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^{241}Pu in the environment: insight into the understudied isotope of plutonium

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Abstract

Studies of plutonium in the environment have focused on the α-emitting isotopes ^{238}Pu, ^{239}Pu and ^{240}Pu, often overlooking the β-emitting isotope ^{241}Pu because of its relatively short half-life (14.4 years). Here, we summarize sources of ^{241}Pu and discuss its distribution and behavior in the environment. In the short term, ^{241}Pu, the largest contributor to the total plutonium radioactivity whereas in the long term its decay products, ^{241}Am and ^{237}Np, are the major contributors as some 46% of current total ^{241}Am is attributable to ^{241}Pu decay. In this context, understanding the fate and transport of ^{241}Pu is crucial to assessing long-term radiological dose.

Keywords ^{241}Pu · ^{241}Am · ^{237}Np · Marine samples · Environmental samples

Introduction

The fate and transport of plutonium (Pu) isotopes, including ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Pu, in the environment are of particular interest because they are potentially hazardous to human health. The primary health risk of ^{238}Pu, ^{239}Pu, and ^{240}Pu isotopes arise from the energetic α-particles they initially emit whereas the risk for ^{241}Pu is from its initial decay by the emission of β-particles. Alpha particles have a much higher relative biological effectiveness than the much lighter electrons that are the primary means of radiation damage by gamma and beta radiation. Nonetheless, these isotopes must enter the body in order to cause significant damage and inhalation is the primary pathway. In fact, lung doses from these transuranics mainly occur via environmental processes such as global dust storms, the resuspension of contaminated soils, and the transport of ash from burnt contaminated biomass. Studies of plutonium in the environment have focused mainly on the ^{238}Pu, ^{239}Pu and ^{240}Pu, isotopes that initially decay by α-radiation. In contrast, ^{241}Pu, initially associated with β-radiation and later γ-radiation, has been overlooked, perhaps due to its relatively short half-life. Being the most abundant plutonium isotope released in the environment, ^{241}Pu is the largest contributor to the total plutonium radioactivity. In the long term, its daughters ^{241}Am (half-life = 432.2 years) and ^{237}Np (half-life = 21.4×10^6 years) become the major contributors to dose.

The primary source of plutonium isotopes in the environment has been atmospheric nuclear tests that were conducted between 1945 and 1980 [1]. Besides atmospheric nuclear tests, satellite accidents and accidents at nuclear power plants, such as Chernobyl, Ukraine in 1986 and Fukushima, Japan in 2011, have contributed to greater plutonium contamination. It is estimated that atmospheric nuclear weapons testing of 1950s and 1960s released about 6.52 PBq (1 PBq = 1×10^{15} Bq) of ^{239}Pu, 5.35 PBq of ^{240}Pu, and 142 PBq of ^{241}Pu globally [1]. The second major source of plutonium contamination was the SNAP-9A accident in April 1964, which released about 630 TBq of ^{238}Pu into the atmosphere [2]. In addition, the B-52 accidents in Palomares, Spain in 1966 and at the Thule Air Base, Greenland in 1968 caused localized environmental contamination with weapons-grade plutonium [3, 4]. Currently, the most significant contributors of plutonium to the environment are nuclear fuel reprocessing facilities such as La Hague in France and Sellafield in the United Kingdom [5, 6].

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Table 1 summarizes the various sources of plutonium released into the environment. Perhaps the most significant observation is that ^{241}Pu is the dominant isotope in five of the eight releases. The ^{241}Pu is produced by the neutron capture of lower atomic weight plutonium and increases its abundance as part of the Pu mixture relative to the irradiation exposure. Plutonium mixtures vary depending on their end use. Reactor-grade plutonium contains the most ^{241}Pu at ~ 11%, almost 30 times higher than weapons-grade plutonium (~ 0.4%) and about 400 times higher than heat-source grade Pu (~ 0,03%) [7]. Consequently, the ^{241}Pu activity is highest for reactor-grade plutonium.

With a half-life of only 14.4 years, ^{241}Pu is the shortest-lived isotope of plutonium found in the environment, which may explain why it is the most understudied. Plutonium-241, unlike other plutonium isotopes, does not emit an α-particle on decay but decays with a primary beta minus (β^{-}) emission, as shown in Scheme 1, which is difficult to detect with standard field instruments.

However, ^{241}Pu decays to the α-emitter, ^{241}Am, which has a half-live of 432.2 years and is also much more radiotoxic and mobile than its parent [8, 9]. The ^{241}Am subsequently decays to ^{237}Np, which is also an α-emitter with a half-life of 2.1 million years. Consequently, in the later years, both ^{241}Am and ^{237}Np will be the major contributors to environmental radioactivity from the disposal of high-or intermediate-level radioactive waste because of their long half-lives and their constantly increasing inventory from both direct ^{241}Pu emissions and in-growth of ^{241}Am during decay.

Plutonium isotopes undoubtedly present a large risk for internal radiation exposure via inhalation or the ingestion of contaminated food. For dose estimation, either from atmospheric testing or severe reactor accidents, the contribution of ^{241}Pu is currently under estimated, not only because it is a β-emitting nuclide but because the risk presented by its progeny, ^{241}Am and ^{237}Np, persist over a much longer term. In this context, understanding the distribution of ^{241}Pu in the environment is crucial for assessing the long-term radiological dose to the general public living in the vicinity of contaminated areas. Currently in the assessment of dose, bioassays are taken for ^{238}Pu, $^{239+240}$Pu and ^{241}Am, without considering ^{241}Pu. Moreover, bio-kinetic models and dose calculation codes, such as the Integrated Modules for Bioassay Analysis (IMBA®), do not account for ^{241}Am in-growth unless the ^{241}Pu activity is specified so knowledge of ^{241}Pu activity is essential for quantifying ^{241}Am. In view of these issues, this paper discusses the sources, distribution and behavior of ^{241}Pu in terrestrial and aquatic environments. It also highlights the progress in analytical methods for detecting ^{241}Pu, discusses the main issues associated with the determination of ^{241}Pu in environmental samples, as well as the fate and transport in the various environmental compartments.

Table 1 Sources of plutonium isotopes in the environment (Bq)

	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu	$^{239+240}$Pu	Total
Specific activity (Bq/kg)	6.33E+14	2.29E+12	8.40E+12	3.82E+15	1.46E+11	1.08E+13	–
Nuclear weapons testing [1]	3.3×10^{14}	6.5×10^{15}	4.4×10^{15}	1.4×10^{17}	1.6×10^{13}	12.6×10^{15}	1.7×10^{17}
Burn-up of SNAP-9A satellite [2]	6.3×10^{14}	–	–	–	–	–	6.3×10^{14}
Aircraft accident in Palomares, Spain [3]	–	–	–	–	–	5.5×10^{10}	5.5×10^{10}
Aircraft accident in Thule, Greenland, 1968 [4]	–	–	–	–	–	1.0×10^{13}	1.0×10^{13}
Reprocessing plant in Sellafield site 1985–1994 [5]	1.2×10^{14}	–	–	2.2×10^{16}	–	6.1×10^{14}	2.2×10^{16}
Reprocessing plant in La Hague site 1995–1999 [6]	2.7×10^{12}	–	–	1.2×10^{14}	1.7×10^{9}	3.4×10^{12}	1.4×10^{14}
Chernobyl nuclear power plant accident, 1986 [1]	3.5×10^{13}	3×10^{13}	4.2×10^{13}	6.0×10^{15}	7.0×10^{10}	7.2×10^{13}	6×10^{15}
Fukushima NPP accident, 2011 [10]	1.9×10^{10}	–	–	1.2×10^{12}	–	6.4×10^{9}	1.2×10^{12}
Fukushima NPP accident, 2011 [96]	$2.9–6.9 \times 10^{10}$	–	–	$1.1–2.6 \times 10^{11}$	–	$1.1–2.4 \times 10^{9}$	$1.4–3.3 \times 10^{11}$

Scheme 1 Decay of ^{241}Pu and the formation of ^{241}Am

$$^{241}\text{Pu (14.35 yr)} \xrightarrow{\beta^-} {}^{241}\text{Am (432 yr)} \xrightarrow{\alpha} {}^{237}\text{NP (2.1 x }10^{6}\text{ yr)} \xrightarrow{\alpha} {}^{233}\text{Pa (26.9 days)} \xrightarrow{\beta^-} {}^{233}\text{U (1.59 x }10^{5}\text{ yr)}$$

Occurrence of ^{241}Pu in the environment

Following $^{239+240}$Pu and ^{238}Pu, ^{241}Pu is the third most common isotope of plutonium found in the environment. Owing to the dependence of activity ratios (i.e., ^{238}Pu/$^{239+240}$Pu, ^{241}Pu/$^{239+240}$Pu, ^{241}Am/$^{239+240}$Pu) and atomic ratios (^{240}Pu/^{239}Pu) on the source, isotopic ratios can act as a fingerprint to identify the origin of the plutonium from different sources released into the environment. For example, the activity ratio of ^{241}Pu to $^{239+240}$Pu ranges from 12 to 16 for global fallout from nuclear tests (ref date: 1963–1972) [8]; 0.5–4 for weapon-grade plutonium (ref date: 1945–1974) [8]; 25 for releases from nuclear fuel reprocessing plants (ref date: 1970–1980) [8]; 70–100 for Chernobyl fallout (ref date: April, 1986) [9] and > 100 for Fukushima fallout (ref date: March 2011) [10]. In addition, ^{241}Pu is almost always present in uranium and plutonium-based nuclear weapons. Therefore, the activity ratios of ^{241}Pu to $^{239+240}$Pu or ^{241}Am to $^{239+240}$Pu and ^{241}Pu/^{239}Pu serve as a good indicator to determine the origin and age of plutonium materials and plutonium contamination [3, 11, 12].

Yet, despite its ubiquity, the ^{241}Pu isotope has received less attention than the other the plutonium isotopes. Owing to the relatively few studies of its environmental and biological behavior, ^{241}Pu can be referred to as the "forgotten isotope of plutonium". The paucity of studies is primarily because: (1) ^{241}Pu is a beta-emitter with maximum energy of only 20.8 keV, representing a lesser radiological risk compared with other alpha-emitting plutonium isotopes, and (2) the precise determination of ^{241}Pu requires additional separation and measurement techniques like liquid scintillation spectrometry or mass spectrometry [13–16].

The global inventory of ^{241}Am activity produced from the decay of fallout ^{241}Pu will be about 60% of ^{239}Pu in approximately 70 years [17]. Allard [18] estimates that some 1.2 × 10^{16} Bq of ^{241}Am has in-grown from the decay of fallout ^{241}Pu. In-grown ^{241}Am from the decay of the ~ 6×10^{15} Bq of ^{241}Pu released from the Chernobyl Nuclear Power Plant (NPP) accident currently amounts to 1.5 × 10^{14} Bq (decay corrected to 2017). Therefore, accurate determination of ^{241}Pu and its distribution is of interest for long-term assessment of dose to the population, for the decommissioning of nuclear facilities, and for radioactive waste management [13, 18].

Analytical techniques for determination of ^{241}Pu

Owing to its primary decay via a 20.8 keV β-emission, ^{241}Pu is difficult to detect with standard field instruments [7]. Traditionally, ^{241}Pu has been determined directly by liquid scintillation counting (LSC) or indirectly by alpha spectrometry to measure the in-grown ^{241}Am daughter. Both of these methods are capable of producing good results. Both methods require pre-concentration, separation of analytes, and long counting times (up to several days) to achieve high counting efficiency and the desired sensitivity.

