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$^{239 + 240}$Pu from "contaminant" to soil erosion tracer: Where do we stand?

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ABSTRACT

As soil erosion is the major threat to one of the most essential resources of humankind, methods to quantify soil redistribution are crucial for agro-environmental assessment as well as for optimisation of soil conservation practices. The use of fallout radionuclides (FRN) as soil redistribution tracers is, next to modelling, currently the most promising approach for assessing soil erosion. This review aims to evaluate the suitability of Plutonium (Pu) in general and the $^{239 + 240}$Pu isotopes in particular as soil redistribution tracers. It provides information on its origin, distribution and behaviour in soils and in the environment. Analytical methods, their recent advances as well as limitations, are discussed. To establish the current state of knowledge and to deepen our understanding, particular attention is given to the main existing achievements and findings based on using $^{239 + 240}$Pu as soil erosion tracer in agroecosystems. We further discuss similarities and differences to other more mature FRN techniques such as the ^{137}Cs based approach which has been until now the most widely used method.

We conclude that $^{239 + 240}$Pu has the potential to become the next generation of soil redistribution tracer compared to the more mature FRN techniques mostly due to (i) its long half-life guaranteeing its long-term availability in the environment, (ii) its analytical advantage in terms of measurement precision and measurement time and (iii) its greater homogeneity at reference sites due to its main origin from past atmospheric nuclear weapon tests. In identifying some key future research opportunities and needs, we hope to refine the efficiency of this promising agro-environmental tracer for effective soil redistribution studies under future climate and land use change.

1. Introduction

Anthropogenic radionuclides are present in the environment globally due to nuclear weapons testing, and more locally mainly due to nuclear power plant (NPP) accidents, releases from nuclear weapons fabrication and nuclear fuel reprocessing plants, and military plane crashes (Hu et al., 2010). While the negative consequences of this contamination are obvious, the ubiquity of the fallout radionuclides (FRN) distribution is one of the pre-requirements for their use as tracers in environmental studies, especially for soil redistribution (erosion and deposition) assessment. As such, the negative connotation most people have of the plutonium element due to its radiogenic threat and high physiological toxicity has been replaced for soil scientists and geomorphologists, since there is a crucial demand for reliable indicators of soil degradation and sediment transport.

Even though fertile soils are one of the most essential resources to sustain humankind in a world of climate variability and land use change, most of the world's soils are in fair, poor, or even very poor condition (FAO and ITPS, 2015). Even in developed countries soil erosion rates still exceed soil formation rates in many areas (Alewell et al., 2014). One of the main threats of soil erosion is soil nutrient depletion. With the imminent threat of soil nutrient shortages in the near future (e.g. peak phosphorous, peak potassium), the negative consequence of soil erosion will dramatically increase not only global prices but also the likelihood of shortages of feed and food worldwide (Koning et al., 2008; Cordell et al., 2009; Gilbert, 2009; Elser and Bennett, 2011) all of which will be connected to substantial sufferings of people due to famines, migration and conflicts.

In spite of this imminent need to assess soil redistribution, there is a striking lack of reliable and affordable methods to quantify soil erosion. In Europe, studies on soil redistribution by sheet/interrill erosion (see Box 1 for definition) recently experienced a revival through the publication of a collection of plot based studies (Cerdan et al., 2010), sediment yields (Vanmaercke et al., 2011), national model assessments

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Box 1

Soil erosion is, strictly speaking, the detachment and transport of soil particles from a source site and its transport to some depositional sink. As such, the processes of erosion and deposition (synonymous to sedimentation) are always coupled; both terms together might be described as soil redistribution.

Soil redistribution encompasses soil redistribution by water and wind as well as mass transfer of soil particles (e.g. landslides). Soil redistribution by water can further be differentiated into transport of single grains (so called sheet or interrill erosion), rill and gully erosion and to a certain extend even landsliding. FRN have mostly been used to trace sheet/interill erosion by water which is the main focus of this review. However, very few studies traced soil redistribution by wind with Pu isotopes, which will be briefly addressed in Section 6.1 for the sake of completeness.

(Panagos et al., 2014) and ultimately the modelling of the new pan-European soil erosion risk assessment (Panagos et al., 2015). The latter triggered controversial discussions within the soil science community regarding the applicability of models to assess soil erosion risks on large scale (Auerswald et al., 2015; Evans and Boardman, 2016b, 2016a; Fiener and Auerswald, 2016; Panagos et al., 2016a, 2016b). The question whether or not it is valid to upscale soil erosion models to a national, continental or even global scale (Borrelli et al., submitted) is still unresolved, since suitable validation data are missing. As such, soil erosion research is in urgent need of methods for reliable soil redistribution measurements. While upscaling from point measurements to large spatial scales (e.g. regional, national or even beyond) is always connected to a certain degree of uncertainty, this uncertainty is even more pronounced at unploughed sites such as grassland or semi-natural sites, where measurements to validate soil erosion models are very scarce (NB: for the definition of unploughed versus uncultivated soils see Box 2).

Fallout radionuclides (FRN) offer a unique alternative to model based approaches in assembling spatially distributed information on soil and sediment redistribution rates within the landscape over different timescales without the need of expensive long-term monitoring (Zapata, 2003; Walling, 2006, 2012; Matisoff and Whiting, 2011; Mabit et al., 2013, 2014; Alewell et al., 2014). Once deposited on the ground, FRN strongly bind to fine particles within the surface soil horizons and move across the landscape primarily through physical processes of soil redistribution (IAEA, 2014a). FRN methods are based on the comparison between the inventory (total radionuclide activity per unit area) at a given sampling site and that of an undisturbed reference site (e.g. located in a flat, well vegetated and unploughed area) with a decrease in the FRN inventory compared to reference indicating erosion, an increase indicating deposition of soil material. The FRN approach possesses important advantages over more conventional means of measuring soil redistribution (such as plots or field mapping), even though the time-averaged or lumped nature can also be considered as a limitation (Porto et al., 2014). Usually anthropogenic FRN based approaches relate to the period extending from the period of the main fallout in the 1950's and 1960's to the time of sampling.

Box 2

Please note that previous studies used the terms ploughed, cultivated and disturbed versus unploughed, uncultivated and undisturbed synonymously. Since the pair ploughed and unploughed are the most precise terms, as unploughed grasslands are indeed mostly cultivated and might be seriously disturbed, we will use the terms ploughed and unploughed throughout this review.

Besides plutonium, the main FRN used as soil redistribution tracers are the anthropogenic Caesium-137 (^{137}Cs) as well as the natural occurring excess Lead-210 (^{210}Pb$_{ex}$) and Berillium-7 (^{7}Be) (Mabit et al., 2008).

Berillium-7 is suitable for evaluating short-term soil redistribution, but cannot be used for evaluating mid- and long-term soil redistribution due to its short half-life of 53 days (Walling et al., 1999; Taylor et al., 2013).

^{210}Pb$_{ex}$ requires the application of self-absorption corrections for its determination using gamma-ray spectrometry. In addition, it suffers from high uncertainty of measurement results at low activity concentrations (Iurian et al., 2016) and from its non-applicability as a soil tracer under specific environmental conditions (Mabit et al., 2014).

As such, ^{137}Cs is currently by far the most common and mature technique used as soil redistribution tracer for assessing mid- and long-term soil redistribution. It is, however, also connected to some impedance. The advantages but also some possible pitfalls of the ^{137}Cs approach to assess soil redistribution rates have recently been discussed controversially (Parsons and Foster, 2011; Mabit et al., 2013). One of the main limitations related to ^{137}Cs is that only around 30% of the deposited ^{137}Cs global fallout is still present due to its radioactive decay (half-life of 30.2 years). In addition, the method is connected to potential errors in areas which have been significantly influenced by fallout from NPP accidents (e.g. Chernobyl, Fukushima) due to the extremely heterogeneous nature of this fallout deposition. As such, soil erosion research was struggling to find alternative isotopic tracers in recent years and the scientific community focused its attention on testing and validating the use of Pu isotopes to investigate soil redistribution processes (Schimmack et al., 2001; Tims et al., 2010a; Xu et al., 2013; Alewell et al., 2014; Lal et al., 2015; Meusburger et al., 2016).

Plutonium isotopes have already been used as tracer and dating tools of aquatic sediments and in water bodies (Ketterer et al., 2002, 2004a; Lind et al., 2006; Tims et al., 2010a, 2010b; Hancock et al., 2011, 2014; Lokas et al., 2013; Sanders et al., 2014, 2016; Lal et al., 2015). However, here our attention is focused on the crucial need of suitable tracers to assess soil redistribution especially for areas or regions where the use of ^{137}Cs or ^{210}Pb$_{ex}$ might be restricted (see discussion below). As such, the present review focuses on the use of Pu isotopes and especially $^{239+240}$Pu as soil redistribution tracer, with soil redistribution being understood as the movement of soils particles in the terrestrial environment.

