950s, the plutonium body burden in the Ozyorsk population was shown to grow at a nearly constant rate and total accumulation amounted to 5.8 Bq at 35 years after the construction of the plant in the city (Suslova et al. 2007).

6.6   EXPOSURES OF CHILDREN

This section focuses on exposures from conception to maturity at 18 years in humans. Differences from adults in susceptibility to hazardous substances are discussed in Section 3.7, Children's Susceptibility.

Children are not small adults. A child's exposure may differ from an adult's exposure in many ways. Children drink more fluids, eat more food, breathe more air per kilogram of body weight, and have a larger skin surface in proportion to their body volume. A child's diet often differs from that of adults. The developing human's source of nutrition changes with age: from placental nourishment to breast milk or formula to the diet of older children who eat more of certain types of foods than adults. A child's behavior and lifestyle also influence exposure. Children crawl on the floor, put things in their mouths, sometimes eat inappropriate things (such as dirt or paint chips), and spend more time outdoors. Children also are closer to the ground, and they do not use the judgment of adults to avoid hazards (NRC 1993).

Children would be exposed to plutonium from fallout by similar routes are adults, such as ingestion of food and water and breathing ambient air. However, levels would generally be low for children not living near areas with known plutonium contamination (e.g., areas where nuclear accidents or former plutonium processing plants). Limited data on exposures of children to plutonium were located.

Compared to adults, the potential for plutonium exposure is greater for children who consume foods (e.g., milk, grains) produced in areas with elevated concentrations of plutonium in the soil and for children with elevated concentrations of plutonium in their drinking water. Children are more likely to be exposed to plutonium in dairy products produced in contaminated areas.

O'Donnell et al. (1997) reported an average ^{239,240}Pu concentration in permanent teeth collected from children within the United Kingdom and Republic of Ireland of 5 mBq/kg (0.1 pCi/kg) ash weight. ^{239,240}Pu concentrations decreased with increasing distance from Sellafield; at 0–50, 50–150, and >150 miles from Sellafield, average ^{239,240}Pu concentrations were 7.1, 5.0, and 3.0 mBq/kg (0.20, 0.10, and 0.08 pCi/kg) ash weight, respectively. These levels are not considered to present a radiological hazard (O'Donnell et al. 1997). Urine collected during a 24-hour period from 17 school-aged children in North London contained 3.5 µBq/day of ^{239}Pu (Priest et al. 1999).

6.7   POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Total plutonium deposition in five Manhattan Project workers exposed to plutonium in 1944–1945 ranged from 98 to 3,300 Bq (2,600–89,000 pCi) according to autopsy data (Voelz et al. 1997).

Individuals living near facilities which utilize plutonium in their operations may have higher exposure potential due to regular releases through stack-emissions or waste water. In addition, atmospheric fallout to the soil can result in secondary releases due to dust generation while farming or due to uptake by crops and subsequent ingestion of contaminated crops (Corey et al. 1982).

Individuals living in Palomares, Spain, were exposed to plutonium after the dispersal of the plutonium in two bombs released during the midair collision of two airplanes (Iranzo et al. 1987). Exposure via inhalation due to the resuspension of contaminated soil was studied for 15 years following the release. Those individuals living near cultivated lands with the highest contamination received a cumulative total of 52.3 mrem (5.2×10^{-1} mSv) from 1966 to 1980 while those in the urban area of Palomares, farther away from the source, received 5.4 mrem (5.4×10^{-2} mSv) (Iranzo et al. 1987).

Kathren et al. (1987) determined levels of ^{239}Pu at autopsy in bones of an individual known to have had occupational exposure to plutonium. Values ranged from 1.9×10^{-4} to 1.14×10^{-2} pCi/g ash (7.0×10^{-6}– 5.0×10^{-5} Bq/g ash), with the highest value detected in the scapula.

Kawamura (1987) estimated the ^{239,240}Pu inhalation intake of visitors to Kiev after the Chernobyl accident to be 0.8 pCi/day (0.03 Bq/day) during peak fallout exposure.

6.8   ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of plutonium is available. Where adequate information is not available, ATSDR, in conjunction with NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of plutonium.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would

reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

6.8.1   Identification of Data Needs

Physical and Chemical Properties.   Table 4-2 summarizes many of the relevant physical and chemical properties of plutonium and selected plutonium compounds. Table 4-3 summarizes the radiological properties of selected plutonium isotopes. There are adequate data for the physical, chemical, and radiological properties of plutonium and plutonium compounds. No data needs are identified.

Production, Import/Export, Use, Release, and Disposal.   According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit substance release and off-site transfer information to the EPA. The TRI, which contains this information for 2004, became available in May of 2006. This database is updated yearly and should provide a list of industrial production facilities and emissions.

The potential for human exposure to plutonium is great due to its ubiquitous presence in the environment, resulting from releases from production facilities and from weapons testing, and its radiological half-life. However, the level of exposure to plutonium will generally be small. The production and use of plutonium 238–243 are well documented. There is little information regarding the production of ^{237}Pu. The amounts of these plutonium isotopes produced for various applications have been documented; however, the most current information is from 1974. More recent data are needed in order to compare past and present production and to project future production. The majority of information on the production and use of plutonium is classified in the nation's defense program. Information on past major releases of plutonium from weapons testing and from the explosion of a navigational satellite is available. However, current information on releases from production facilities is unavailable and is needed in order to monitor populations that might be exposed. The disposal of plutonium prior to 1970 is documented, but again, more recent information regarding amounts being held for mandated disposal in the proposed high-level disposal facility is needed. Rules and regulations for the disposal of plutonium have been established and these are reported in Chapter 8.