The chemical separation procedure used for the α-emitting isotopes of plutonium can also be used for ^{241}Pu. Chemical separation is typically performed with anion exchange columns or TEVA® chromatography columns (from Eichrom Technologies in the US or Triskem International in Europe), which have a high affinity for plutonium. Following separation, the stainless steel planchet used to electroplate plutonium isotopes for alpha spectrometric measurement is then subjected to LSC of ^{241}Pu, after alpha spectrometric measurement. A detection limit of 7–11 mBq has been reported using low background LSC [11].

Techniques have been developed to count alpha discs directly, with no further purification of the plutonium isotopes, by placing the planchet in the bottom of a liquid scintillation vial and adding the scintillant on top [19, 20]. However, variable deposition thickness on the alpha planchet may result in low and variable counting efficiencies for both ^{241}Pu and alpha isotopes of plutonium. Accounting for these low efficiencies can be difficult, even with conventional external-standard quench-correction techniques. One of the main challenges of the LSC method is the accurate determination of the counting efficiency [14]. The counting efficiency of ^{241}Pu in LSC usually varies from 30 to 43%, depending on the spectral quench parameter of the external standard (SQP[E]).

To maximize the counting efficiency of ^{241}Pu, a technique was developed whereby plutonium is leached from the alpha planchet with concentrated HNO_3 and then extracted into tri-octylphosphine oxide (TOPO)/toluene. The Pu-bearing organic extract is then mixed directly with scintillation cocktail and counted using LSC [21]. A detection limit of 105 mBq has been achieved with 5 g of LGC sediments [20]. This technique has also been used to determine ^{241}Pu in soils [22]. These authors compared several organic extractants (TOPO/cyclohexane, HDEHP/toluene, Aliquot 336/xylene, and DEDA/toluene) and observed that HDEHP/toluene can effectively extract ^{241}Pu from the sample. Lee and Lee [12] proposed a new approach in which they combined LSC with pulse-shape analysis (PSA) for the determination of ^{241}Pu co-existing with alpha-emitting plutonium isotopes and americium in soil samples. The indirect method uses alpha spectrometry to measure the in-grown ^{241}Am. In applications of this method, the separated plutonium planchets were kept for at-least six months for the in-growth of ^{241}Am. In the literature, the typical in-growth period for ^{241}Am ranged from 6 months to several years for environmental samples [20, 23]. The generated ^{241}Am was then separated from plutonium and measured by alpha spectrometry. The detection limit of the method varies with in-growth time. A typical detection limit with alpha spectrometry is 0.3 mBq, achieved with an in-growth period of 13 years [23]. There are two main disadvantages to this method: (1) it takes at least six months for measurable in-grown ^{241}Am to be produced and (2) an incomplete spectral separation of ^{241}Am from ^{238}Pu interferes with the precise determination of ingrown ^{241}Am by alpha spectrometry. Reliable results can be achieved only if appropriate sample preparation is applied, which not only involves sample pre-concentrations but also effective matrix removal steps and multistage radiochemical separation processes. Livingston et al. [24] determined ^{241}Pu activities in environmental samples by measuring in-grown ^{241}Am produced by the decay of ^{241}Pu. Koide et al. [25, 26] also used this technique to measure ^{241}Pu activities in polar glaciers.

In recent years, several mass spectrometry techniques have also been used for the determination of ^{241}Pu. Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Thermal Ionization Mass Spectroscopy (TIMS), Accelerator Mass Spectrometry (AMS), and Resonance Ionization Mass Spectroscopy (RIMS) have all been used to determine Pu isotopes, including ^{241}Pu [27]. Sturup et al. [28] used SF-ICP-MS for the determination of plutonium isotopes in sediment and seawater and obtained detection limits of 0.0115 mBq for ^{239}Pu, 0.0084 mBq for ^{240}Pu and 3.8 mBq for ^{241}Pu. Donard et al. [29] successfully applied SF-ICP-MS to the simultaneous detection of ^{239}Pu, ^{240}Pu and ^{241}Pu and ^{242}Pu in sediments. Using the same technique and operating conditions, Varga et al. [15] reported detection limits of 0.034 mBq for ^{239}Pu, 0.08 mBq for ^{240}Pu, and 54 mBq for ^{241}Pu with 1-g soil and sediment samples. The formation of hydride and oxide interferences (e.g., $^{238}U^{1}H^{+}$ or $^{207}Pb^{16}O_2^{+}$), usually encountered in the low-level determination of plutonium isotopes by ICP-MS, were minimized by using a desolvation sample introduction system with Ar-N_2 mixed gas plasma. Although the introduction of nitrogen might increase nitrogen containing polyatomic interferences, it decreases the UH^{+}/U^{+} ratio to $< 10^{-5}$. In the latter procedure, they reported improved detection limits of 0.021 mBq for ^{239}Pu, 0.014 mBq/g for ^{240}Pu, and 11.9 mBq for ^{241}Pu by using similar operating conditions, minus the Ar-N_2 mixed gas plasma [16]. A survey of the literature indicates that Multi Collector ICP-MS (MC-ICP-MS), coupled with ultrasonic nebulizers (USN) or MCN-6000, and Sector Field-ICP-MS (SF-ICP-MS), coupled with a microconcentric desolvating nebulizer (MCN-6000) are the most commonly utilized ICP-MS techniques for determination of the ^{241}Pu.

Among the mass spectrometric techniques, AMS is the most sensitive detection techniques for many long-lived radionuclides. Detection limits as low as 10^{6} atoms (ca. 0.001 mBq) can be achieved for ^{239}Pu [30]. Additionally, matrix interferences are less in AMS than in ICP-MS and determination of the ^{240}Pu to ^{239}Pu ratio is readily accomplished. For Pu isotopes, the major advantage of AMS over the conventional MS (TIMS or ICP-MS) is the complete destruction of molecular isobars (e.g., $^{238}UH^{+}$ for ^{239}Pu) by stripping to highly positive charged states in the terminal of the tandem accelerator. The determination of ^{241}Pu can be achieved without additional sample processing steps, if the concentrations of ^{241}Pu in the sample are high enough. The major drawback of this technique in that the determination of ^{241}Pu has a low detection efficiency [30–32].

Table 2 compares the radiometric method and mass spectrometric methods for the determination of plutonium isotopes. Studies indicate that AMS, TIMS and RIMS are more sensitive than alpha spectrometry for the determination of $^{239+240}$Pu, whereas the sensitivity of ICP-MS is comparable to LSC for the measurement of ^{241}Pu. The chemical separation methods for both radiometric and mass spectrometric methods can be similar; however, the counting time of mass spectrometric methods are much shorter than that of radiometric methods (a few minutes vs. a few hours and sometimes days). Lee et al. [33] compared alpha spectrometry, LSC, AMS, and ICP-MS techniques by analyzing a set of environmental reference materials. It was concluded that the alpha spectrometry obtained results for $^{239+240}$Pu were in reasonably good agreement with those of ICP-MS and AMS, whereas values obtained by LSC and ICP-MS were only in fair agreement for ^{241}Pu. The determination of ^{241}Pu by ICP-MS is hampered by its low abundance and by polyatomic interference peaks, which can be expected at m/z of 239–242, up-mass tailing of ^{238}U and non-spectral interferences resulting from matrix constituents [34]. This is particularly important in the analysis of environmental samples since the level of uranium is approximately 6–7 orders of magnitude higher than that of plutonium. Furthermore, the relative precision obtained by SF-ICP-MS has a mean value of 32%, which is lower than

Table 2 Typical detection limit of ^{241}Pu in the environmental samples by various analytical methods

Sample	Detection method	Detection limit	Count time	References
Marine sample	LSC	11 mBq	5 h	[11]
Sediment, soil	LSC	41 mBq	1 h	[97]
Air filter, grass, sediment	LSC with PSA	7 mBq	600 min	[13]
Sediment, 5 g	LSC	105 mBq	300 min	[20]
Soil, 200 g	LSC	28 mBq	500 min	[97]
Soil, 10 g	LSC	1.0–11 mBq	1440 min	[98]
Soil, 0.5–40 g	LSC	73–90 mBq	–	[70]
Lichen	LSC	37 mBq	120 min	[71]
Lichen, peat	LSC	7 mBq	600 min	[9]
Soil, 100 g	LSC with PSA	8.7 mBq	700 min	[12]
Moss, 20 g				
Contaminated soil from Chernobyl	Alpha ^{241}Pu (via ^{241}Am)	0.5 mBq	3 h	[23]
Sea water and soil	LSC	2.2 mBq	1000 min	[19]
Urine	TIMS	0.0014 mBq for ^{239}Pu 0.0009 mBq for ^{240}Pu 0.4 mBq for ^{241}Pu	20–30 min	[27]
Sediment, soil, biological samples	SF-ICP-MS	0.021 mBq for ^{239}Pu 0.014 mBq for ^{240}Pu 11.9 mBq for ^{241}Pu	20 min	[15, 16]
Marine soil, sediment off the Fukushima site (> 10 g)	SF-ICP-MS	2 mBq for ^{241}Pu 0.14 fg/ml	~ 5–10 min	[34]
Marine sediment, Urine	RIMS	0.01 mBq for ^{239}Pu 0.03 mBq for ^{240}Pu 20 mBq for ^{241}Pu	1–2 h	[27]
Sediment, soil	ICP-MS	0.0025 mBq for ^{239}Pu 0.0078 mBq for ^{240}Pu 3.09 mBq for ^{241}Pu	~ 5–10 min	[97]
Ocean water	AMS	~ 0.0001 mBq (1.0–1.2 × 10^4 atom)	~ 5 min	[30, 32]
Soil, plant, sediment	AMS	~ 0.001 mBq (~ 10^6 atom)	~ 5 min	[30, 31]

with alpha spectrometry (5 ± 1%) and liquid scintillation counting (19 ± 2%) [29].

Another detection technique that has been used for the determination of ^{241}Pu is gas-flow proportional counting. This technique uses a gaseous ionization detector to measure the energy of incident α and β ionizing radiation by generating a detector output proportional to the radiation energy. The major advantage of this technique is that the background β count rate is often lower that of LSC [27, 35]. However, the efficiency of the gas-flow proportional counter method is low due to the absorption of low-energy β particles emitted by ^{241}Pu into the counter window. A detection limit of about 10 mBq per sample has been reported by Rosner et al. [35], which is comparable to LSC.

These studies show that the main disadvantage of ICP-MS techniques is the relatively low abundance sensitivity that results in relatively large measurement uncertainties for ^{241}Pu reported at low signal intensity. In addition, there is a risk of interferences from polyatomic species and tailing of ^{238}U, which overlap the peaks for ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{237}Np isotopes. The ICP-MS technique, therefore, may not be a very useful method for low level determination of ^{241}Pu generally found in the environmental samples. Environmental concentrations of ^{241}Pu are expected to be low because most of the ^{241}Pu released from atmospheric nuclear weapons testing has decayed to ^{241}Am. In fact, the ^{241}Pu/^{239}Pu atom ratio in the atmospheric fallout samples has decreased from ~ 0.014 in 1963 to ~ 0.00194 in 2000 [36]. Owing to its short half-life and correspondingly high specific activity, radiometric determination of ^{241}Pu is the preferred technique. On the other hand, the mass spectroscopy technique is preferred if high concentrations of ^{241}Pu are present in the sample e.g., Chernobyl contaminated samples.