Until recently, there have been relatively few attempts to exploit the full potential of Pu isotopes as soil redistribution tracers especially when compared to the much more common use of ^{137}Cs. Even though there were early studies on soil redistribution already 25 years ago (Joshi and Shukla, 1991), plutonium was marginally used until the beginning of this century when the potential of Pu as soil redistribution tracer was demonstrated at a southern German site (Schimmack et al., 2001, 2002). It took almost another decade for additional studies to follow (Everett et al., 2008; Tims et al., 2010a; Hoo et al., 2011; Lal et al., 2013; Xu et al., 2013, 2015; Alewell et al., 2014; Zollinger et al., 2015; Arata et al., 2016a; Meusburger et al., 2016; Zhang et al., 2016). One major obstacle was the analytical limitations connected to the measurements of plutonium at environmental level. Until recent years, it was restricted mostly to the traditional radiometric alpha-particle spectrometry technique and to some extent to the accelerator mass spectroscopy technique (AMS), whose availability was limited to a few facilities worldwide (Chamizo et al., 2006; Bisinger et al., 2010). However, the advances in mass spectrometric techniques, in particular with the development and improvement of the ICP-MS techniques, and the higher availability of those techniques in laboratories worldwide, opened possibilities of using Pu isotopes for a wide application in tracing soil redistribution and sediment transfer (Ketterer and Szechenyi, 2008; Cizdziel et al., 2008; Ketterer et al., 2002). An additional obstacle in the use of plutonium as soil redistribution tracer was the non-availability or the inadequacy of existing conversion models to convert $^{239+240}$Pu inventories to soil redistribution rates (Alewell et al., 2014; Arata et al., 2016a, 2016b). As both of these key limitations have been overcome in the last few years, the time is ripe for further testing and validation of $^{239+240}$Pu under various agro-environmental conditions to recognize this tracer as an efficient tool for soil redistribution assessment.

The aim of this review is to present and discuss the existing knowledge using plutonium isotopes as soil redistribution tracer in terrestrial agroecosystems. A description of the origins of the main Pu isotopes (238, 239, 240, and 241) is given first; followed by a presentation of their existence in the environment which opens up possibilities for their use as tracers (please note that ^{242}Pu and ^{244}Pu will not be discussed in this review due to their rare existence in the environment). In discussing possible measurement and analytical strategies using radiometric and mass spectrometric measurement techniques, we then aim to provide guidance to the readers not only for potential future applications but also for project planning and design. As we want to highlight the ultimate possibilities of this unique tracer approach, we also point out its limitations, which are mainly connected to the environmental behaviour of Pu. The latter will be partly addressed in comparison to the most widely used soil redistribution tracer ^{137}Cs. The core of this review will not only present and discuss the concept of Pu as soil redistribution tracer but it will as well summarize the major findings of existing case studies which have successfully applied this innovative approach. Our overarching aim is to promote innovative assessment of soil redistribution in order to encourage international research teams to make use of these techniques. Further research using those techniques would enable us to increase our understanding of soil erosion processes and their associated on-site and/or off-site agro-environmental impacts.

2. Origins of Pu in the environment and its main isotopic signatures

Plutonium (atomic number $Z = 94$) belongs to the actinide series, which encompasses 15 different metallic elements from atomic numbers 89 to 103 (actinium through lawrencium). It is one of the transuranium elements (also known as transuranic elements) with atomic numbers > 92 (uranium). All transuranium elements are unstable and decay radioactively into other elements.

Two of the plutonium isotopes (238 and 239; $T_{1/2} = 88.74$ y and 24,110 y, respectively) occur naturally in trace amounts within uranium minerals as a result of neutron capture (Pentreath, 1995). The anthropogenic creation of an element with a mass of 238 and 239 was achieved in the 1940's by firing deuterons at ^{238}U (Pentreath, 1995). Today, evidence of plutonium isotopes with masses between 232 and 246 have been documented, but from an environmental point of view only isotopes with a mass between 238 and 241 are of importance (Pentreath, 1995). With the exception of ^{241}Pu ($T_{1/2} = 14.35$ y, beta-decay), which decays by beta particle emission to Americium-241 (^{241}Am), other Pu mass isotopes such as ^{238}Pu, ^{239}Pu, and ^{240}Pu ($T_{1/2} = 6563$ y) decay by alpha particle emission (Hardy et al., 1973; Harley, 1980; Pentreath, 1995; Kelley et al., 1999).

The major fraction of plutonium deposited onto the earth's surface was introduced by the past atmospheric weapon's testing programs. Generally, the intensive testing of nuclear weapons in the atmosphere from 1954 to 1958 and then from 1961 to 1962 (including crashes of ^{238}Pu-powered US-satellites in the late 1950's and early 1960's, (Bossew et al., 2007)) made transuranium nuclides widely distributed (Pentreath, 1995). Results from airborne radionuclide measurements indicate that plutonium operations were of most concern between 1948 and 1961, in 1967, and then from 1970 until 1973 (Le et al., 2011). Based on fission yield estimates of atmospheric nuclear tests through 1987, the total global fallout inventory has increased only by approximately 5% since 1971 (Kelley et al., 1999). Radioactive waste reprocessing and disposal sites, deep sea disposal of packaged waste, lost weapons as well as open uranium mines might locally or regionally contribute significantly to Pu contamination of the environment (Pentreath, 1995).

Because of the similarities of the deposition pattern and accumulation rates between strontium (^{90}Sr, $Z = 38$, $T_{1/2} = 28.9$ years) and plutonium associated with the past bomb tests fallout, derived information from ^{90}Sr allows to estimate an average overall Pu deposit of around 52 mBq km^{-2} (Masarik, 2010). About two thirds of the Pu releases from weapon testing have been deposited in the oceans and other aquatic systems (Choppin, 2006; Harley, 1980). It is estimated that 1.6×10^{16} Bq of plutonium have been deposited in the oceans of the world from weapons testing (Perkins and Thomas, 1980). These releases include the residual fissionable nuclides in the weapon (e.g. ^{235}U, ^{239}Pu) and those which are produced during its explosion (so called fission products (e.g. ^{137}Cs, ^{90}Sr etc. (Choppin, 2006)). Radioactive particles (IAEA, 2011) containing plutonium oxide formed in the very high temperature weapon explosions were also released into the environment (e.g. as fused with soil particles or embedded into refractory cladding fragments) and may remain as refractory material into the environment for long periods of time (as such called source dependent species) (Choppin, 2006). When these refractory source specific species are exposed over time to specific environmental conditions (e.g. low or high redox potential, acid or alkaline conditions) they might eventually be modified in the environment to become source independent species whose behaviour is dependent on the conditions of the ecosystem in which they exist (e.g. oxic or anoxic, high or low pH (Choppin, 2006), see also Section 4.2).

The distribution of Pu associated to NPP accidents such as Chernobyl in 1986 or Fukushima in 2011 is confined mostly to the proximity of the NPP sites. In this, Pu differs fundamentally from ^{137}Cs, because Pu, in contrast to ^{137}Cs, is contained in the non-volatile fraction of nuclear fuel debris released from reactors during accidents (Ketterer and Szechenyi, 2008). Accordingly, deposition of plutonium occurred mostly in the particulate fraction and is relatively local or regional (Matisoff et al., 2011; Kirchner et al., 2012; Schwantes et al., 2012; Evrard et al., 2014; Steinhauser, 2014; Yamamoto et al., 2014). Starting on 26th April 1986, Chernobyl's emissions were transported first northwestwards over Poland, the Baltic States, Finland, Sweden and Norway and on April 27th to eastern-central Europe, southern Germany, Switzerland, Italy and Yugoslavia (Paatero et al., 2010). While all of the above countries experienced significant deposition of ^{137}Cs, the geographic distribution of Pu fallout is, in the case of the Chernobyl NPP accident, confined to specific areas such as the proximal portions of Russia, Ukraine, Belarus, Poland, the Baltic countries, and Scandinavia (Mietelski and Was, 1995; Eikenberg et al., 2001; Ketterer et al., 2004c; Matisoff et al., 2011). (Mietelski and Was, 1995) estimated maximum Pu surface activity for Chernobyl fallout in eastern Poland at 25 Bq m^{-2} (for all alpha-emitting Pu isotopes) with up to 30% of the total originating from global fallout. A study by Ketterer et al. (2004c) on ^{241}Pu activity showed 40–62% Chernobyl-derived deposition in southern Poland, and 58–96% Chernobyl-derived deposition in northeastern Poland. In Finland, despite its geographic proximity to Russia, the deposition of $^{239+240}$Pu due to the Chernobyl accident was much lower (< 0.25 Bq m^{-2}) (Paatero et al., 2010) than the $^{239+240}$Pu contribution from the weapons testing between the 60° and 70° northern latitudes (50 Bq m^{-2}) (Hardy et al., 1973).

After the Great East Japan Earthquake and resulting Tsunami on March 11, 2011, the Fukushima nuclear accident (FNA) led to hydrogen explosion, core meltdown, and the subsequent release of radioactivity both into the atmosphere and the Pacific Ocean (Hirose, 2012; Koo et al., 2014). Plutonium and other transuranium elements derived from the FNA were widely observed in the terrestrial environment (Lin et al.,

2015) and it was the most serious NPP accident in terms of radioactive pollution of the marine environment, with 80% of the radioactive material being deposited into the ocean (Lin et al., 2016). It has, however, to be noticed that the absolute increase in activity of these radionuclides in the marine environment after the FNA was rather small - only 0.1% of the inventory of these transuranium elements in the marine sediment compared to the activity before FNA (100 Bq m^{-2}) (Lin et al., 2015). Obviously, most of the refractory radionuclides (Sr, Pu and other transuranic elements) stayed in the reactor (Lin et al., 2016).