Environmental Fate.   The major transport processes involved in the environmental fate of plutonium, as it relates to potential human exposure, have been fairly well defined. These processes include transport in the atmosphere when adsorbed to particulate matter and dry or wet deposition on land and water. Information on environmental compartments, such as flux rates, and the mechanisms and rates of several processes involved in the biogeochemical cycling of plutonium are still undefined. The data available regarding uptake of plutonium by plants are limited. There is some information regarding the conversion of the oxidized forms of plutonium to reduced forms followed by uptake into plants. Information regarding the influence of inorganic complexes on transport and regarding the media-specific effects of pH on the oxidation states of plutonium would be useful in order to more fully understand transport processes. The persistence of plutonium isotopes is well documented. Transformation of plutonium is through radioactive decay or chemical oxidation/reduction reactions. These processes have been well characterized.

Bioavailability from Environmental Media.   Plutonium is known to be absorbed following inhalation exposure. Bioavailability following oral and dermal exposure is very low; however, plutonium can be absorbed from contaminated wounds. Bioassay data are available on absorption from contaminated air and water.

Food Chain Bioaccumulation.   Plutonium has been shown to bioconcentrate in aquatic organisms at the lower end of the food chain (WHO 1983). However, data do not indicate that plutonium is bioconcentrated in plants, higher aquatic organisms, or animals. In addition, there is no indication that plutonium is biomagnified in terrestrial or aquatic food chains. No additional information on bioaccumulation appears to be necessary at this time.

Exposure Levels in Environmental Media.   Reliable monitoring data for the levels of plutonium in contaminated media at hazardous waste sites are needed so that the information obtained on levels of plutonium in the environment can be used in combination with the known body burden of plutonium to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites.

A number of studies have been performed throughout the years on the fallout associated with the testing of nuclear weapons. Information is available on levels in air, water, soil, plant materials, and foodstuffs (Ahier and Tracy 1995; Arimoto et al. 2005; Dai et al. 2002; DOE 1999a, 2005a, 2005c, 2005d, 2005e, 2005f, 2006a; Hirose and Aoyama 2003; Ibrahim et al. 1997; Lee and Clark 2005; Lehto et al. 2006;

Litaor 1999; Mulsow et al. 1999; Struminska and Skwarzec 2004). In particular, information is very limited on levels in media associated with areas surrounding waste sites. Such information is needed in order to quantify the potential exposure via these sources. Limited data are available on estimates of human intake via specific media (e.g., food) (Cooper et al. 1992; Pietrzak-Flis and Orzechowska 1993; Sanchez et al. 1999). This information would be important in determining the impact of exposure through each of these media. In general, plutonium levels found in environmental media that resulted from fallout are low and exposure would also be expected to be low. Plutonium exposure would likely only be relevant to individuals living near areas with known plutonium contamination (e.g., nuclear accident sites or waste sites).

Exposure Levels in Humans.   Plutonium concentrations have been reported in various tissues and biological fluids, including urine, and in lung, liver, and bone tissues obtained from autopsy (Filipy et al. 2003; Ibrahim et al. 1999; Ivanova et al. 1995; Popplewell et al. 1988; Takizawa 1982; Voelz et al. 1997; Wrenn and Cohen 1977). Occupationally exposed populations are likely routinely biomonitored through urinalysis. However, such data are not made available and are needed to quantify exposure to these individuals. In addition, no information is available on biomonitoring of individuals around NPL sites where plutonium has been found or of the general public.

This information is necessary for assessing the need to conduct health studies on these populations.

Exposures of Children.   Children would be exposed to plutonium from fallout by similar routes are adults, such as ingestion of food and water and breathing ambient air. However, levels would generally be low for children not living near areas with known plutonium contamination (e.g., areas where nuclear accidents or former plutonium processing plants). Limited data on exposures of children to plutonium were located. O'Donnell et al. (1997) reported [239,240]Pu levels in permanent teeth collected from children in the United Kingdom and Republic of Ireland. Priest et al. (1999) reported [239]Pu content in urine in North London school children.

There do not appear to be any childhood-specific means to decrease exposure to plutonium. However, as levels of plutonium in food and ambient air are generally low, exposure to plutonium would also be expected to be low.

No data were located on plutonium concentrations in breast milk or infant formulas. Additional studies on daily intake of plutonium in children and infants would be useful to estimate the exposure of this

population to plutonium, particularly in areas contaminated with plutonium where exposure may be of greater concern.

Child health data needs relating to susceptibility are discussed in Section 3.12.2, Identification of Data Needs: Children's Susceptibility.

Exposure Registries.   No exposure registries for plutonium were located. This substance is not currently one of the compounds for which a sub-registry has been established in the National Exposure Registry. The substance will be considered in the future when chemical selection is made for sub-registries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to exposure to this substance.

USTUR established a database to document levels and distribution of uranium and transuranium isotopes in human tissues for occupationally exposed workers who donate their bodies to science (USTUR 2003). The Department of Energy (DOE) has developed the Comprehensive Epidemiologic Data Resource (CEDR) Program to provide public access to health and exposure data concerning DOE installations. In addition, studies relating to populations residing near DOE installations, as well as other studies of radiation exposures and health effects, such as atomic bomb survivors, are included in CEDR (CEDR 2007).

6.8.2   Ongoing Studies

No ongoing studies pertaining to the environmental fate of plutonium or plutonium compounds were identified in a search of the Federal Research in Progress database (FEDRIP 2007).