^{241}Pu in the environment: distribution and behavior

There have been several studies of plutonium in the environment since the early 1960s but most have investigated the concentration, distribution, and migration behavior of $^{239+240}$Pu and ^{238}Pu in the various environmental compartments with little attention paid to ^{241}Pu. One of the earliest studies of ^{241}Pu is that reported by Livingston et al. [24] in which ^{241}Pu concentrations and ^{241}Pu/$^{239+240}$Pu activity ratios were measured in several environmental samples (sediment core, beach sand, harbor sediment, seaweed, and starfish) collected from the Cape Cod area (41.34°N, 70.42°W) to identify the source of ^{241}Pu contamination. They found only low activity concentrations of ^{241}Pu, ranging from 0.28 to 18.8 mBq/g, mostly with the signature of global fallout. One of the few subsequent studies was that of Gasco et al. [3] who measured ^{241}Pu, other alpha isotopes of plutonium, and their isotopic ratios in soil samples collected from Palomares to evaluate the impact of the B-52 accident. Struminska-Parulska and Skwarzec [37] studied ^{241}Pu occurrence and its distribution in seabirds from northern Eurasia to identify its source and to quantify bio-accumulation. There was a non-uniform distribution of ^{241}Pu with the highest concentrations in the digestive organs and feathers and the lowest in muscle tissue. The internal dose from the accumulated ^{241}Pu in seabirds showed no significant effects. Moreno et al. [38] studied the spatial distribution of ^{241}Pu and the ^{241}Pu/$^{239+240}$Pu ratio in Irish Sea Plankton. The data were used to estimate transit times from Sellafield to locations farther away and the age of plutonium in Plankton. The estimated mean age in this study was 17 ± 2 years (n = 10) for plutonium and 18.6 ± 0.8 years (n = 13) for phytoplankton and zooplankton. The spatial distribution was reasonably homogeneous across the Irish Sea.

Another major source of plutonium contamination in the environment is the Chernobyl NPP accident, which occurred on April 26, 1986. It is estimated that the Chernobyl accident released about 6.1 PBq of plutonium isotopes. It increased the concentration of $^{239+240}$Pu, ^{238}Pu and ^{241}Pu in surface air during the 1986–1987 period, particularly over Europe, and contributed slightly to the global plutonium inventory [1]. An important characteristic of the radioactive material released to the atmosphere by Chernobyl was the presence of highly irradiated fuel particles known as “hot particles” or “Chernobyl dust”. Most of the plutonium was associated with larger particles (10–15 μm) causing the majority of the released plutonium to be deposited near the plant.

The accident at the Fukushima Daiichi NPP on March 11, 2011, also released a small amount of plutonium. Releases were confirmed by the detection of plutonium in environmental samples at a site 1.7 km from the Fukushima NPP and at several other sites within a 20–30 km zone around the plant [10, 39]. Although several studies have attempted to estimate the total released fission products, such as ^{131}I and ^{137}Cs, very few have tried to estimate the total amount of plutonium released. Schwantes et al. [40] estimated a release of only 0.002% (± 0.003%) of the overall plutonium inventory (5.6 kg in Units 1 and 3). Recent analyses by Zheng et al. [10] reported an even lower release, totaling only 0.00002% of the core inventory (about 1.0×10^9 to 2.4×10^9 Bq of $^{239+240}$Pu and 1.1×10^{11} to 2.6×10^{11} Bq of ^{241}Pu.)

The baseline data of dispersal of fallout plutonium from nuclear weapon tests are provided by Hardy et al. [2]. The minimum baseline level of ^{239}Pu contamination in the northern hemisphere was determined to be between 0.04 and 0.15 Bq/m^2, based on 65 soil samples collected around the world. The global integrated deposition of ^{241}Pu was about 440 Bq/m^2 with an air concentration of about 0.8 Bq/m^3 [1]. The majority of plutonium released into the atmosphere as a result of nuclear weapon tests is now associated with sub-surface soils, bottom sediments, or particulates suspended in the water column. Table 3 lists ^{241}Pu concentration levels measured in various environmental samples.

^{241}Pu in surface air

Data on ^{241}Pu in air are very sparse because of its short half-life and difficulty in quantification by conventional radiometric techniques. Concentrations of ^{241}Pu in surface air were not systematically monitored during 1959–1964, the period with the heaviest contributions from global fallout. The annual average concentration of ^{241}Pu in surface air in the mid-latitudes of the northern hemisphere resulting from nuclear weapons testing between 1950s and 1980s was estimated using an atmospheric transport model and the known amount of ^{241}Pu released to the stratosphere as a result of the weapons testing. The results show a rapid increase in ^{241}Am surface air concentrations, which reached a maximum of 0.60 mBq/m^3 in 1963–1964. Since 1973, levels have been around 0.01 mBq/m^3 or less and are continuing to decline. Figure 1 shows the predicted air concentrations of ^{241}Pu from global fallout [41]. Aerosol concentrations of ^{241}Pu were measured in the lower stratosphere (10.1–14.2 km altitude) over Switzerland for

Table 3 The ^{241}Pu concentrations in environmental samples contaminated from different sources

Sample media/location	Sample date	^{241}Pu activity (mBq/g)	Sources	References
Air filter, Finland[a]	1963	< 0.016–1.73	Nuclear weapons testing	[44]
Lichen Top, Finland	1967	2.3–3.0	Nuclear weapons testing	[69]
Lichen, Bottom, Finland	1967	4.1–93	Nuclear weapons testing	[69]
Soil, Japan	1969–1977	0.06–21.25	Nuclear weapons testing	[55]
Sediment, Santa Barbara Basin, USA	1973–74	11–116.33	Nuclear weapons testing	[17]
Sediment, Soledad Basin USA	1973	9.7–123.83	Nuclear weapons testing	[17]
Soil, South Korea	1995	0.66–10.4	Nuclear weapons testing	[12]
Moss, South Korea	1995	1.28–15.5	Nuclear weapons testing	[12]
Soil, Hungary	1998	0.043–1.70	Nuclear weapons testing	[98]
Soil, Palomares, Spain[c]	July, 1994	0.6–7.41	B-52 accident	[3]
Sediment, Bikini Atoll	–	19.3–33.4	PPG close in fallout	[94]
Soil, Semipalatinsk Nuclear Test Site	Oct, 1994	4830	Soviet nuclear test site	[99]
Air filter, Finland[a]	April–May, 1986	< 0.05–13.3	Chernobyl NPP accident	[13]
Air filter, Belgrade[a]	May 1–15, 1986	0.24–7.77	Chernobyl NPP accident	[49]
Air dust	Jan-Dec, 1986	0.001–3.50	Chernobyl NPP accident	[52]
Hot particle, Finland[b]	April 1986	1005	Chernobyl NPP accident	[69]
Forest soil, Poland	April/May, 1986	< 90–254	Chernobyl NPP accident	[63]
Soil, Bragin, Chernobyl	1986	820–1480	Chernobyl NPP accident	[22]
Peat, Finland	May, 1986	4.6–77	Chernobyl NPP accident	[69]
Ash fodder, Hungary	1998	131	Chernobyl NPP accident	[98]
Lichen, Top, Finland	May, 1986	40.6–204	Chernobyl NPP accident	[9]
Lichen, Bottom, Finland	May, 1986	10.6–168	Chernobyl NPP accident	[9]
Lichen, Bottom, Kalanti, Finland	July, 1986	30–184	Chernobyl NPP accident	[69]
Alpine soil, valley of Piora, Switzerland	Jan, 2009	0.5–21	Nuclear weapons testing + Chernobyl	[56]
Alpine soil, France, Switzerland	Jan, 2009	1–53	Nuclear weapons testing + Chernobyl	[56]
Lichen Top, Kalanti, Finland	July, 1986	71–689	Nuclear weapons testing + Chernobyl	[69]
Baltic sediments, Finland	April–May, 1986	< 0.5–27	Nuclear weapons testing + Chernobyl	[13]
Baltic sediments, Poland	May, 1987	0.9–14.2	Nuclear weapons testing + Chernobyl	[87]
Phytobenthos, Puck Bay, Baltic sea	1986–1987	0.24–1.01	Nuclear weapons testing + Chernobyl	[88]
Zoobenthos, Puck, Bay, Baltic sea, Poland	1986–1987	0.13–9.20	Nuclear weapons testing + Chernobyl	[88]
Black sea sediment		1.4–15	Nuclear weapons testing + Chernobyl	[85]
Ravenglass Saltmarsh, Cumbria, UK	1997	6670–55,900	Sellafield discharge	[20]
Soil, Tomsk-Seversk site	–	0.3–104.7	Nuclear weapons testing + discharge from SCC	[99]
BOMARC, Soil, USA	2003	0.33–8.17	Missile fire at BOMARC	[58]
Soil, litter, Japan	March, 2011	4.52–34.8	Fukushima NPP accident	[10]
Marine sediments, 30 km off Fukushima site	March, 2011	0.93–4.02	Global fallout + PPG close in fallout	[92]

PPG Pacific Proving Ground, *SCC* Siberian chemical combine

[a] mBq/m^3

[b] Activity of total sample (mBq)

[c] Activity (Bq)

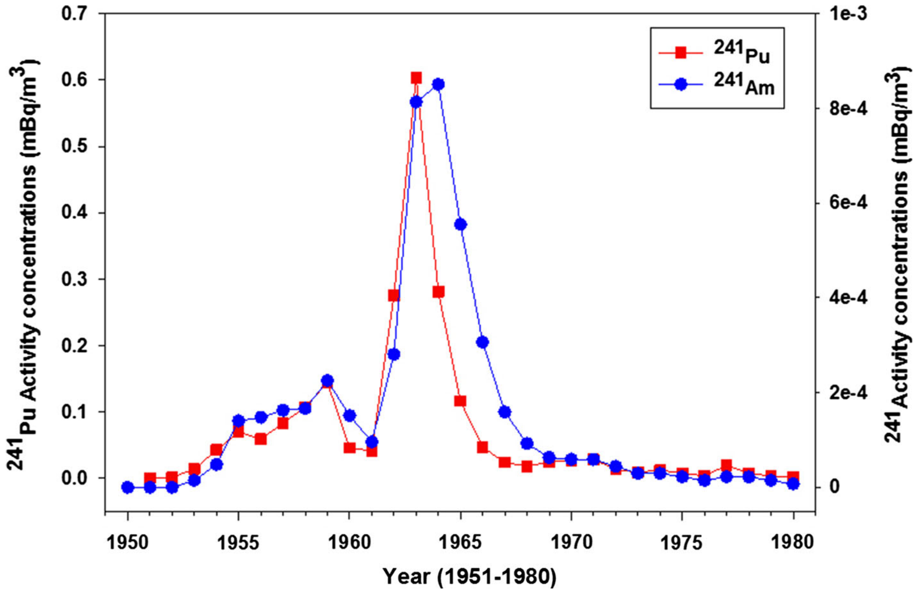

Fig. 1 Predicted surface air concentrations of ^{241}Pu and ^{241}Am (mBq/m^3) during 1951–1980. Data from Bennet [41]

the periods 1973–1977, 2007–2008 and 2010 [42]. Concentrations of ^{241}Pu in the stratosphere show a steady decrease from 1.34 ± 0.150 mBq/m^3 in 1977 to 0.004 ± 0.001 mBq/m^3 in 2010 [42]. The ^{241}Pu levels were more than one order of magnitude higher than those for $^{239+240}$Pu during the period 1973–1977. These authors used a ^{241}Am/^{241}Pu age-dating model to determine the deposition history of plutonium into the atmosphere. Their calculations suggest plutonium contamination dates between 1964 and 1982.