Pu isotopes originating from the Fukushima NPP accident determined through the presence of the relatively short-lived ^{241}Pu have been detected in top soil samples collected within the 20–30 km area around the Fukushima NPP. However, no additional Pu contribution was measured in the soil samples collected in Chiba, Kamagaya and Mito, Japanese cities located > 100 km south from the NPP site (Zheng et al., 2012). Recently, similar findings were reported by Cao et al. (2017) when investigating the ^{239}Pu and ^{240}Pu content of the sediments deposited in Lake Inba located in the Chiba prefecture around 200 km from the NPP site. The latter is confirmed by a model simulation of the atmospheric dispersion pattern of Pu, which pointed to a relatively small fraction of atmospheric deposition (Lin et al., 2015). Calculated $^{239+240}$Pu releases during FNA by METI (Ministry of Economy, Trade and Industry, Japan) and by Zheng et al. (2012) were 6.4×10^9 Bq and 1.0×10^9 to 2.4×10^9 Bq, respectively. As reported by Zheng et al. (2012), this estimated value is around 4 orders of magnitude lower than the Chernobyl $^{239+240}$Pu release (i.e. 8.7×10^{13} Bq).

Overall, the total amount of radioactivity released by FNA was about 10% of that released by the Chernobyl nuclear accident and < 1% of the global fallout from the atmospheric nuclear weapon's testings (Lin et al., 2016) (excluding the noble gases ^{85}Kr and ^{133}Xe, which were traveling as far as Australia (Orr et al., 2013)).

To summarize, the two major Pu isotopes in the environment are ^{239}Pu with a half-life of 24,110 years and ^{240}Pu with a half-life of 6,561 years. Both are alpha-emitting actinides which originate mainly from past nuclear weapon tests, while contributions by other more localized sources, e.g. NPP accidents, nuclear weapons manufacturing and nuclear fuel reprocessing, added locally Pu content in the environment (Ketterer and Szechenyi, 2008).

2.1. *The use of isotope ratios to differentiate between different contamination sources*

To differentiate between different sources of Pu contamination, Pu isotope ratios can be used (Mietelski and Was, 1995; Mitchell et al., 1997; Chiappini et al., 1999; Ketterer et al., 2004c; Lind et al., 2006; Evrard et al., 2014). The ^{240}Pu/^{239}Pu atomic ratio can provide an important fingerprint for source identification of Pu in environmental samples because this ratio significantly varies with the source and production process (Kelley et al., 1999). The ^{240}Pu/^{239}Pu atomic ratio of northern hemisphere mid-latitude weapons testing fallout is typically in the range of 0.18 with values reported in the literature varying from 0.14 to 0.24 (Mitchell et al., 1997; Kelley et al., 1999); in contrast, several studies of ^{240}Pu/^{239}Pu atomic ratio of Chernobyl fallout indicate values of 0.37 to 0.41 (Muramatsu et al., 2000; Boulyga and Becker, 2002; Ketterer et al., 2004c). For FNA ^{240}Pu/^{239}Pu ratios were reported as 0.395 and 0.447 and for ^{241}Pu/^{239}Pu as 0.174 and 0.196 by Kirchner et al. (2012)) and Schwantes et al. (2012), respectively. For the FNA reactor 1–3 (Nishihara et al., 2012) calculated ^{240}Pu/^{239}Pu ratios of 0.344, 0.320 and 0.356 and for ^{241}Pu/^{239}Pu of 0.192, 0.192 and 0.183. To date, only a limited number of studies have measured ^{241}Pu, because ^{241}Pu is not measurable by alpha-spectrometry and its analysis by liquid scintillation counting has a relatively poor detection limit (Rosner et al., 1992). As summarized by Lokas et al. (2013) using evidence from the existing literature, the activity ratio of ^{238}Pu/$^{239+240}$Pu can also be used as an indicator for distinguishing the Pu source: a ratio around 0.025 is expected for the global fallout, 0.50 for Chernobyl (ratio corrected to 2012) with other anthropogenic sources exhibiting average values ranging from 0.18 to 0.49.

The ^{137}Cs/$^{239+240}$Pu ratios can also be used to identify and to apportion ^{137}Cs input originating from Chernobyl from the global fallout. The ^{137}Cs/$^{239+240}$Pu ratios in soils and sediments from the northern hemisphere due to the global fallout from atmospheric weapons testing have average ratio values of 36 (Turner et al., 2003). In contrast, reference top soils (0–3 cm) of two Alpine sites with predominantly Chernobyl input of ^{137}Cs had average ^{137}Cs/$^{239+240}$Pu ratios of 136 (range 99–249) and 413 (range 90–898) for the Northern Alpine and the Southern Alpine site, respectively (Alewell et al., 2014). In areas substantially affected by the Chernobyl fallout (e.g. > 20% of the total ^{137}Cs fallout), this additional key information provided by plutonium isotopes determination is an asset for the application of the ^{137}Cs inventory conversions model to deduce more reliable yearly soil redistribution rates.

The ^{137}Cs and $^{239+240}$Pu contribution from Chernobyl versus global fallout in environmental samples can also be attributed through the use of ^{134}Cs ($T_{1/2} = 2.06$ y) and ^{238}Pu isotopes, based on the known isotopic ratios in global and Chernobyl fallout (Schimmack et al., 2001; Bossew et al., 2007).

Releases from other sources can also be characterized using Pu isotope ratios. Mitchell et al. (1997)) as well as Chamizo et al. (2006) applied Pu isotope ratios (^{240}Pu/^{239}Pu as well as ^{238}Pu/^{239}Pu and ^{241}Pu/^{239}Pu) to identify the main and significant proportions of weapons grade plutonium at Palomares (Spain) and Thule (Greenland) respectively, following the 1966 mid-air collision of two US aircrafts in 8500 m above the Mediterranean village Palomares. Originating mainly from fuel weapon core fragments and radioactive particles, the ^{240}Pu/^{239}Pu atomic ratio from the samples of the Palomares soils had a characteristic ratio of 0.0657 (Chamizo et al., 2006). In contrast, both global weapons fallout and spent fuel from civil reactors have higher ^{240}Pu/^{239}Pu ratios between 0.18 and 0.52 (Oughton et al., 2000).

To establish typical ^{240}Pu/^{239}Pu ratios for specific production sites is more difficult since Pu isotope ratios are known to vary with reactor type, nuclear fuel burn-up time, neutron flux, and energy (Oughton et al., 2000). At the "Mayak" Production Association (Mayak PA) which was established in the late 1940's to produce plutonium for the Soviet nuclear weapons program, ^{240}Pu/^{239}Pu ratios in the surrounding environment were found to be increasing from 1949 to present days (Oughton et al., 2000). Generally weapons-grade plutonium is characterized by a low content of ^{240}Pu, with ^{240}Pu/^{239}Pu ratios below 0.07 because it is produced by leaving the nuclear fuel in the reactor for only a short time to minimize neutron activation of ^{239}Pu (Oughton et al., 2000). Other studies used isotopic ratios to distinguish global fallout plutonium from weapons tests, e.g. at the Nevada Test Site in the USA (Turner et al., 2003) or in Australia (Tims et al., 2013, 2016), since the fallout composition also depends on the nuclear detonation, weapon type and yield (Oughton et al., 2000).

3. Analytical methodologies for the determination of Pu isotopes

Two types of techniques are available for the determination of Pu isotopes in environmental samples: the traditional radiometric techniques based on decay counting, such as alpha-particle spectrometry and liquid scintillation counting (LSC), and the mass spectrometric techniques based on atom counting, such as inductively coupled plasma mass spectrometry (ICP-MS) and accelerator mass spectrometry (AMS).

3.1. *Radiometric techniques*

3.1.1. *Alpha-particle spectrometry*

The ^{238}Pu and $^{239+240}$Pu isotopes are frequently measured in environmental samples using alpha-particle spectrometry (Aggarwal, 2016; Vajda and Kim, 2010, 2011). While the ^{238}Pu isotope can be measured easily using alpha-particle spectrometry, the ^{239}Pu and ^{240}Pu isotopes cannot be resolved using this analytical method due to similar energies for their alpha particles (5.16 MeV for ^{239}Pu and 5.17 MeV for ^{240}Pu). Therefore, the sum of their activities (i.e. $^{239+240}$Pu) is usually reported in environmental radioactivity monitoring programs. For counting times in the range of days/weeks, detection limits as low as 0.1 mBq can be achieved in routine analysis for those isotopes. The relatively low cost of the instrumentation, the high sensitivity due to the low background, the high selectivity for alpha particles against other types of radiation, the increased potential for higher throughput routine analyses using multi-chamber spectrometers, and the uniqueness of the technique for the measurement of the relatively short-lived ^{238}Pu ($T_{1/2}$ = 87.7 y), make alpha-particle spectrometry attractive for the routine investigation of Pu isotopes in environmental samples.

3.1.2. Liquid scintillation counting (LSC)

The pure beta-emitting ^{241}Pu isotope ($E_{\beta max}$ = 20.8 keV, 100% yield) can in addition be easily measured by LSC using the remaining Pu alpha source following its analysis by alpha-particle spectrometry for the determination of the Pu alpha-emitting radionuclides present in the sample (Moreno et al., 1998). If Pu was electrodeposited on a stainless steel disc for its counting by alpha-particle spectrometry, the disc is leached with concentrated nitric acid and neodymium fluoride co-precipitation is carried out to scavenge Pu in the lower oxidation states. The precipitate is then recovered in a H_3BO_3/HNO_3 based dissolver and mixed with the scintillation cocktail (Kwong et al., 2004). Alternatively, if Pu was deposited on a membrane filter of small pore size (0.1–0.2 µm) using micro-co-precipitation with neodymium fluoride, the micro-co-precipitate can be dissolved in diluted nitric acid directly in the LSC vial and the scintillation cocktail added to the vial. The vial is then shaken prior measurement. Care has to be taken to ensure that, following shaking, the membrane filter is deposited at the bottom of the vial and not on the wall not to interfere with the measurement process. A detection limit in the range of 10 mBq has been reported for the measurement of ^{241}Pu using LSC (Kwong et al., 2004).

3.2. Mass spectrometric techniques

The advances in mass spectrometric techniques, in particular with the development and improvement of the ICP-MS techniques, make those techniques relevant alternatives for the analysis of ^{239}Pu and ^{240}Pu isotopes and for determining their isotope ratio (Ketterer et al., 2002; Kim et al., 2007; Ketterer and Szechenyi, 2008; Cizdziel et al., 2008).

3.2.1. Inductively coupled plasma mass spectrometry (ICP-MS)

A typical quadrupole ICP-MS (Q-ICP-MS) has a detection limit in the range of 10–100 fg mL^{-1}, which corresponds to a detection limit in the range of 0.1–1 mBq for ^{239}Pu and ^{240}Pu. The main advantage of the mass spectrometric technique in this case is that the ^{239}Pu and ^{240}Pu are individually measured and that the $^{239}Pu/^{240}Pu$ isotope ratio can thus also be established. On the other hand, the short-lived ^{238}Pu cannot be determined by mass spectrometry, which means that radiometric and mass spectrometric techniques are complementing and not replacing each other. The sector field ICP-MS (SF-ICP-MS) and multi-collector ICP-MS (MC-ICP-MS) have about 1 to 2 orders of magnitude lower detection limits than Q-ICP-MS, i.e. 0.01–0.1 mBq, which makes them more suitable than alpha-particle spectrometry for those nuclides that have half-lives longer than about 100 years (if there are no isobaric interferences). The overall sensitivity is, however, strongly influenced by the sample preparation and radiochemical separation performed to prevent major isobaric and molecular interferences. The major interference in ^{239}Pu determination using mass spectrometric techniques is the ^{238}U tailing and the formation of UH^+ in the plasma, leading in general to comparable detection limits using alpha-particle spectrometry and SF-ICP-MS for $^{239+240}$Pu. Whereas ICP-MS techniques allow considerably faster measurement times than alpha-particle spectrometry, costs of those equipment are higher than the traditional alpha-particle spectrometry equipment, i.e. 3 to 4 times the cost of an alpha-particle spectrometry equipment for a quadrupole ICP-MS, 8 to 10 times the cost of an alpha-particle spectrometry equipment for a sector field ICP-MS, and 12 to 15 times the cost of an alpha-particle spectrometry equipment for a MC-ICP-MS in 2017, to give orders of magnitude for budgeting purposes.

3.2.2. Advanced mass spectrometry techniques

Besides ICP-MS, there are other highly advanced mass spectrometric techniques that are more sensitive for the detection of Pu isotopes, such as thermal ionization mass spectrometry (TIMS), resonance ionization mass spectrometry (RIMS) and accelerator mass spectrometry (AMS). TIMS has a higher sensitivity for ^{239}Pu and ^{240}Pu than ICP-MS, and interferences due to U traces are less significant. It requires, however, a time-consuming sample preparation to produce a thin filament source. RIMS, an analytical technique using tuned laser beams for the selective excitation of the Pu atoms, is highly sensitive for the measurement of ^{239}Pu as it can detect ^{239}Pu activities as low as 10^7 atoms per sample, which is in the range of 0.01 mBq. AMS has the highest sensitivity for the ^{239}Pu isotope due to the absence of isobaric and molecular interferences (Chamizo et al., 2006; Bisinger et al., 2010). Limits of detection can go down to 10^6 atoms per sample that refers to approx. 0.001 mBq. However, the application of these advanced mass spectrometry techniques is limited by the low availability and high cost of those very specific facilities. RIMS is available at only a few laboratories worldwide whereas AMS facilities are available only at national or regional levels, and scientists have therefore to apply for beam time for access to those facilities.

3.3. Sample preparation prior measurement

In order to get accurate and reliable results at environmental soil and sediment levels, chemical separation and pre-concentration steps are a prerequisite for both radiometric and mass spectrometric techniques (Rollin et al., 2009; Ayranov et al., 2005).

The complete separation of Pu from the sample matrix is required in alpha-particle spectrometry to obtain ‘infinitely’ thin alpha source of Pu for its measurement. Because of the short range of alpha radiation in matter, the source thickness should not exceed a few micrometers, otherwise the alpha spectrum becomes degraded and the resolution of the Pu peaks in the alpha spectrum is altered. A radiochemical procedure is applied to the sample to separate Pu from the major and minor components of the sample matrix (IAEA, 2009, 2014b). The main spectrometric interferences in Pu analysis by alpha-particle spectrometry are ^{241}Am overlapping with ^{238}Pu, and ^{210}Po and ^{228}Th partially overlapping with the ^{238}Pu peak. Occasionally other interferences, e.g. ^{224}Ra, ^{229}Th, ^{231}Pa, ^{232}U and ^{243}Am can be identified in the Pu spectra. Traces of U, Th and Np can contaminate the Pu source if the radiochemical separation is not effective.

For mass spectrometric techniques, the radiochemical separation aims at increasing the Pu concentration in solution and at eliminating or at least limiting the potential isobaric and molecular interferences during the measurement process. The radiochemical separation of Pu for ICP-MS and alpha-particle spectrometric analysis is usually performed in a similar way. The requirements for ICP-MS analysis are, however, somewhat different to the ones of alpha-particle spectrometry, namely, the strict requirement of low concentration of U and salt content in the purified solution due to the strong interference from $^{238}U^1H^+$ with ^{239}Pu at the mass on charge ratio (m/z) 239, and problems of clogging of the sample introduction system and corrosion/accumulation of salt in the interface parts of the ICP-MS.

For soil and sediment samples, pre-treatment includes the drying, ashing and digestion of the sample using acid leaching, total digestion, microwave oven digestion or fusion (Dirican and Sahin, 2016; Jurecic et al., 2014). Total digestion and acid leaching can be easily carried out on hot plates and are therefore commonly used in laboratories for the digestion of up to 10 g of soil and sediment samples. Although the use of microwave oven digestion and fusion systems for Pu digestion in soil and sediment samples has increased lately due to the rapidity and simplicity of the methods, their applications are limited to a few grams of sample, which, in some cases, may be a limitation in terms of achievable detection limits. If refractory particles potentially embedding Pu inside the sample may exist, a full digestion method is recommended to ensure a complete dissolution of all Pu components. After preparation of the sample solution from large amounts of sample, co-precipitation procedures can be used as an initial step of purification. Selective separation of Pu using precipitation, co-precipitation, ion exchange, solvent extraction, or extraction chromatographic techniques are then used for the radiochemical separation of the Pu isotopes from the sample matrix components (Varga et al., 2007; Vajda and Kim, 2010). The affinity and distribution coefficient to resin or solvent depend on the Pu oxidation state. It is well known that Pu can exist in several oxidation states from + 3 to + 6 in the sample (see Section 4), and that Pu(IV) will disproportionate into Pu(III) and Pu(VI) under acidic conditions. Therefore, the adjustment of the Pu oxidation state is a necessary step for the quantitative radiochemical separation of Pu using an ion exchange or extraction chromatography column with liquid-liquid extraction (IAEA, 2009; Xu et al., 2014b). Anion exchange resins are often used for the Pu radiochemical separation in ICP-MS analysis (Qiao et al., 2011).

3.4. Support to high-quality Pu measurement in environmental samples

To support high-quality measurement results for the determination of radionuclides in environmental and food samples worldwide, the International Atomic Energy Agency (IAEA) is organizing on an annual basis an ALMERA proficiency test (PT) exercise and a worldwide PT exercise open to all laboratories, in which the determination of the Pu isotopes in soil and sediment samples is regularly included. As a recent example, the determination of $^{239+240}$Pu in a soil sample was requested to the participating laboratories as part of the 2015 IAEA PT exercises. Among laboratories reporting measurement results for the determination of $^{239+240}$Pu in soil, approx. 75% of the laboratories member of the ALMERA network and approx. 55% of the worldwide laboratories obtained accepted values for their measurement results (Osvath et al., 2016; Pitois et al., 2016). Several IAEA soil and sediment reference materials with certified massic activities of ^{238}Pu and $^{239+240}$Pu are also available to laboratories as quality control materials for their Pu analyses. The moss soil IAEA-447, the Fangataufa sediment IAEA-384 and the Irish Sea sediment IAEA-385 can be ordered at the IAEA website.[1]

3.5. Summary

To recapitulate, both radiometric and mass spectrometric measurements require a thorough sample preparation consisting of the digestion of the soil sample and the radiochemical separation of the element plutonium from the rest of the soil matrix. This step, which can be carried out in the laboratory for several samples in parallel, requests at least a few days of laboratory work depending on the digestion method used. Following the sample preparation, either radiometric or mass spectrometric detection can be used for the measurement process. Radiometric measurements using alpha-particle spectrometry and LSC are simple and cost-effective measurement techniques for the determination of ^{238}Pu, $^{239+240}$Pu and ^{241}Pu, but not for ^{239}Pu and ^{240}Pu individually. They require, however, long counting times for accurate quantification of Pu at environmental levels, i.e. usually several days. However, several samples might be counted simultaneously in separate alpha spectrometry multi chambers. On the contrary, mass spectrometric techniques provide fast measurements, are highly sensitive (sensitivity dependent on the type of instrument) and capable of providing the individual concentrations of ^{239}Pu and ^{240}Pu (but not of ^{238}Pu). However, the availability/cost of some of those techniques may sometimes be a clear limiting factor. The selection of the proper measurement technique is dependent on the intended purpose of the analysis (Michel et al., 2007; Xu et al., 2014b). If the comprehensive characterization of Pu isotopes in the sample is requested, the combination of both radiometric and mass spectrometric techniques may be necessary (Hou and Roos, 2008; Qiao et al., 2009).