Thomas and Perkins [43] calculated ^{241}Pu concentrations in surface air at Richland, Washington, USA, as a function of time. They used measured concentrations of ^{239}Pu in the atmosphere and an estimated ^{239}Pu/^{241}Pu ratio of 0.015, based on the November 1952 “Ivy Mike” nuclear explosion at Enewetak Atoll, to derive concentrations of ^{241}Pu in surface air. Figure 2 shows the calculated surface-air concentrations of ^{241}Pu at Richland for the period 1963 through 1973, together with the measured concentrations of ^{241}Am. The surface-air concentration of ^{241}Pu ranged from 0.02 to 1.83 mBq/m^3 with a ^{241}Pu/$^{239+240}$Pu ratio of about 15 [43]. As expected, the concentration of ^{241}Pu was highest ($\sim$ 1.83 mBq/m^3) in 1963, after which it decreased steadily to 0.02 mBq/m^3 by 1973. Salminen and Paatero [44] measured ^{241}Pu concentrations in archived filters collected in 1963 at Sodankylä, Finland. The ^{241}Pu concentrations in this study, which ranged from < 0.016 to 1.73 mBq/m^3 with a mean ^{241}Pu/$^{239+240}$Pu ratio of 18, agree well with the ^{241}Pu concentrations estimated by Thomas and Perkins [43]. The ^{241}Pu/$^{239+240}$Pu ratio indicates that the source of ^{241}Pu in the surface air is largely due to the atmospheric weapons tests of 1950s and 1960s. During these decades, plutonium concentrations in surface air varied widely due continued contributions from nuclear weapons testing with concurrent depositions of fallout materials on the earth surface and resuspension of contaminated soil. However, due to the short half-life of ^{241}Pu, concentrations in the surface air have fallen below the conventional analytical detection level since the mid-1970s.

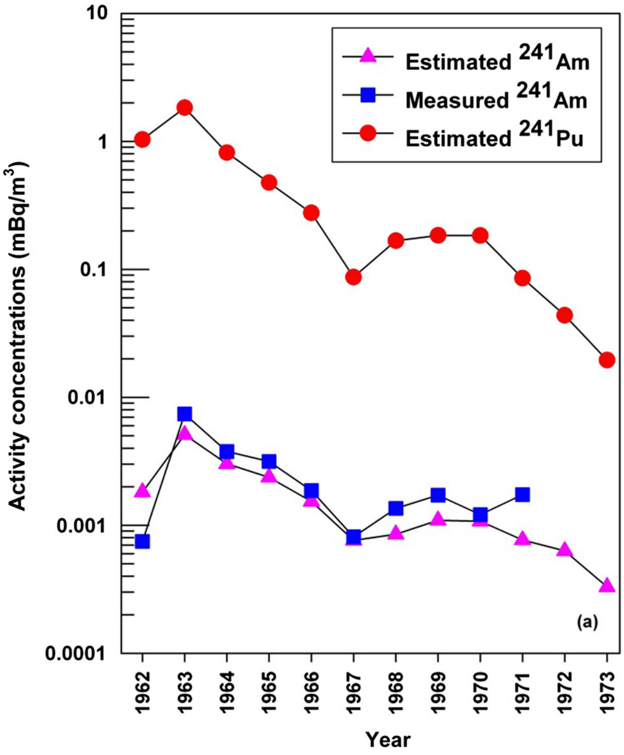

Fig. 2 Surface air concentrations of ^{241}Pu and ^{241}Am (mBq/m^3) during 1962–1973 in Richland, Washington, USA. Data from Ref. [43]

While only limited data exist on the atmospheric dispersion of ^{241}Pu resulting from weapons testing, the existing surface-air concentrations of ^{241}Pu, like $^{239+240}$Pu, show a seasonal dependence. The 1963 data set from Sodankylä, Finland, reported by Salminen and Paatero [44] show the highest concentrations of ^{241}Pu occurred during the spring and summer, with the lowest concentrations in the winter (Fig. 3a). The seasonal cycle of plutonium concentrations in air has been observed since the early days of atmospheric monitoring. Seasonal variations in $^{239+240}$Pu concentrations have been confirmed by much of the data collected in the northern hemisphere. For example, Kierepko et al. [45] showed seasonal variations of $^{239+240}$Pu concentrations in surface air at Krakow and Bialystok, Poland for the period 1991–2008. Arnold and Wershofen [46] observed a similar seasonal cycle for $^{239+240}$Pu in surface air over Germany during the period 1991–2003.

Figure 3b shows the estimated concentrations of ^{241}Am in surface air of Sodankylä, Finland in 2017, produced from the decay of ^{241}Pu measured in 1963 by Salminen and Paatero [44]. The ^{241}Am concentrations obtained were in the range from 0.001 to 0.050 mBq/m^3. As with $^{239+240}$Pu, a seasonal cycle of ^{241}Am concentrations in air has also been observed. In the United States, surface-air concentrations of ^{241}Am at the Waste Isolation Pilot Plant (WIPP), a transuranic waste repository site in southeastern New Mexico, have been monitored since 2002 [47, 48]. The activities of ^{241}Am range from 2.0 to 61.8 nBq/m^3 (Fig. 4). Approximately 50% of the ^{241}Am activity concentration was found in the PM$_{10}$ particle size fraction. Concentrations of ^{241}Am in surface air closely tracked those of $^{239+240}$Pu. Although the concentrations are quite low, strong springtime peaks in ^{241}Am activity concentrations are evident.

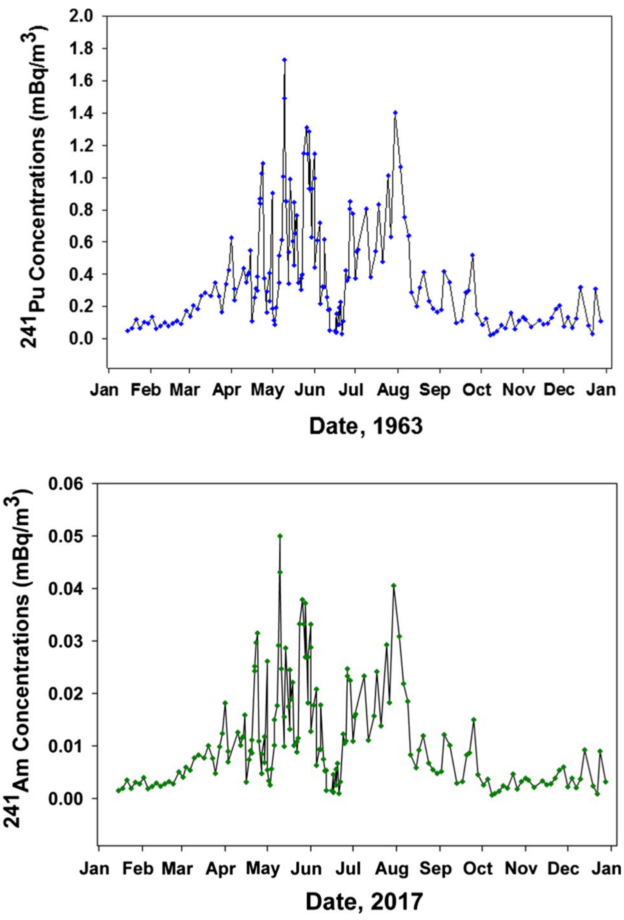

Fig. 3 The ^{241}Pu concentrations (from Ref. [44]) in surface air of Sodankyla, Finland during 1963 (top) and the estimated ^{241}Am concentrations in surface air of Sodankyla, Finland during 2017 (bottom)

The seasonality in surface-air concentrations are attributed to the seasonal variation in the elevation of the tropopause, the boundary between troposphere and the stratosphere. In the winter, the tropopause is at a lower elevation thereby enhancing transport of radioactive aerosols into the stratosphere and lowering surface-air concentrations. In the summer months, the tropopause is at a higher elevation and transport of radioactive aerosols into the stratosphere decreases thereby increasing surface-air concentrations. Data from the WIPP suggest another mechanism may be active. Using recent measurements of $^{239+240}$Pu concentrations obtained in the early 1980s, and the estimated mean residence times for plutonium in the troposphere and stratosphere, it seems more likely that the observed ^{241}Am concentrations are due to a combination of the resuspension of contaminated soil particles and local contamination. At the WIPP, the windier part of the year occurs from January to June with April being the windiest month.

The ^{241}Pu in surface air were detected at several locations in Europe following the Chernobyl accident. Surface air

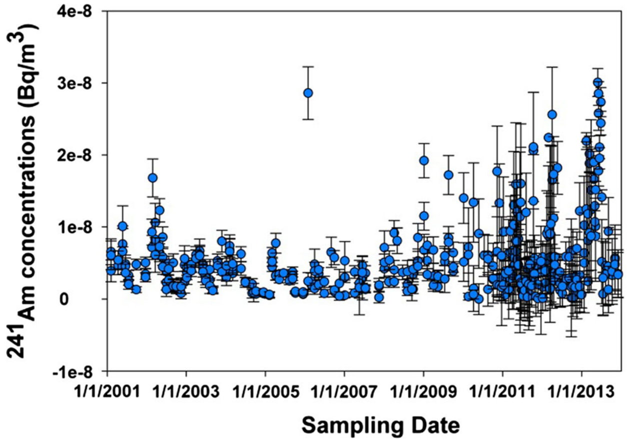

Fig. 4 The ^{241}Am concentrations in ambient air in the vicinity of WIPP site during 2001–2013

samples taken during May 1–15, 1986 from Belgrade showed ^{241}Pu levels in the range 0.2–7.8 mBq/m^3 [49]. In Finland, the activity concentrations in air were ~ 0.15–13.3 mBq/m^3, which is about 80 times higher than the corresponding value measured for $^{239+240}$Pu in April, 1986 [49]. Concentrations measured in Austria were in the range 0.011–0.089 mBq/m^3 for $^{239+240}$Pu, 0.0042–0.041 mBq/m^3 for ^{238}Pu and 0.0002–0.0061 mBq/m^3 for ^{241}Pu [50]. Average surface air concentration of ^{241}Am in Roskilde, Denmark were in the range from 5.2 to 11.0 µBq/m^3 during April–May, 1986 [51]. The ^{241}Pu concentrations in airborne dust samples from Gdynia (northern Poland) reached a maximum of 3.50 mBq/g during April–May time frame and then decreased gradually to 0.001 mBq/g by December, 1986 [52].

The ^{241}Pu/$^{239+240}$Pu activity ratio in atmospheric samples was 85 ± 20 in south Sweden, 74.6 in Austria, and 86 ± 8 in Denmark [13]. Russian researchers reported ^{241}Pu/$^{239+240}$Pu ratios in the range 67–82 at the height of the Chernobyl event [13]. Paatero and Jaakkola [9] reported a ^{241}Pu/$^{239+240}$Pu activity ratio of 94.8 in Finland compared to a ratio of 83 estimated from Chernobyl core inventory. Prior to the Chernobyl NPP accident, the ^{241}Pu/$^{239+240}$Pu activity ratios in airborne dust collected from Gdynia ranged from 33 and 39. In contrast, at Tsukuba, Japan, a ratio of 14.5 was reported and attributed mostly to Chinese nuclear tests in the 1980s [52].

There is report of the detection of airborne plutonium at a sampling station located 120 km from the Fukushima NPP [53]. The highest levels detected were 0.00028 mBq/m^3 of $^{239+240}$Pu and 0.025 mBq/m^3 of ^{241}Pu (decay corrected to March 15, 2011). The authors noted that the concentrations of plutonium, and predominantly anthropogenic ^{236}U, increased in the environment after the incident. However, levels detected were still very low and would have contributed negligibly to the total dose at the time of the incident. Furthermore, the ^{240}Pu/^{239}Pu ratios of 0.318 ± 0.10 (global fallout ratio of 1.7–0.25) and ^{241}Pu/^{239}Pu ratios of 0.117 ± 0.032 (global fallout ratio of 0.00255–0.00314) in five Pu-rich samples, analyzed by AMS, were clearly different from the global fallout ratios in Japan and correspond to the ratio observed in the litter sample near the Fukushima NPP. The discharge of actinides from Fukushima was expected to be low due to their low volatility. The detection of atmospheric $^{239+240}$Pu at a concentration of 44.5 ± 2.5 nBq/m^3 after the Fukushima accident, which is four orders of magnitude lower than after Chernobyl, further confirmed that Fukushima was a negligible source of plutonium, at least outside Japan [54].