4. Environmental behaviour of Pu

4.1. Plutonium from atmosphere to pedosphere to biosphere

Plutonium has been identified as one of the most toxic elements and is known to cause lung, liver and bone cancer as well as having detrimental effects on the immune system (ATSDR, 2010). Depending on the specific isotopes, their half-lives vary from 14 years (^{241}Pu) to 8×10^7 years (^{244}Pu) with the two major Pu isotopes ^{239}Pu and ^{240}Pu having half-lives of 24,110 and 6,561 years, respectively. As such, plutonium contamination does not decay notably within time horizons significant for the humankind and its transport and mobilization are crucial for ecological or health assessment as well as for its use as an environmental tracer.

As the last weapons testing took place several decades ago, plutonium concentrations in the air are generally low today. Baseline ^{239}Pu air concentrations range from 5.9×10^{-5} to 1.4×10^{-4} mBq per cubic meter (ATSDR, 2010). The low content in the troposphere is due to relatively rapid dry and wet deposition (so called atmospheric fallout) which efficiently removes radionuclides within a period of a few weeks to months (Alvarado et al., 2014). In contrast, radionuclides including plutonium are present in the stratosphere at higher levels than in the troposphere and have mean residence times of 2.5–5 years (Alvarado et al., 2014).

Levels of $^{239+240}$Pu in the first 30 cm of the earth's surface measured at around 60 worldwide locations have been re-calculated by Taylor (2001) from the work originally published by Hardy et al. (1973). On average, Pu soil content originating from weapons fallout is a factor of five greater in the northern hemisphere (7.1 ± 3.1 Bq kg^{-1}; n = 33) than in the southern hemisphere (1.4 ± 0.9 Bq kg^{-1}; n = 30) as most of the nuclear tests took place in the northern latitudes (Taylor, 2001).

Plutonium inventories as reported from soil redistribution studies performed around the world point to a surprisingly uniform background contamination between 55 and 90 Bq m^{-2} (Table 1) with the exception of one study from Australia reporting 18 Bq m^{-2} (only one reference site considered which was affected by fire (Hoo et al., 2011)). Average plutonium concentrations in surface soil from global fallout range from 0.37 to 3.7 Bq kg^{-1} of soil (ATSDR, 2010). However, local or regional differences might be due to differing deposition regime, caused by factors like altitude or vegetation cover. Present day background $^{239+240}$Pu concentrations of top soil layers in Switzerland vary between 0.1 and a few Bq kg^{-1} depending on the soil type and altitude, with contribution of atmospheric fallout being higher in the Alps compared to the flat landscapes of northern Switzerland (Eikenberg et al., 2001). Soils from forest ecosystems exhibit generally higher levels than ploughed areas because of the greater filtration effect of forests for aerosol deposition on leaves (interception deposition) as compared to arable land or grassland having a less specific plant surface area (Eikenberg et al., 2001).

The DOE (1980) found no evidence of bioaccumulation through the food chain from soil to plants to rodents. Akleyev et al. (2000) reported

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[1] https://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/Radionuclides/index.htm.

Table 1
Comparison of published studies reporting soil redistribution assessments using plutonium isotopes.
Please note that all studies involved $^{239+240}$Pu isotopes (= Pu) for the calculation of soil redistribution with the exception of Lal et al. (2013) who used ^{239}Pu only. NONE = none of the established conversion models used. NA = information not available. IM = Inventory Method (Lal et al., 2013), PM = Proportional Model (Walling et al., 2002), PDM = Profile Distribution Model (Walling and Quine, 1990), MBM = Mass Balance Model, (Walling et al., 2002), DMM = Diffusion and Migration Model (Walling et al., 2002).

Reference	Location	Climate	Land use/land cover	Main study objective	Pu mean reference inventory (Bq m^{-2})	Other FRN mean reference inventory (Bq m^{-2})	Net soil redistribution (range in t ha^{-1} yr^{-1}) and conversion model(s) used	Comparison to other erosion assessments
Schimmack et al. (2001)	Scheyern, Southern Germany	Temperate	Arable	Potential of Pu as tracer, comparison to ^{137}Cs	58.6 ± 8.5	^{137}Cs: 2800 ± 800	12.5 (with assumed sampling date in 1991, overall loss was given as 350) NONE	^{137}Cs: 10 USLE: average 10 with maximum up to 100
Schimmak et al. (2002)	Scheyern, Southern Germany	Temperate	Arable	Potential of Pu as tracer	NA	NA	Erosion: 32 sedimentation: 39 NONE	Erosion: ^{137}Cs: 37 USLE plus tillage: 29 sedimentation: ^{137}Cs: 52
Hoo et al. (2011)	Lower Cotter catchment, Canberra, Australia	Dry temperate	Eucalyptus forest, bush vegetation	Using Pu as soil erosion tracer at scale of several hundred km^2	18.5 ± 1 (STDEV) to 28 ± 1 (STDEV)	NA	2–6 cm (modified IM)	NA
Xu et al. (2013)	Liaodong Bay, Northeast China	Temperate with monsoonal	From native vegetation to forest to cropland	potential of Pu as tracer compared to ^{137}Cs	Sampling site: 44–86.9 reference sites: 0.023 to 0.938 Bq kg^{-1}	^{137}Cs: Sampling sites: 764–1704 reference sites: NA	6 cm (only a very rough estimated given) NONE	NA
Lal et al. (2013)	Daly basin, Northern Territory, Australia	Monsoonal wet-dry	Natural eucalyptus (90%) intensive grasslands	Assess land management measures using ^{239}Pu	^{239}Pu 88 ± 7 (STDEV) $^{239+240}$Pu: 99.4*	NA	Erosion unploughed: IM 4.4 erosion ploughed: PM 7.5–19.5 MBM 8.5–29.7	Parshall flumes: 19–29
Alewell et al. (2014)	Swiss Central Alps, Urseren Valley, Canton Uri	Temperate, subalpine to alpine	Permanent grasslands	Assess Pu as tracer	83 ± 11 (STDEV)	^{137}Cs: 6892 ± 2199	Sedimentation PM: 1.9–7 erosion IM 0.2–16.4 PDM 0.2–8.9	^{137}Cs (assessed as not suitable because of Chernobyl fallout)
Alewell et al. (2014)	Swiss Southern Alps, Val Piora, Canton Ticino	Temperate, subalpine to alpine	Permanent grasslands	Assess Pu as tracer	77 ± 13 (STDEV)	^{137}Cs: 10,355 ± 10,107	Sedimentation PM: 0.4–20.2 erosion IM 0.1–4.5 PDM 0.2–7	^{137}Cs (assessed as not suitable because of Chernobyl fallout)
Xu et al. (2015)	Liaodong Bay, Northeast China	Temperate with monsoonal	From native vegetation to forest to cropland	First assessment in China of Pu as tracer	Reference: 86.9–90.0 unploughed sites: 12–51 ploughed: 50–62	^{137}Cs: reference: 1688 unploughed: 422–1043 ploughed: 981–1300	Unploughed: IM 20–72 ploughed: MBM 26–29	^{137}Cs unploughed: 14–40 ploughed: 18–28
Arata et al. (2016a)	Swiss Central Alps, Urseren Valley, Canton Uri	Temperate, subalpine to alpine	Permanent grasslands	Validation of the new conversion model MODERN	83 ± 11 (STDEV)	NA	Erosion: DMM: 0.3–2.4 MODERN: 1.6–8.4 PDM: 0.6–5.4 IM: 0.9–9.2 Deposition: PM: 8.7–25.1 MODERN: 3.2 to 9.8	NA
Meusburger et al. (2016)	South Korea, headwater catchment of Lake Soyang	Temperate, intense monsoon events	Forest, arable (cereals to legume)	Suitability of Pu compared to ^{137}Cs and ^{210}Pb$_{ex}$	55 ± 8 (STDEV)	^{137}Cs: 1607 ± 292 (STDEV) ^{210}Pb$_{ex}$: 6463 ± 1832 (STDEV)	erosion: MODERN: 1.24–25.8 IM: 1.47–48.5 MBM: 7.7–98.3 deposition: MODERN: 0.15–11.9 IM: 0.34–15.8 MBM 22.1–26.2	^{137}Cs achieved comparable erosion rates. ^{210}Pb$_{ex}$ was not suitable because of measurement uncertainty
Zollinger et al. (2015)	Swiss High Alps	Subalpine to alpine	Tundra, forest	Quantifying the effect of permafrost on soil erosion	Reference: 92 ± 10 non permafrost: 246 ± 185 permafrost: 80 ± 47	^{137}Cs: Reference: 3139 ± 688 non permafrost: 4371 ± 985 permafrost: 3852 ± 2660	Permafrost sites: erosion: IM 1.8 ± 3.7 PDM 0.3 ± 0.6 non-permafrost sites sedimentation: IM 0.2 ± 1.8 PDM 0.9–2.2	^{137}Cs: permafrost: sedimentation IM 0.03 ± 2.2 PDM 0.01 ± 0.9 non-permafrost sedimentation IM 0.5 ± 0.5 PDM 0.4–0.4
Zhang et al. (2016)	Liaodong Bay, Northeast China	Temperate with monsoonal		Estimate soil erosion rate using Pu atmospheric deposition	Reference: 86.9 to 90.0	NA	MBM considering atmospheric deposition: unploughed: 27–41 ploughed: 26–52	NA

*calculated from ^{240}Pu/^{239}Pu ratios and ^{239}Pu activities.

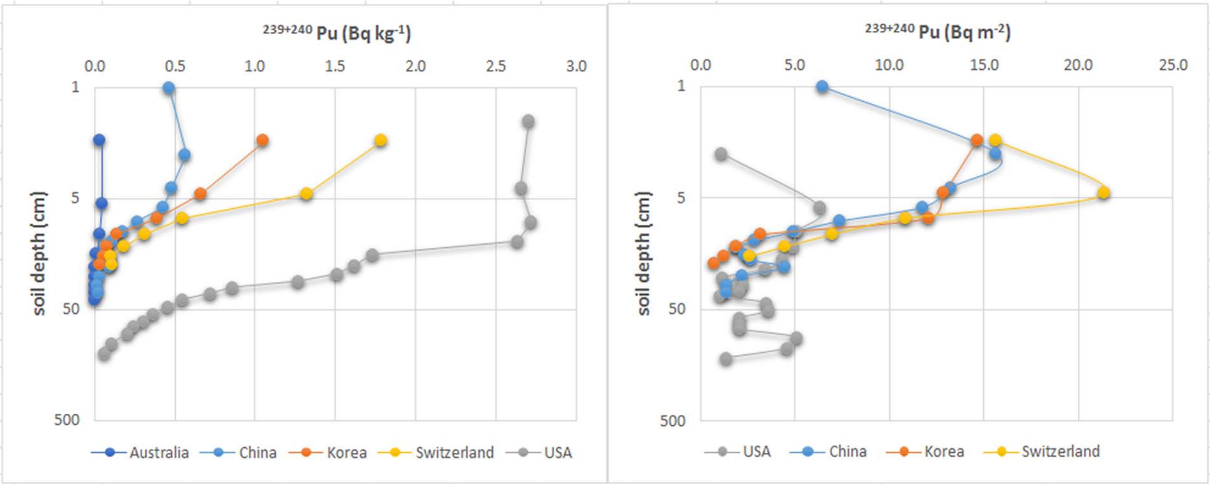

Fig. 1. Examples of $^{239+240}$Pu concentration (left panel) and inventories (right panel) soil depth profiles from sites around the world (Australia (Lal et al., 2013), China (Xu et al., 2013), the Republic of Korea (Meusburger et al., 2016), Switzerland (Alewell et al., 2014), USA (Ketterer et al., 2004b)). Please note that inventories of China have been calculated with a general bulk density value of 1.385 g cm^{-3}.

plutonium accumulation coefficients (as the ratio of concentration in the plant to the concentration in the soil) to be highly species-dependent with a wide range from 2×10^{-4} to 0.8, which is on the lower end compared to the common heavy metals (Blume et al., 2016). In a comparison between ^{239}Pu and ^{236}U regarding their plant availability and uptake, the enrichment factors of Pu were lower by factors between 7 and 52 compared to uranium (Froehlich et al., 2016). The plant dry weight/soil dry weight concentration ratios (CR) range from 0.033 to 0.126 for ^{236}U but only between 0.0015 and 0.0116 for ^{239}Pu, thus being at least an order of magnitude lower (Froehlich et al., 2016). The relatively low plant availability and uptake of plutonium has also been confirmed in comparison to ^{137}Cs (Nisbet et al., 1993; Akleyev et al., 2000; Froehlich et al., 2016). The low plant availability of ^{239}Pu compared to other FRN has been explained by its relatively high association with colloidal and higher molecular weight materials (see Nisbet et al. (1993) and Section 4.2). Higher plant uptake of ^{137}Cs has been discussed to be partly caused by being analogue to potassium (Nisbet et al., 1993). However, caesium is very reactive and binds rapidly and strongly to fine soil particles, so potassium is more likely to be incorporated into the plants than caesium (Mabit et al., 2013; Wakabayashi et al., 2016). There is no nutrient chemical analogue to Pu, but the uptake of Pu may occur in response to a nutrient requirement for iron (Neu et al., 2002), which is, however, relatively low.

Thus, most of the plutonium released to either natural waters or terrestrial environments is rather efficiently sorbed to suspended particles, organic matter or sediments with a high potential of long-term retention. As the aim of this review is the use of plutonium as soil redistribution tracer, we focus in the following on soils as sinks of plutonium and on its comparability to ^{137}Cs which is considered the most widely utilized soil redistribution tracer.

4.2. *Soils as sinks of Pu*

As with all heavy metals, soils and sediments are also efficient sinks for actinides. Generally, actinide solubility depends on pH, redox potential (EH), reaction with complexants such as carbonate, phosphate and humic acids as well as sorption to surfaces of minerals and colloids (Choppin, 2006; Bryan et al., 2007). In comparison to other FRNs, the mobility of plutonium has been discussed controversially. While several studies claimed that Pu appears to be the least mobile, as it is rapidly adsorbed onto organic matter and mineral oxides of the soil (Bunzl et al., 1992; Choppin, 1992; Litaor and Ibrahim, 1996; Ryan et al., 1998; Lee and Lee, 1999), others have interpreted this preferential association of Pu to higher organic molecular fractions as an increase in mobility because of a reduced sorption to soil particles, lower plant uptake (Nisbet et al., 1993) and thus potentially higher downward vertical migration in the soil profile (Alewell et al., 2014; Meusburger et al., 2016). The latter results in some soils in a peak concentration of $^{239+240}$Pu activity often slightly below the surface with a rather polynomial and not an exponential depth distribution (Fig. 1, (Xu et al., 2013;Alewell et al., 2014;Arata et al., 2016a)). However, other studies report a clear exponential depth function of $^{239+240}$Pu in soils ((Lal et al., 2013; Meusburger et al., 2016), Fig.1). In this respect, it is of crucial importance to differentiate between the depth distribution pattern of concentration and inventories, which might differ considerably (Fig. 1). For instance, at the US site where the soil is comprised of decomposed forest litter on top of volcanic cinders, we observe the highest concentrations because of the high Pu sorption capacity, but rather low inventories due to the low bulk density of the material. The polynomial depth distribution of inventories at some sites might originate from exponentially distributed concentration profiles (in our example data set that would apply to the sites from the Republic of Korea and Switzerland, Fig. 1). The latter is due to the low bulk density of the upper most horizon, which is common at grassland or semi-natural (e.g. unploughed) sites if they are not intensively grazed. In contrast, high livestock density leads to compaction and greater bulk densities in the upper horizons.

The downward migration of $^{239+240}$Pu in soils was shown to be influenced by changes in pH, ion strength/salinity, carbonate concentration and organic matter content and composition (Choppin, 1992; Ryan et al., 1998). The distribution coefficients between particulates and solution differ with respect to Pu oxidation states which are known to show markedly different biogeochemical properties (Nelson and Lovett, 1978). The concentrations of the different oxidation states of actinides are generally dependent on pH, redox potential, and the presence of suspended particulates. Each oxidation state has quite a different chemical behaviour, complicating prediction of the geochemical dynamics. Increasing pH and/or redox potential favours higher oxidation states (Choppin, 2006). Plutonium has six chemical oxidation states (i.e. 0, + 3, + 4, + 5, + 6 and + 7) but under environmental conditions it exists in four oxidation states: Pu(III), Pu(IV), Pu(V) and Pu(VI). Because it can be present simultaneously in these four oxidation states, plutonium is considered to have a complex environmental redox chemistry (Xu et al., 2014a). The environmental mobility of Pu is highly affected by its oxidation state, and both reduced forms of Pu - especially Pu(IV) - are considered the less mobile. The two oxidation states Pu(III) and Pu(IV) show a high affinity for particulate matter compared to the more soluble pair, Pu(V) and Pu(VI) (Nelson and Lovett, 1978) and the higher oxidation states Pu(V) and Pu(VI) exceed in their solubility the lower oxidation values (Pu(III) and (IV)) by about two to three orders of magnitude (Nelson and Lovett, 1978; Xu et al., 2014a). As such, the reduction to Pu(IV) by organic matter can be a major path of plutonium immobilization (Choppin, 1992).

In anoxic or strongly acidic waters (e.g. soil solutions), Pu(III) can play a crucial role, while the dominant soluble state of plutonium in aerobic waters is $Pu(V)O_2{}^+$ (Nelson and Lovett, 1978; Choppin, 2006). The dominant state as Pu(III) under reducing conditions is often also due to the presence of enhanced levels of organics and occurs as such often as a complex to humics (Choppin, 2006). The complex role of organics and its dependency on redox conditions has generally been confirmed in many studies for both sorption and mobilization of Pu (Choppin, 1992). Generally humic acids can reduce Pu(VI) or Pu(V) to Pu(IV) (Penrose et al., 1987; Choppin, 1992). Penrose et al. (1987) found that a silt loam rich in organics appeared to reduce Pu(VI) to Pu (IV) which was subsequently strongly absorbed to the soil, while this sorption behaviour was not observed for high capacity montmorillonite free from organics. However, the further reduction of Pu(IV) to Pu(III) will occur under aerobic conditions only if pH is below 3 (Choppin, 1992). In summary, organic matter can potentially lower oxidation values of plutonium and this transfer to the more reduced states (e.g. Pu (III) or Pu(IV)) might then increase sorption affinity to the soil matrix.