Figure 5 shows predicated increase in ^{241}Am/$^{239+240}$Pu activity ratio from the global fallout, Chernobyl fallout and Fukushima fallout as a function of time. The ^{241}Pu/$^{239+240}$Pu activity ratios from the global fallout, Chernobyl fallout, and Fukushima fallout were used to estimate the in-growth of ^{241}Am as described previously [10]. The ^{241}Am in-growth from the global fallout was based on the ^{241}Pu/$^{239+240}$Pu ratio of 12.8 reported by Livingston et al. [24]. For the Chernobyl ratios, the value of 96 from Paatero and Jaakkola [9] was used, while for the Fukushima NPP, initial ratio 107.8 reported by Zheng et al. [10] was used. Currently, the ^{241}Pu/$^{239+240}$Pu activity ratio is about 0.83 for global fallout from nuclear tests, approximately 28 for the Chernobyl fallout and about 86 for Fukushima. As shown in Fig. 5, the ^{241}Am/$^{239+240}$Pu ratio for global fallout never reached 1.0 but is projected to reach a maximum of 0.36 by the year 2042. For Chernobyl fallout, a ratio of 1.0 occurred in 1994 and a peak of 2.83, almost an order of magnitude higher than global fallout, is expected to occur in the year 2058. The ratio reached 1.0 for the Fukushima fallout in 2018 and is expected to peak at 3.18, more than one order of magnitude higher than global fallout in 2081, followed by a gradual decrease. Owing to the much longer half-life, ^{241}Am is expected to remain in the environment for a long time, potentially contributing to internal radiation doses.

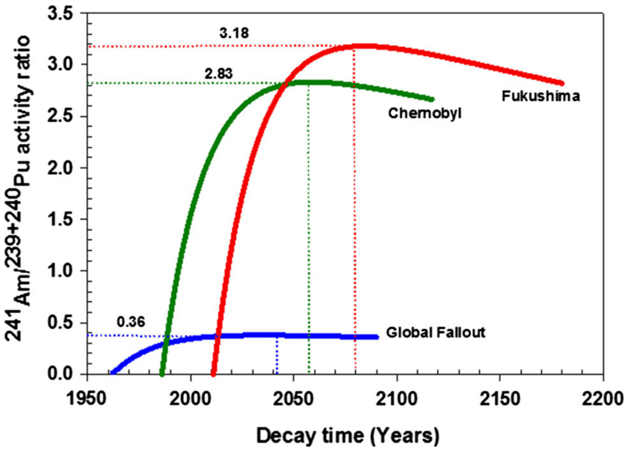

Fig. 5 The calculated activity ratios of ^{241}Am/$^{239+240}$Pu from the global fallout, the Chernobyl and the Fukushima plutonium with time

^{241}Pu in soils and sediments

The fallout-based concentrations of plutonium isotopes, including ^{241}Pu, in soil samples collected during the period 1969–1977 in Japan were reported by Yang et al. [55]. Concentrations of ^{241}Pu in this study were estimated using the ^{241}Pu/^{239}Pu atom ratio detected in fallout reference materials. Estimated concentrations of ^{241}Pu in these soils were in the range 0.06–21.24 mBq/g (decay corrected to January, 1964), whereas the measured concentrations of $^{239+240}$Pu were in the range 0.004–1.46 mBq/g. The plutonium deposition was higher in the northern prefectures of

Japan than in the southern prefectures. The spatial distribution of measured $^{239+240}$Pu and estimated ^{241}Pu concentrations were highly correlated with a ^{241}Pu/$^{239+240}$Pu activity ratio of 14.8 [55], which is slightly higher than the global fallout ratio of 12.1 reported for lake sediments. Plutonium in these soils is mainly derived from nuclear weapons testing, with a minor contribution from Chinese nuclear tests.

There have been several studies of the vertical distribution of plutonium in soil profiles, contaminated as a result of nuclear fallout and/or by accidental releases. Generally, these studies show higher concentrations in surface soils than in subsurface soils. Depth-profile studies of ^{241}Am, ^{238}Pu and $^{239+240}$Pu in soil at the Atolls of Mururoa and Fagataufa, where French nuclear weapons tests were conducted over the period 1977–1974, show that more than 95% of the plutonium and americium remained in the top 5-cm layer. The ^{241}Pu concentrations in alpine soils from France and Switzerland show depth profiles similar to those observed at other sites. Maximum ^{241}Pu concentrations were generally found in the top 10 cm of the soil profiles. A similar depth distribution profile has been reported for ^{241}Am and plutonium isotopes (^{238}Pu, $^{239+240}$Pu) at these sites [56]. However, in the Mercantour wetlands where soils have high organic matter content (69–70%), significant differences in the vertical distributions of plutonium and americium have been observed [57]. This difference is probably due to the different migration behavior of these radionuclides in fully-saturated wetlands or to the complexation of these radionuclides with organic matter in the soil. While americium is strongly retained in the organic-rich layers of the wetlands, plutonium seems to be slightly mobilized, likely due to the formation of colloids. Hence, a slight enrichment of americium, with respect to plutonium, was observed at depths with high organic contents. Another important parameter affecting the distribution of ^{241}Pu in soil is particle size distribution. Lee and Clark [58] observed that majority of both ^{241}Pu and ^{241}Am in soil at the McGuire Air Force Base and Boeing Michigan Aeronautical Research Center (BOMARC) accident site in New Jersey, USA, was associated with the small size fraction (75–147 µm; very fine sand to fine sand) [58]. In a sub-surface oxic soil near Los Alamos National Laboratory, New Mexico, USA, plutonium is relatively mobile and has been transported by soil particles in the 25–450 µm (medium silt to medium sand) size range [58]. In contrast, in wet anoxic soils near Sellafield, most of the plutonium was immobilized in the sediments although a small fraction remains mobile. These differences in mobility of plutonium is attributed to differences in the oxidation state, i.e., Pu(IV) versus Pu(V), as well as the humic content of the soils. Several authors have also reported exponentially decreasing relationships between plutonium concentration and soil depth [59]. The concentration profile of $^{239+240}$Pu in the sandy loam soil at the Trinity nuclear test site in New Mexico shows that about 50% of the plutonium initially residing in the top 0–5 cm layer of soil in 1953 had moved downward to 5–20 cm by 1973 [59]. The authors noted that the mobility of plutonium in soil profiles is greatest when plutonium is present as PuO_2, or when the soil is low in clay content, high in soluble organic material, and covered with vegetation. Most of the radioactivity was found on the < 100 µm particle size fraction, which corresponds to very fine sand and smaller. In the WIPP's arid environment in southeastern New Mexico, even though the surface soils are quite coarse, leaching and colloidal transport are not major factors affecting the vertical migration of plutonium. Lateral movement of soil by wind erosion is the dominant mechanism in the redistribution of the radionuclides in this ecosystem.

Several studies have reported deposition of plutonium from Chernobyl NPP accident, particularly in the 30-km exclusion zone surrounding the NPP [60, 61]. The total ground deposition of plutonium in Chernobyl soil was reported to be around 2540 Bq/m^2 for ^{241}Pu and 77.4 Bq/m^2 for $^{239+240}$Pu. About 99% of the released plutonium accumulated within the top 0–4 cm layers where there was significant humic acid content [60]. However, some of the plutonium remained in the surface soil layers because the radionuclides were released as hot particles that remain in the near-surface weathered zone. The 34.6 Bq/m^2 of ^{241}Am deposited in the soil profiles, as of 2000, is attributed to decay of ^{241}Pu. A 1998 study of soil profiles at Kapachi (7 km south of the Chernobyl NPP) showed total activities of 177 kBq/m^2 for ^{241}Pu, 17.1 kBq/m^2 for $^{239+240}$Pu, and 13.7 kBq/m^2 for ^{241}Am in the top 5 cm layer, indicative of very slow vertical movement of the actinides in that soil type [61]. The authors noted that ^{241}Am appeared to migrate faster than plutonium. A study of forest soils from the Chernobyl 30-km exclusion zone suggests that plutonium was retained very effectively by the soil organic layers. On the basis of the almost equal distribution of plutonium between organic and mineral layers, it was suggested that plutonium is redistributed in forest soil by migrating from the organic to the underlying mineral layers. The majority of plutonium in sandy and podzolic soils was confined to the surface horizons whereas it migrated to a depth of 10–15 cm in peat soils [62].

Outside of 30-km exclusion zone, the deposition of Chernobyl fallout plutonium has been much less. For example, northeast Poland received about 1.0 kBq/m^2 of ^{241}Pu and 25 Bq/m^2 of $^{239+240}$Pu [63, 64]. Southern Finland received up to 430 Bq/m^2 of ^{241}Pu [9] while Romania received between 156 and 385 Bq/m^2 of ^{241}Pu [63]. The ^{241}Pu level in coniferous forest soils taken from Poland was about 254 mBq/g with an average ^{241}Pu/$^{239+240}$Pu ratio of 86 ± 47, which is characteristic of Chernobyl fallout. No measurable Chernobyl fallout plutonium has been reported for soils from Western Europe.

Chernobyl plutonium exhibits higher abundances of ^{240}Pu and ^{241}Pu. Activity ratios of 0.30 ± 0.03 for ^{238}Pu/$^{239+240}$Pu and 115 ± 14 for ^{241}Pu/$^{239+240}$Pu in 1986 are representative to the Chernobyl fallout [64]. The ^{241}Am/$^{239+240}$Pu ratio of 1.6 ± 0.2 (in 2000) reported by Carbol et al. [60] is consistent with measurements in other environmental samples contaminated with Chernobyl fallout. In forest soils, ratios of ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu co-vary and range from 0.186 to 0.348 and 0.0029 to 0.0412, respectively. In hot particles collected in soil from the Ukraine, the ^{241}Pu/$^{239+240}$Pu activity ratio ranged from 54.7 to 73.1 with a mean of 60.2 [65] whereas the range in Polish soils was 86–87 [63, 64].

A few studies from Japan provided solid, mass-spectrometric, isotopic evidence for the detection of Fukushima-derived plutonium in the soil and litter samples in the 20–30 km around the Fukushima NPP [10]. These authors found only low soil concentrations of $^{239+240}$Pu in the Fukushima prefecture with values ranging from 0.019 ± 0.003 to 1.4 ± 0.023 mBq/g. These values are within the range of 0.15–4.31 mBq/g typically measured in Japanese soil samples and attributed to global fallout from nuclear weapons testing. In another study [66], soil samples collected outside of 20 km exclusion zone had $^{239+240}$Pu levels in the range 0.0067–0.347 Bq/kg. Furthermore, the ^{238}Pu/$^{239+240}$Pu activity ratio in these soil samples was close to 0.03 (range 0.028–0.034), indicative of global fallout. However, high activities of ^{241}Pu, ranging from 4.52 to 34.8 mBq/g, and ^{241}Pu/$^{239+240}$Pu activity ratios > 100 were detected in surface at the J-Village (about 20 km south of Fukushima NPP) and in litter samples collected from Namie Town and Iitate Village northwest of the Fukushima NPP. The release of ^{241}Pu is known to have occurred during the time of atmospheric nuclear weapons testing, but due to a half-life of 14.4 years, residual activity in Japanese soils is very low (^{241}Pu/$^{239+240}$Pu activity ratio of $\sim$ 1.2, ^{241}Pu decay corrected to March 15, 2011). Thus, the detection of high ^{241}Pu activity in these samples suggested an additional source of plutonium. The levels detected were extremely low and ^{241}Am produced from the decay of Fukushima-derived ^{241}Pu will reach only 3% of the already low levels of soil ^{241}Pu. At sites most contaminated with ^{241}Pu, this will result in a maximum ^{241}Am concentration of about 1 Bq/kg by the year 2081, which is about the same found in many soils in Japan, and worldwide, as a result of nuclear weapons testing in the 1950s and 1960s. However, based on a reported ^{241}Pu/$^{239+240}$Pu activity ratio of > 100 for Fukushima (compared to 83 ± 5 from the Chernobyl accident), the authors emphasized the need for a long-term dose assessment of ^{241}Pu and ^{241}Am, which has a high radiotoxicity. Recently, Ikeuchi [67] confirmed the widespread distribution of Fukushima-derived ^{241}Pu in surface soils from the Fukushima prefectures. Based on their findings, these authors also suggested the need for a long-term dose assessment of ^{241}Pu and ^{241}Am, which has a high radiotoxicity.

Perturbations of plutonium isotopic and atom ratios in various environmental samples were also significant after the Fukushima NPP accident. For example, the ^{241}Pu/^{239}Pu atom ratio (^{241}Pu decay corrected to March 15, 2011) of 0.122 ± 0.038, the ^{240}Pu/^{239}Pu atom ratio of 0.319 ± 0.047 in soil [10], and 0.381 ± 0.046 in vegetation samples [68] were much higher than the corresponding ratios of 0.180 ± 0.007 and 0.00194 ± 0.00014, respectively for the global fallout. Shinonaga et al. [53] found similarly high plutonium atom ratios (0.32 ± 0.10 for ^{240}Pu/^{239}Pu and 0.117 ± 0.032 for ^{241}Pu/^{239}Pu) in aerosol samples collected 120 km from the Fukushima NPP. The ^{238}Pu/$^{239+240}$Pu activity ratios (range 1.64–2.64) reported in black roadside dust, collected from the highly contaminated area of Fukushima prefectures (Minamisoma and Namie), were also higher than the global fallout value of $\sim$ 0.03.

No ^{241}Pu activity was detected in surface soils at Mito, Kamagaya, and Chiba, located 100–200 km from the Fukushima NPP. Additionally, the ^{240}Pu/^{239}Pu atom ratios in samples from these cities were similar to that of the global fallout ratio, indicating that the plutonium released from the Fukushima NPP was deposited within 20–30 km around the plants. The atom ratios of ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu found in the surface soil of J-Village were slightly lower than those in litter samples in Namie Town and Iitate Village in the NW direction of the Fukushima NPP. Using a simple two-term mixing model, Zheng et al. [10] estimated that the contribution of Fukushima-derived $^{239+240}$Pu in the J-Village soil was 87% and the remaining 13% of $^{239+240}$Pu was of a global fallout origin.

^{241}Pu in biomass

Several studies have been made on the occurrence of ^{241}Pu in lichens. Lichens have been identified as an important environmental medium in understanding the time deposition of plutonium. Fallout-based concentrations of ^{241}Pu were measured in several lichen samples taken between 1967 and 1976 in Finland [69, 70]. Lichen ^{241}Pu concentration ranged from 2.3 to 93 mBq/g (ref date: July 1 of sample year), some ten times higher than $^{239+240}$Pu. In another study by Hakanen et al. [71] lichen samples taken from same region over the period 1960–1977 showed ^{241}Pu concentrations in the range 22–123 mBq/g, which is consistent with the levels (22–118 mBq/g) detected in lichens sampled in Sweden during 1966–1975 period [72]. Higher depositions of ^{241}Pu were generally observed at the bottom of the lichen than at the top. A similar distribution pattern was reported for $^{239+240}$Pu, suggesting downward migration of deposited plutonium. This may be because lichens, which are the first to colonize bare rock, secrete carbonic and organic acids as products of metabolism. These metabolites collect at the rock surface (base of the lichen colony) where they start the process of rock weathering. Radionuclides that penetrate the colony and those transported downward by metabolites would accumulate at the low permeability rock surfaces. Activity ratios for ^{241}Pu/$^{239+240}$Pu in lichens were consistent with the typical global fallout ratio observed during 1960s and 1970s. Activity ratios for lichen samples collected during the period 1967–1976 ranged from 7.3 to 12.8. Samples collected during 1966–1971 period showed ratios ranging from 7.2 to 9.1. Ratios for samples collected over the period 1966–1975 ranged from 7.1 to 14. There was no difference in ^{241}Pu/$^{239+240}$Pu activity ratios at the top and bottom sections of these lichens. Studies also concluded that biological mean residence time of ^{241}Pu in lichens is on the order of 4–6 years. The distribution pattern of ^{241}Am in the lichen carpet was different from that of ^{241}Pu. No pronounced peak in activity was observed over the study period. The average ^{241}Am/$^{239+240}$Pu activity ratios measured were in the range from 0.12 to 0.18 [73].

The distribution of ^{241}Pu in lichens provide further insight into behavior of Chernobyl-derived plutonium. Lichen samples from Finland in 1986 had ^{241}Pu concentrations in the range 30–686 mBq/g with ^{241}Pu/$^{239+240}$Pu activity ratios of 37–120 (reference date July 1986), which are typical of the Chernobyl fallout ratio [69]. Since these samples were collected immediately following the Chernobyl accident, higher levels of ^{241}Pu were generally detected at the top part of the lichen than at the bottom. The downward migration of ^{241}Pu, as observed in the lichens contaminated due to global nuclear testing, was not seen in these samples. In another study, the lichen samples taken during 1987–1988, from the same regions, show ^{241}Pu levels in the range10–204 mBq/g and ^{241}Pu/$^{239+240}$Pu activity ratios between 37 and 115 (ref date: May 1986). A non-uniform distribution of ^{241}Pu was also reported in these lichens. The ^{241}Am levels in lichens after the Chernobyl accident were also determined. The highest concentration measured was 1.8 mBq/g [74]. The ^{241}Am/$^{239+240}$Pu activity ratio of 1.6 (in 2000) was characteristic for Chernobyl-derived plutonium in the environment.

There is no reported detection of Fukushima-derived plutonium in lichens. Since the Fukushima NPP accident seemingly did not release significant amounts of plutonium, no widespread distribution of plutonium in the environment samples is expected. However, positive detection of plutonium ($^{239+240}$Pu) has been reported in only two vegetation samples sampled at different hot spots in Japan, at the level of 0.49 and 0.17 mBq/g. The detection of Fukushima-derived plutonium in these samples indicates a very non-uniform distribution of plutonium, most probably in particulate form [68].

^{241}Pu in ice cores

Polar glaciers typically exhibit a detailed historical record of anthropogenic radionuclides, including fallout from nuclear weapons testing. Therefore, it is not surprising that ice cores have been used to reconstruct atmospheric transport and distribution of fallout from nuclear weapons testing. A few of the studies aimed at quantifying the plutonium recorded in Antarctic and Arctic ice cores have focused on ^{241}Pu distribution [26]. For the 1950s and 1960s, a good chronology exists from Arctic and Antarctic ice cores [26]. The ^{241}Pu in the glacier deposit of South Dome, Greenland showed two distinct fallout maxima for the periods 1950–1960 and 1963–1965 (Fig. 6a). The maximum activities measured in South Dome were 30 mBq/kg in 1955 and 27.8 mBq/kg in 1963. The first set of thermonuclear tests was conducted in the 1950s and included the "Ivy Mike" test at the Enewetak Atoll in 1952 and the "Bravo Castle" test at the Bikini Atoll in 1954. These tests were reflected in both Arctic and Antarctica ice cores with increased activity concentrations of ^{241}Pu from 1955 to 1959. A second peak from 1960 to 1963 reflects the post-moratorium weapon testing conducted by the former Soviet Union (USSR) at Novaya Zemlya (Russian Arctic) and Semipalatinsk (Kazakhstan) in the autumn of 1961. However, unlike the Arctic core in which the ^{241}Pu concentration peaked again in the early 1960s, the ^{241}Pu activity in the Antarctic core remained relatively low after 1958, with only a slight increase in the early 1960s. Although the tests conducted in the 1960s were large, there was minimal transport of fallout plutonium from the Russian Arctic to Antarctica, resulting in lower ^{241}Pu levels during the post-moratorium period. In contrast, the 1970s ice core from Dome C, Antarctica showed a large increase in ^{241}Pu activity, to about 72.2 mBq/kg in 1956, and a significantly lower value in the 1960s [26]. No significant activity was measured in the Dome C core prior to 1955. A similar depositional pattern has also been reported for ^{239}Pu at Dome C. The highest ^{239}Pu level, 9.4 mBq/kg, was observed in 1956, followed by a decreasing trend during the 1960s [75]. At the J-9 site, also in Antarctica, ^{241}Pu levels between 1955 and 1962 were too small to be measured by the LSC technique (Fig. 6b) The Partial Test Ban

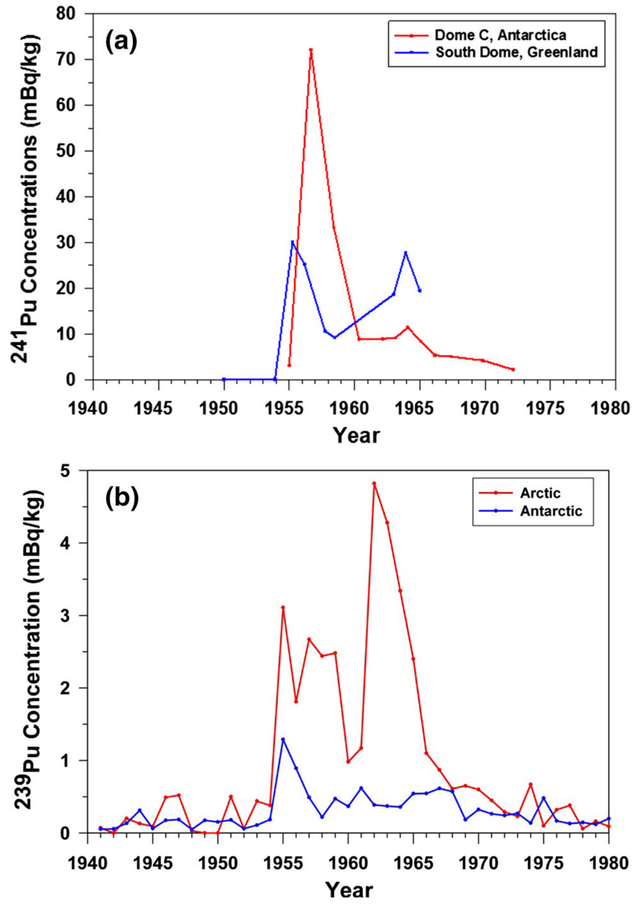

Fig. 6 The ^{241}Pu in the glacier deposit of South Dome, Greenland and Dome C, Antarctica during 1950–1973 (**a**) and annual average ^{239}Pu in Arctic and Antarctic during 1945–1980 (**b**). Date from Ref. [27] for ^{241}Pu and from Ref. [68] for ^{239}Pu

treaty of 1963 resulted in a decline in ^{241}Pu activity concentrations, both in the Arctic and Antarctic, but the concentrations remained above the baseline because of limited atmospheric testing by the French and Chinese through late 1970s.

Overall, ^{241}Pu levels in the Antarctic were lower than those observed in the Arctic, which is consistent with the distribution pattern of fallout plutonium from nuclear weapons testing. Global fallout from these tests shows the highest deposition in the mid-latitudes of the northern hemisphere and lowest in the southern hemisphere. A similar distribution profile has also been observed for ^{239}Pu and ^{241}Am in polar glaciers. For example, ice-core data from Greenland sites Belukha Glacier, Colle Gnifetti, and Colle du Dome, and from the Antarctic all showed increased ^{239}Pu activity concentration from 1955 to 1960 with the highest activity recorded between 1963 and 1965 [76].