As such and because of the large differences in the distribution coefficients between soil solid phase and solutions of different oxidation states of Pu, the initial distribution of plutonium between soluble and particulate phases in the soil will be highly dependent on the distribution coefficients of oxidation states of the source material (e.g. what is called source dependent species). It also leaves us to conclude that to understand the ultimate sorption-desorption dynamics of plutonium in soils, knowledge of the status or even the changes in oxidation state over time is needed.

The depth profile of the $^{239+240}Pu/^{137}Cs$ activity ratios in undisturbed references sites of the headwater catchment of Lake Soyang (Republic of Korea) pointed to higher downward migration of $^{239+240}Pu$ compared to ^{137}Cs (Meusburger et al., 2016). A relatively higher mobility of plutonium compared to caesium was also determined by Schimmack et al. (2001). However, even though plutonium is more mobile in relation to ^{137}Cs or even other FRNs, the overall sorption to soil particles can still be considered to be very high. The latter is confirmed by measurements at Hanford (USA) just 2 km from a reprocessing plant which have shown that 96% of the Pu released to the atmosphere in the late 1940's was still retained in the top 5 cm of the arid soil half a century later (Choppin, 1992). Thus, the lower plant uptake (or probably no plant uptake in this arid ecosystems), and the association to the colloidal and higher molecular weight fraction which caused the Pu to migrate downwards in the soil profile does obviously not result in a general higher export from the soil system even half a century later.

The overall conclusion for the use of $^{239+240}Pu$ as soil redistribution tracer must be that a detailed determination of soil depth profiles at reference sites is required to account for site specific differences in migration and diffusion behaviour as well as the possible transport of $^{239+240}Pu$ with the illuviation of fine soil/clay fractions (see Sections 5.1. and 5.2 below). To assess soil redistribution rates, not only the absolute retention of $^{239+240}Pu$ in the soil profile is crucial, but even more so the shape of the inventories' depth profile which is determined by downward migration. In contrast to other FRNs, which exhibit a rather exponential depth distribution (e.g. uranium (Froehlich et al., 2016) or caesium (Kato et al., 2012; Xu et al., 2013; Alewell et al., 2014)), the depth distribution concentrations and/or inventories of $^{239+240}Pu$ at undisturbed sites can follow rather a polynomial than an exponential function ((Matisoff et al., 2011) for Poland; (Lal et al., 2013) for Australia), (Van Pelt and Ketterer, 2013) for USA; (Alewell et al., 2014; Arata et al., 2016a) for Switzerland and (Xu et al., 2013) for China). The latter might be explained by the downward migration of Pu during the last 50–60 years since the major bomb fallout events (Everett et al., 2008) or the above discussed slightly higher mobility of Pu compared to other FRNs depending on its oxidation state. A second explanation might be the very low plant bioavailability of Pu (Nisbet et al., 1993). As Pu is basically not taken up by the vegetation (Iurian et al., 2015), its depth profile will only represent the combined effects of diffusion and migration, bioturbation (if any) and other physical processes that move soil grains down through the profile (Froehlich et al., 2016) or results in erosion or deposition processes. This is in contrast to other radionuclides which might potentially be slightly more taken up by plants, like, e.g. uranium or caesium, which will then be recycled back to the ground surface in fallen leaves, bark and twigs (Nisbet et al., 1993; Froehlich et al., 2016), thus enhancing the exponential shape of the depth distribution in soils.

5. Concept of $^{239+240}Pu$ as soil redistribution tracer

5.1. General concept

When FRNs reach the soil surface by wet or dry deposition, they are tightly adsorbed to fine soil particles. The subsequent lateral redistribution of adsorbed FRN is mainly associated with soil particle transport. Soil erosion is indicated by lower FRN inventories, while sedimentation is indicated by higher FRN inventories compared to the reference site (Mabit et al., 2008). The FRN method provides information on soil redistribution processes affecting a specific study area since the time of deposition of the selected FRN and can be performed during a single sampling campaign, thus avoiding time-consuming and costly procedures commonly required to monitor sites over extended time periods (Mabit et al., 2008, 2013). The method is based on a targeted FRN comparison: the inventory (total activity per unit area) at a given sampling site versus the inventory measured in an adjacent and undisturbed and unploughed reference site, where no soil redistribution has occurred. Mass activities of the FRN ($Bq\ kg^{-1}$) have to be converted into areal activities also termed inventories ($Bq\ m^{-2}$) with measured mass depth (xm) of fine soil material ($kg\ m^{-2}$ sampling depth^{-1}). The inventory change (Inv_{change}) between reference and sampling site can be calculated as:

$$Inv_{change} = \frac{Inv - Inv_{ref}}{Inv_{ref}} \times 100 \tag{1}$$

where Inv_{ref} is the local reference total inventory as mean of all reference sites ($Bq\ m^{-2}$) and Inv is measured total inventory at the sampling point ($Bq\ m^{-2}$). Negative values of Inv_{change} indicate erosion, whereas positive values indicate deposition. The conversion of FRN inventories to soil erosion/deposition rates requires conversion models considering land use and the FRN being used (see Section 5.2 below).

While there are many advantages of the FRN method (global distribution of FRN and thus global applicability, retrospective assessment of soil redistribution, spatially distributed data depending on sampling sizes, only one sampling campaign required which can simultaneously assess both erosion and deposition), there are also some limitations. One constraint valid for all FRN based approaches is the need for specific detections systems depending on the FRN used (see Section 3). While the main analytical limitations are already overcome or are expected to be solved in the near future at least for the use of plutonium as soil erosion tracer, another key requirement for using the method appropriately is the availability and the proper selection of suitable reference sites. Indeed, the measured total FRN inventory at the reference sites represents the baseline fallout (i.e. reference inventory), a fundamental parameter for the qualitative and quantitative assessment of soil redistribution rates (Loughran et al., 2002). It is used for the comparison with the total FRN inventories of the sampling sites, and therefore determines if and how strongly a site is eroding or accumulating sediments. Sutherland (1996, 1998) suggests that the sample size should be increased until the allowable error reaches 10% at 90% confidence level. (IAEA, 2014a) suggested that if the coefficient of variation (CV) of the FRN inventory at a specific reference site exceeds 30%, this provides an indicator of its unsuitability. The latter leaves the possibility of increasing sampling numbers to reduce the CV value below 30%. Moreover, the depth profile of the FRN inventory distribution in the soil at the reference site of unploughed soils plays a crucial role, as the shape of this profile is used in the conversion models to convert changes in FRN inventory into quantitative estimates of soil redistribution rates (Section 5.2). Recent studies demonstrated the sensitivity of conversion models to uncertainties or bias in the reference inventory (e.g. (Kirchner, 2013; Iurian et al., 2014; Arata et al., 2016a)).

5.2. Measuring inventories is only half the way: the critical need of suitable conversion models to derive soil redistribution rates

For all FRN based soil redistribution assessments conversion models are needed to derive quantitative estimates of soil erosion and deposition rates from FRN inventory measurements. Different conversion models have been proposed by the scientific community and differ mainly in their underlying assumptions of soil stratification and descriptions of FRN transport processes (Table 2) (IAEA, 2014a). Current available models range from relatively simple models assuming homogenous FRN distribution in the considered soil profiles such as the Proportional Model (Walling et al., 2002, 2014) or exponential depth distribution of FRN inventories such as the Profile Distribution Model (Walling and Quine, 1990) or the Inventory Method (Lal et al., 2013) to more complex models considering vertical migration of the FRN (e.g. the Mass Balance Model and the Diffusion and Migration Model (Walling et al., 2002)). As the depth distribution of FRN is strongly dependent on cultivating measures especially ploughing, different models have been developed for ploughed or unploughed soils.

Table 2

Models available to convert FRN inventories into soil redistribution rates. MBM = Mass Balance Model, DMM = Diffusion and Migration Model, IM = Inventory Method, MODERN = MOdelling Deposition and Erosion rates with RadioNuclides. E = suitable to derive erosion rates. D = suitable to derive deposition rates.

	Ploughed			Unploughed		
	^{137}Cs	$^{239+240}$Pu	^{210}Pb$_{ex}$	^{137}Cs	$^{239+240}$Pu	^{210}Pb$_{ex}$
Proportional Model[a]	E + D	E + D	E + D			
MBM 1–3[a]	E + D*	§	E + D*			
DMM[a]				E + D*		E + D*
PDM[a]				E + D*	E + D*	
IM[b]					E	
MODERN[c]	E + D	E + D	E + D	E + D	E + D	E + D

§Simplified version by Xu et al. (2015)) or (extended by atmospheric deposition) of Zhang et al. (2016) available.

D* deposition can be roughly estimated but only if FRN inventories of an upslope catena is known.

[a] Walling et al. (2002, 2014).

[b] Lal et al. (2013).

[c] Arata et al. (2016a, 2016b).

While the Proportional Model (PM) is the most simple model algorithm but only suitable for ploughed soils, the Profile Distribution Model (PDM) is a very convenient model to estimate erosion rates at unploughed locations. However, as highlighted by Walling et al. (2014) as well as by Alewell et al. (2014) and Arata et al. (2016a,b), it involves a number of simplifying assumptions on the inventory depth distribution of FRN in the soil (e.g. the exponential depth distribution).