Tables 4 and 5 summarize ^{241}Pu/$^{239+240}$Pu activity ratios and ^{241}Pu/^{239}Pu atom ratios originating from various sources. The early 1950s, fallout in the Antarctic had a ^{241}Pu/$^{239+240}$Pu ratio of 25–30 but this decreased to about 10 in the late 1950s [26]. In the Arctic cores, the ratio showed essentially the same trend. Sources other than atmospheric nuclear weapons testing are not a significant source of plutonium contamination in the Arctic and Antarctic and are therefore not discussed here.

^{241}Pu in the marine environment

The World's oceans are a major repository of plutonium released to the environment. The three major sources of plutonium in oceans are atmospheric nuclear weapons testing, the Chernobyl accident, and the discharge of effluents from nuclear reprocessing plants [77]. Both global as well as regional fallout contributed to the present levels of plutonium in seawater and sediment. The oceans contain an estimated 30 PBq of ^{241}Pu [77], attributed to weapons testing (decay corrected to Jan, 2000). In the marine environment, the majority of plutonium released is found in sediment layers. Marine sediments then become a source of plutonium to seawater. Sediment mixing by actions of benthic organisms and physical processes, such as waves and currents, further facilitate re-introduction of radionuclides to seawater. Plutonium exchanged from contaminated sediment to seawater is then available to be transported via ocean currents. A variety of biogeochemical processes such as changes in oxidation state, dissolution, hydrolysis, complexation, sorption, colloid formation, and microbial activity all influence the dispersion, mobility, and long-term behavior of plutonium in the marine environment [77]. The most common oxidation state of plutonium in marine waters are Pu(IV) and Pu(V). The Pu(IV) state is highly particle-reactive and is therefore easily scavenged by suspended matter and colloids, whereas Pu(V) is relatively soluble and can be transported in the dissolved phase over long distances. However, in anoxic marine waters, Pu(III) is the dominant oxidation state [78].

The first ocean-wide study of plutonium in seawater originated with the Pacific GEOSECS sampling program in the early 1970s [79]. At present, seawater concentrations of ^{241}Pu originating from nuclear weapons testing vary between 20 and 40 mBq/m^3 (ref. date 2000) whereas the concentration of ^{241}Am is less than 1–2 mBq/m^3 [80, 81]. The $^{239+240}$Pu activity concentration in surface seawater varies from a few mBq/m^3 in the open ocean to greater than 100 mBq/m^3 in semi-enclosed waters close to the source, e.g., in the Irish Sea [82]. However, elevated concentrations in the water column have been observed in some locations as a result of local or regional fallout. For example, surface seawater concentrations of $^{239+240}$Pu in the vicinity of the Enewetok Atoll were around 3000 mBq/

Table 4 The ^{241}Pu/$^{239+240}$Pu activity ratio in environmental samples

Sampling media	Date	^{241}Pu/$^{239+240}$Pu activity ratio	References
Fallout from weapons test, Northern Hemisphere	1963–1972	15–16	[43]
Soil, Japan	1961–1968	4.1–20.3	[100]
Greenland Glaciers	1955–1963	10–30	[26]
Antarctica, Glaciers	1953–1963	10.8–23.4	[26]
Air filter, Sodankyla, Finland	1963	18 (7.6–41)[a]	[44]
Sediments, Cape cod	1 Jan, 1970	5.6–10.8	[24]
Seaweed, Star fish	1 Jan, 1970	8.0–9.0	[24]
Sediment, Santa Barbara Basin	1973–1974	5.3–8.1	[17]
Sediment, Soledad Basin	1973	6.5–8.2	[17]
Alpine soil of France and Switzerland	Jun, 2009	0.8–2.2	[56]
Alpine soils of Coglio, in Ticino	2008	1.6 ± 0.4	[56]
Soil, Moss	1995	1.80–5.11	[15]
Soil, Semipalatinsk Nuclear Test Site	Oct, 1994	0.173 ± 0.005	[99]
Sediment core	1 Jan, 1970	8.4–22.0	[25]
Lichen, Finland	1 July, 1967	11.3–12.7	[69]
Lichen, Sweden	1961–1975	6–13	[101]
Lichen, NE Greenland	1980	4.2 ± 0.6	[101]
Soil, Svalbard	1980	4.3 ± 0.9	[101]
Reindeer, bone, Sweden	1968	8 ± 2	[101]
Weapons grade plutonium	1945–1974	0.75–7.5	[102]
Sediment, Thule	1968	3.3 ± 0.4	[101]
Sediment, Thule	2001	0.87 ± 0.12	[4]
BOMRAC missile test	2003	0.15–0.24	[58]
Chernobyl NPP accident			
Soil, Chernobyl	1986	115 ± 14	[60]
Air filter, Austria	1986	31.6–74.6	[50]
Air filter, Finland	1 July, 1986	98	[69]
Air filter, Soil	May 1, 1986	85	[63, 101]
Air filter, Denmark	May, 1986	96 ± 3	[101]
Lichen, Peat from Finland	May 1, 1986	94.8 (41–115)[a]	[9]
Lichen, Finland	1 July, 1986	37–120	[69]
Peat, Finland	1 July, 1986	4.1–60	[69]
Hot particle, Finland	1 July, 1986	96–107	[69]
Sellafield	1997	25	[5]
Ash fodder, Hungary	1998	68.57 ± 6.7	[98]
Discharge from nuclear facility			
La Hague discharge	1966–1996	71.8 (2.0–124.3)[a]	[103]
Sellafield discharge	1952–1996	25 (2.0–52)[a]	[103]
Ravenglass, saltmarsh	1997	11.5–14.8	[20]

Table 4 (continued)

Sampling media	Date	^{241}Pu/$^{239+240}$Pu activity ratio	References
Fukushima NPP accident			
ICP-Ms analysis of Pu isotopes in litter and surface soil.	March, 2011	107.8	[10]
Fukushima NPP accident: ORIGEN-ARP simulations of the average inventories in rectors unit 1 and unit 3	March, 2011	123.7	[40]
METI estimation on the amounts of Pu	March, 2011	187.5	[104]
Mean inventories of Pu isotopes in reactor units 1–3	March, 2011	118.1	[105]

[a] Values in parentheses are range

Table 5 The ^{241}Pu/^{239}Pu atom ratio in environmental samples

Sampling media	Date	^{241}Pu/^{239}Pu atom ratio	References
Fallout from weapons test, Northern Hemisphere	Jan, 1995	0.00264 ± 0.0002	[4, 106]
	Jan, 2000	0.00194 ± 0.00028	[107]
Fallout from weapons test, Southern Hemisphere	Jan, 2000	0.00197 ± 0.00093	[107]
Bravo Test, Bikini Atoll		0.0038 ± 0.0002	[107]
Sea water, Enewetak Atoll	Jan, 2015	0.00030–0.00117	[79]
Weapon-grade plutonium		0.005–0.007	[103]
Reactor grade plutonium		0.04–023	[103]
Chernobyl fallout	May,1986	0.123 ± 0.007	[108]
Chernobyl soil	Mar, 2009	0.0384 ± 0.0022	[109]
Sediment, Bikini Atoll	Mar, 2011	0.0021–0.0025	[94]
Waste from Sellafield	Jan, 1995	0.0116	[106]
Kyshtym accident, weapon grade plutonium	Jan, 1995	0.000231 ± 0.000006	[99]
Fukushima NPP accident	Mar, 2011	0.103–0.135	[10]
Atmospheric fallout in Japan, 1963–1979	Jan, 2000	0.00287 ± 0.00056	[10]
Soil in Tokyo, Japan	Jan, 2000	0.00171 ± 0.00010	[10]
Savannah River site, USA (aerosol particles, mineral fragments, vegetation debris, soil)	2003–2014	0.00106–0.03131	[110]
Pacific Proving Ground, close in Fallout		0.0017–0.0024	[66, 111]
NTS integrated fallout	1980	0.000445	[112]
Soil, Semipalatinsk Nuclear Test Site		0.000116 ± 0.000005	[99]

m^3 (measured in 1997) [80]. Localized elevated seawater concentrations of plutonium, especially near the bottom water, have also been observed at sites like Chernaya Bay in the Arctic sea, the Irish Sea near Sellafield, the nuclear weapon test site near Novaya Zemlya, and the Thule accident site [80–83]. Owing to their particle-reactive nature, plutonium isotopes and ^{241}Am are easily attached to particles and effectively scavenged from surface water to be released again at medium depths. Typical profiles of these radionuclides in the open ocean showed minimum values at the surface and maxima at medium water depths [82].

Since April 1986, Chernobyl has been a new and significant source of plutonium in Eastern European and the Baltic Sea. Following a 1986 peak in plutonium isotopes from Chernobyl, radionuclide concentrations decreased continuously [84]. The fallout from Chernobyl to the marine environment was reasonably small and localized, e.g., in the Baltic Sea and the Black Sea [84]. The total inventory of ^{241}Pu in the Baltic Sea in 1986 was estimated at 138 TBq, of which about 64% (88 TBq) is believed to have originated from the Chernobyl accident [84]. Approximately 99% of the inventory is assumed to have been rapidly transferred to the bottom sediments. Being the closest marine body to the Chernobyl site, the Black Sea has also received, and continues to receive, an additional input of Chernobyl-derived radionuclides through runoff from the Danube and Dnieper Rivers. The most significant radionuclides carried into the Black Sea from these sources were ^{137}Cs and ^{90}Sr. However, plutonium isotopes (^{238}Pu, $^{239+240}$Pu and ^{241}Pu) and ^{241}Am have also been detected in Black Sea sediments at concentrations ranging from 1.4 to 15 mBq/g for ^{241}Pu and 0.07 to 0.75 mBq/g for $^{239+240}$Pu [85, 86].

An initial survey of ^{241}Pu in marine sediments and biological samples was provided by Livingston et al. [24]. The ^{241}Pu concentrations in marine sediment samples were in the range 21–950 mBq/g, whereas the range in biological samples was 17–58 mBq/g. Analysis of the vertical migration of ^{241}Pu in marine sediments show that most of the fallout ^{241}Pu still remains in the first few centimeters of sediment cores [24]. The ^{241}Pu/$^{239+240}$Pu activity ratio in these sediments averaged 9.4 at the time of collection (12.8, if decay corrected to 1962), which agrees with the fallout ratio of 13–14 for the 1961–1962 USSR/USA tests and the 1967 Chinese tests. Koide et al. [17] reported representative ratios of 14–16 (12.4, if decay corrected to July 1, 1962) for the fresh fallout debris in sediments from coastal basins off California and Mexico.

Several studies have reported the distribution of ^{241}Pu in the Baltic Sea ecosystems [37, 87, 88]. The most significant source of plutonium in the Baltic Sea is the Chernobyl NPP accident. The second most important source is fallout from nuclear weapon tests. Surface waters of the southern Baltic, sampled during 1986–1988, contained 170 mBq/m^3 of ^{241}Pu in Gulf of Gdańsk samples and 90 mBq/m^3 in Gdańsk Deep samples with ^{241}Pu/$^{239+240}$Pu activity ratios of 74 and 89, respectively [88]. In a separate campaign, surface waters collected from four different regions of the Baltic Sea (Gulf of Gdańsk, Słupsk Bank, Bornholm Deep and Pomeranian Bay), during the period 1997–2001, show an increase in concentration of ^{241}Pu to about 2210–3350 mBq/m^3. The study showed that colloidal plutonium (> 1 kDa) is only a minor fraction of the total plutonium in Baltic waters. The largest percentage of plutonium (50–80%) in these waters was found in the dissolved fraction [89]. The highest total activity concentration of ^{241}Pu was found in Słupsk Bank and lowest in Pomeranian Bay. The ^{241}Pu/$^{239+240}$Pu activity ratios are higher than the global fallout ratios and reflect a mixture of Chernobyl and global fallout plutonium [89].

The vertical distribution of ^{241}Pu in sediments from these four regions of the Baltic Sea was reported by Struminska-Parulska [87]. A non-uniform depth distribution was reported for ^{241}Pu, with most ^{241}Pu occurring at shallower depths that did not exceed 10 cm. There was no evidence of the downward migration of ^{241}Pu. The sandy sediments from the Gulf of Gdansk appear to contain less plutonium (average ^{241}Pu 7.92 mBq/g; range 0.02–20.0 mBq/g) than the silty and organic-rich sediments from the Gdańsk Deep (average ^{241}Pu conc. 22.3 mBq/g; range 1.5–62 mBq/g). The ^{241}Pu/$^{239+240}$Pu activity ratio in the Gulf of Gdańsk was characteristic of Chernobyl fallout (44 ± 13) in the top 1-cm sediment layer, whereas the ratio (< 10) at the bottom layer (2–8 cm) was reflective of global fallout. In the Gdańsk deep, the ratio obtained was similar to that of global fallout.

In areas contaminated by the Thule accident, concentrations of $^{239+240}$Pu, ^{238}Pu, ^{241}Pu and ^{241}Am were one to three orders of magnitude higher than the fallout level. In sediments, the highest concentrations of ^{241}Pu and $^{239+240}$Pu were 5900 and 7600 mBq/g, respectively. The vertical distribution of Thule sediments showed the downward migration of radionuclides to 20 cm, somewhat deeper than reported by Smith et al. [90] where radionuclides reached down to 15 cm with maximum concentrations at a depth of 3–6 cm.

Another major source of ^{241}Pu in marine environment has been the discharge of waste from nuclear fuel reprocessing facilities such as La Hague, France and Sellafield, United Kingdom. The estimated release of total plutonium into the Irish Sea from Sellafield for the period 1951–1992 amounts to 0.12 PBq of ^{238}Pu, 0.61 PBq of $^{239+240}$Pu, and 21 PBq of ^{241}Pu with a ^{241}Pu/$^{239+240}$ ratio between 30 and 40 [5]. Most of the discharge occurred from the mid-1960s through the mid-1980s. The ^{241}Pu/$^{239+240}$ ratio peaked at around 50 in the mid-1970s and has remained between 30 and 40 ever since. Plutonium release from the La Hague into the north coast of France has been small, about 0.4% of that of Sellafield, with a total plutonium release of less than 0.005 PBq [6]. More than 95% of the plutonium released from Sellafield to the Irish Sea has been rapidly transported to the seabed in association with particulate matter. It has also been demonstrated that the spatial distribution of ^{241}Pu is controlled by the tidal currents and the clay contents in the sediments. Particle transport is considered to be the most important transport mechanism for the dispersion of plutonium to intertidal and offshore sediments in the Irish Sea [20].

The depth profile of ^{241}Pu and ^{241}Am in sediment cores from the Irish Sea indicates that both ^{241}Pu and ^{241}Am concentrations increase with depth, reaching a peak at about 19–20 cm (Fig. 7). The ^{241}Am/^{241}Pu, which varies from 0.06 to 0.11, reached a maximum near the surface and at the depth of the ^{241}Pu and ^{241}Am peaks. The ^{241}Am in the profile is due to in-growth from the decay of ^{241}Pu, but

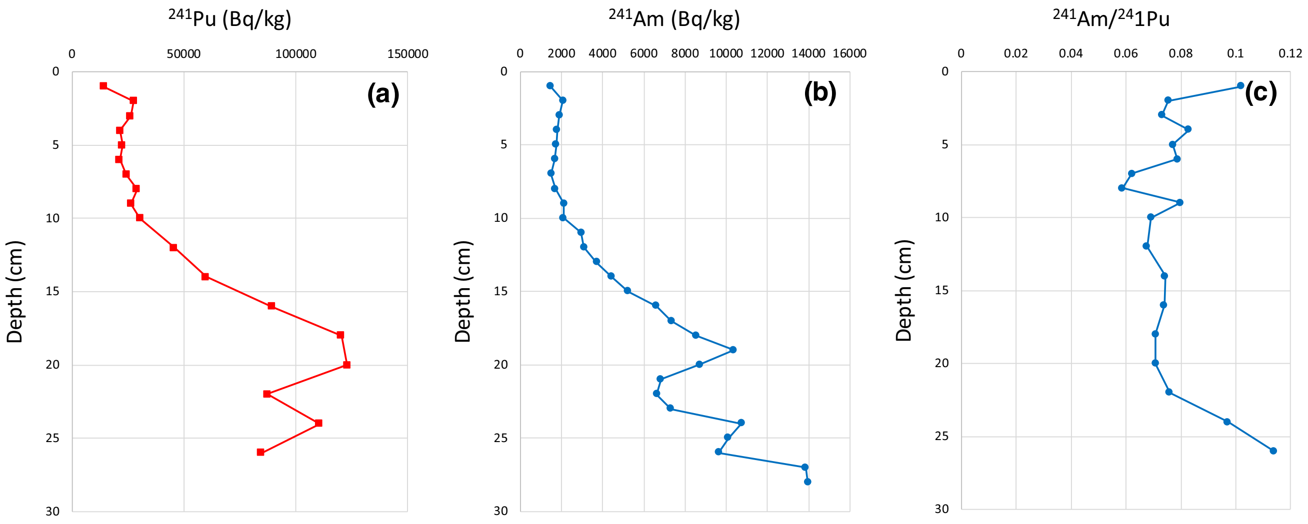

Fig. 7 Depth distribution profile in Irish Sea sediments: **a** distribution of ^{241}Pu, **b** distribution of ^{241}Am and **c** ^{241}Am/^{241}Pu. Data from Ref. [20]

the ratio does not necessarily reflect this. It is believed that mixing of sediments largely contributes to the changes in isotopic ratio of radionuclides. Studies have shown that the sediment mixing rate for the plutonium isotopes was approximately 90%.

The ^{241}Pu, like $^{239+240}$Pu, is accumulated by marine organisms and plants. Plutonium in fine sediments is slowly remobilized by benthic organisms through sorption onto their cell surfaces or by accumulation within cells. This plutonium is ultimately transported from the sediments up through the food chain. The redistribution of plutonium from sediments back to the water column has been observed in several investigations of contamination from global fallout at the Enewetak and Bikini Atolls [80].

Studies have shown that in the Baltic ecosystems approximately 80% of plutonium can be found in zoobenthos, 10% in phytobenthos and the rest in phytoplankton, zooplankton and fish [88]. In general, plutonium bio-accumulation in marine organisms is higher compared to that in terrestrial organisms. The target organs and tissues for ^{241}Pu bio-accumulation are mainly the digestive gland, gill, and skeleton [89]. However, sorption and retention by benthic organisms is quite variable. The average ^{241}Pu concentrations in Baltic plankton, benthos and fish varied in the range 0.006–9.88 mBq/g [88], whereas those in Baltic seabirds varied between 0.01 and 0.228 mBq/g. Struminska-Parulska [89] measured bio-accumulation factors of 0.01–3.90 for Baltic fish and 0.8–99 for seabirds, algae and plankton. The distributions of ^{241}Pu in the marine environment follow the order: marine birds $<$ fish $<$ zooplankton $<$ phytoplankton $<$ zoobenthos $<$ phytobenthos [87, 88]. Therefore, the uptake of ^{241}Pu into marine biota is dependent on the species. Sediment-dwelling species play a significant role in the remobilization process as they may redistribute plutonium deposited in the sediments by mixing and agitation. In general, levels of radionuclides in marine biota are related to the corresponding levels in seawater and sediment via accumulation through food chains. The distribution of ^{241}Pu in marine organisms generally follows the same trend as $^{239+240}$Pu.

The Fukushima NPP accident introduced contamination into the marine environment through the deposition of the radionuclides released to the atmosphere and also through the direct discharge of thousands of tons of radioactive fluids into the western North Pacific Ocean. However, the amount of plutonium isotopes released directly into the marine environment remains unknown. Several studies have been conducted to find Fukushima-derived plutonium in the marine environment [10, 91]. However, none of these studies found elevated levels of plutonium that could be attributed to the Fukushima NPP accident. Studies of plutonium in marine sediments, sampled 30 km from the Fukushima NPP, suggest negligible contributions of the Fukushima NPP accident to plutonium in marine sediments. Both activities and isotopic composition in these samples reflect the presence of global fallout and Pacific Proving Ground (PPG) close-in fallout rather than plutonium from the Fukushima NPP accident. Similar findings were reported by Bu et al. [92] who have continued their marine monitoring work in the search for Fukushima-derived plutonium in the Pacific. Sediment cores collected from the western North Pacific had a ^{241}Pu activity of 7.42 mBq/g, which is typical of the background levels of ^{241}Pu detected in this region. Furthermore, the ^{241}Pu/$^{239+240}$Pu activity ratio (2.5) is comparable to the background ratio reported before the accident and was significantly lower than derived ratios associated with

Fukushima. Several other studies had measured ^{241}Pu levels in marine sediments off the coast of Japan prior to the Fukushima NPP accident. The ^{241}Pu activity concentrations and ^{241}Pu/$^{239+240}$Pu activity ratios in these studies were in the range 3.3–8.4 and 1.1–1.9 mBq/g, respectively (ref. date: March 11, 2011) [34, 93] suggesting the presence of global fallout plutonium rather than Fukushima fallout. Furthermore, ^{241}Pu activities as high as 33.4 mBq/g (range 19.3–33.4 mBq/g), and ^{241}Pu/$^{239+240}$Pu activity ratios of 2.2–2.7 (ref. date: March 11, 2011) have been reported in sediments near the Bikini Atoll due to PPG close-in fallout [94]. However, contamination within the 30 km exclusion zone around the plant remains unknown, suggesting a need for further study of the few "hotspots" close to the Fukushima NPP. Additional research is required to fully understand the long-term effects of Fukushima-derived plutonium in the marine environment.

A few studies dedicated to actinides in environmental waters were published by Sakaguchi et al. [95] and Hain et al. [32]. These authors studied river water, paddy field water, and Pacific Ocean water for plutonium and uranium isotopes. Both the concentrations and isotopic composition of plutonium in sea water reflect the presence of global fallout and Pacific Proving Ground (PPG) close-in fallout rather than plutonium from the Fukushima NPP.

Summary and conclusion

Despite being the most abundant plutonium isotope released from the atmospheric nuclear tests and from the other sources, ^{241}Pu is still the most understudied isotope of plutonium. This review provides a summary of the sources, distribution, and behavior of shortest-lived, yet important, isotope of plutonium (^{241}Pu) found in the environment. The ^{241}Pu inventory in low-level nuclear waste and in environmental samples is of interest because ^{241}Pu is a precursor of other transuranium nuclides (^{241}Am and ^{237}Np) that have longer half-lives, greater environmental mobility, and greater toxicity. In addition, the global inventory of ^{241}Am activity produced from the decay of fallout ^{241}Pu will reach about 60% of ^{239}Pu in approximately 70 years. Vertical profiles of ^{241}Pu in soils and sediments exhibit distribution patterns similar to those of $^{239+240}$Pu and ^{241}Am. However, ^{241}Am is observed to migrate faster than plutonium isotopes in some soil and sediment profiles.

Liquid scintillation counting remains a powerful technique for determination of ^{241}Pu because of its simplicity, high selectivity, and acceptable sensitivity and is expected to remain a frequently used technique in ^{241}Pu analyses for a long time. Over the last decade, because of the increasing sensitivity of ICP-MS and the improvement in sample introduction systems, the detection of ^{241}Pu has been achieved. Techniques like AMS, TIMS, and RIMS are very sensitive, but expensive, techniques that can be utilized for ^{241}Pu determination. A major advantage of mass spectroscopy techniques is that ^{241}Pu isotope can be measured together with other isotopes of plutonium without any additional sample preparation step. However, the short half-life and correspondingly high specific activity of ^{241}Pu favor its determination radiometrically.

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