The Mass Balance Model (MBM) and the Diffusion and Migration Model (DMM) consider different vertical distribution of the FRN in the soil depending on the land use (ploughed or unploughed) and on the migration processes of the specific FRN since the main fallout. In ploughed soils, the MBM assumes the FRN content to be mixed uniformly within the plough layer. In unploughed soils, the DMM simulates the downward diffusion and migration of FRN in the soil profile over time, and assumes that most of the FRN was located near the surface after the fallout (Walling et al., 2002). As such, the DMM considers that following the fallout a relatively high inventory change would have resulted in a small soil loss which leads to generally lower values as compared to exponential models. The MBM and the DMM algorithms include constants which should accurately describe the physical processes affecting FRN distribution in the soil since the main fallout (e.g. migration constant, diffusion constant). The empirical or experimental determination of these constants is not trivial and, if not carefully selected, can significantly bias the resulting soil redistribution rates (Poreba and Bluszcz, 2008; Iurian et al., 2014). As such, most of the soil redistribution studies using either the DMM or the MBM relied on literature values for these parameters, which originate from different environmental conditions, timing and atmospheric fallout scenarios. The IAEA has supported the development of a Microsoft Excel Add-in (Walling et al., 2014) which allows the conversion of FRN inventories into soil redistribution rates through the application of different models (Table 2). This Add-in, which was initially developed for ^{137}Cs and later extended for ^{7}Be and ^{210}Pb$_{ex}$ (Walling et al., 2014), can be freely downloaded from the IAEA website, but its code is not editable and thus cannot be adapted to specific agro-environmental conditions (e.g. a particular inventory depth profile of the FRN distribution) or to other FRNs such as $^{239+240}$Pu.

As such, one of the past main limitations to use $^{239+240}$Pu as soil redistribution tracer was, until recently and next to the analytical limitations (see Section 3), the inadequacy of existing conversion models (Alewell et al., 2014; Arata et al., 2016a, 2016b). In 2016, a new conversion model was developed, which was called MOdelling Deposition and Erosion rates with RadioNuclides (MODERN) (Arata et al., 2016a, 2016b; Meusburger et al., 2016). The MODERN concept enables to convert FRN inventories to soil redistribution rates with several noticeable advantages:

1. MODERN does not make any distinct assumptions on the FRN inventory depth profile, but accurately describes the measured soil profile shape of any selected FRN at the reference site;
2. MODERN is based on an algorithm to convert FRN inventories into both erosion and deposition rates independently from the land use type, whereas other conversion models are specifically developed to quantify rates of only one redistribution process (i.e. erosion or deposition) connected to one specific type of land use (Table 2);
3. MODERN allows adapting the depth profile to simulate the precise behaviour of the selected FRN under different agro-environmental conditions (e.g. ploughing activities, erosion and deposition processes, anthropogenic disturbance) assuming that reference and sampling sites experienced the same treatments;

4. MODERN is applicable and adaptable to all FRN and as such opened the possibility to extend the FRN approach to other radionuclides such as $^{239+240}$Pu;
5. MODERN code is freely available and editable either as MatLab or R package (modeRn).[2]

Until the development of MODERN, previous conversion models for unploughed sites with natural FRN depth distribution (e.g. permanent grasslands, steppes) were based on the assumption of an exponential FRN depth distribution (Lal et al., 2013; Walling et al., 2014). As discussed above, the depth distribution of Pu at unploughed sites may follow a polynomial or an exponential function (see Section 4.2). As such, with the implementation of an exponential function as reference soil depth distribution, conversion models were bound to systematically overestimating the Pu content in the uppermost horizons of the reference soil profile for many regions in the world, which resulted in underestimating the redistribution of sediments (Alewell et al., 2014; Arata et al., 2016a; Meusburger et al., 2016). In a few recent studies, MODERN was successfully validated with rigorous comparison to published conversion models as well as to ^{137}Cs based soil redistribution assessments and visual surveys of soil damage in the field (Arata et al., 2016a, 2016b; Meusburger et al., 2016, submitted). The DMM turned out to be generally considerably lower in erosion rates compared to MODERN as well as to PDM and IM. The latter three compared fairly well, showing only deviations at the high or low end ratios (Arata et al., 2016a). The deviation between the models may be explained by the assumption of an exponential depth function of the Pu at reference sites by the algorithm of the PDM and IM, whereas MODERN reproduces precisely the depth profile following the accuracy of the depth incremental measurements. However, differences between means of sites were not significant (Arata et al., 2016a) which might, nevertheless, be very different at sites differing even more from the assumed exponential depth distribution (e.g. less organic matter content might shift equilibria to higher oxidations states with higher mobility and thus higher downward migration, see Section 4.2). A model comparison by Meusburger et al. (2016) at the Lake Soyang headwater catchment in the Republic of Korea resulted in comparable results of MODERN, the PDM and the MBM for ^{137}Cs (except for one outlier where ploughing started recently). However, in the case of $^{239+240}$Pu a close relation between the IM and MODERN for unploughed sites was observed ($R^2 = 0.90$; $p = 0.0001$), but the erosion estimates based on the IM were twice as high (Meusburger et al., 2016). The latter was most likely attributed to an overestimation of the surface soil concentration by the exponential function of the IM. For the ploughed sites, the simplified MBM introduced by Xu et al. (2015) also resulted in considerably higher soil redistribution assessments as compared to MODERN. As the authors noted that the simplified MBM was particularly insensitive to inventory changes, MODERN results of $^{239+240}$Pu derived soil redistribution rates were favoured (Meusburger et al., 2016).

So far, the application of MODERN seem to provide realistic assessments not only for $^{239+240}$Pu but also for ^{137}Cs and $^{210}Pb_{ex}$ based soil redistribution assessments (Arata et al., 2016b; Meusburger et al., 2016). However, additional investigations are needed to apply and test this model in using the different FRN under varying conditions (e.g. environmental conditions, soil types, land use).

6. Applications and implications of using $^{239+240}$Pu as soil redistribution tracer

6.1. Main achievements using $^{239+240}$Pu as soil redistribution tracer

The earliest studies to connect plutonium to soil redistribution rates were utilizing plutonium as qualitative tracer with no quantification of soil redistribution magnitudes (Muller et al., 1978). A decade later (Foster and Hakonson, 1987) used modelled soil erosion rates to assess plutonium export from non-federal land of the US, resulting in only 0.002% export of the initial plutonium fallout for the Savannah River basin, 0.01% for the Columbia River basin, 0.02% for the Hudson and Rio Grande River basins, and 0.08% for the Mississippi River basin. After another preliminary evaluation of plutonium as soil redistribution tracer by Joshi and Shukla (1991)) where the study mainly aimed at developing a model to decipher the impact of atmospheric pollutants on watershed quality, the first to make use of plutonium isotopes to assess soil redistribution rates was a study in southern Germany one decade later (Schimmack et al., 2001, 2002). To date, as summarized by Table 1, only a few applied studies using Pu as a tracer for soil redistribution have been performed, with a clear emphasis in the southern hemisphere (Australia; (Everett et al., 2008; Tims et al., 2010a; Hoo et al., 2011; Lal et al., 2013)), East Asia (one region in Northeast China, Liaodong Bay: (Xu et al., 2013, 2015; Zhang et al., 2016) as well as one headwater in the Republic of Korea (Meusburger et al., 2016)) with the exceptions of a few areas located in central Europe (one agricultural site in southern Germany (Schimmack et al., 2001, 2002) and four Swiss Alpine grassland sites (Alewell et al., 2014; Zollinger et al., 2015; Arata et al., 2016a)).

Peer-reviewed existing studies presented in Table 1 have emphasized and/or concluded that Pu as soil redistribution tracer:

(i) has the advantage of generally not being influenced by fallout from NPP accidents (with the exception of specific areas in the close vicinity of the accident site) which results in relatively low variability of reference site inventories, thus increasing the applicability and decreasing uncertainty of this FRN method;
(ii) has the advantage that the sensitivity of both main isotopes, i.e. ^{239}Pu and ^{240}Pu, remains essentially at the same level than when they were deposited throughout time horizons of anthropogenic dimension, because of their long half-lives. The latter is of major advantage in terms of its use as tracer compared to the most commonly used soil redistribution tracer ^{137}Cs and has thus the potential of being a reliable soil redistribution tracer in future studies;
(iii) seems to be a more applicable tracer approach than $^{210}Pb_{ex}$, as several studies under specific environmental conditions report $^{210}Pb_{ex}$ unsuitability because of low concentrations associated to high uncertainty in its determination (Iurian et al., 2016);
(iv) can potentially be advanced to assessment of short-term soil redistribution assessment if resampling approaches are applied (Porto et al., 2014; Arata et al., 2017).
(v) has the analytical advantage of higher accuracy as compared to $^{210}Pb_{ex}$ (Iurian et al., 2015) and higher sample throughput, in particular if ICP-MS techniques are applied for the Pu measurements.

Few studies attempted to trace soil redistribution by wind with $^{239+240}$Pu isotopes. Van Pelt and Ketterer (2013) concluded that advantages/limitations of using $^{239+240}$Pu to trace wind erosion compared to other FRNs, especially ^{137}Cs, are basically the same as when assessing soil redistribution by water erosion: smaller sample sizes needed and the ease and speed of measurement when using ICP-MS analytical facilities, which could allow more spatially extensive sampling strategies, resulting in more accurate estimates. Further, the long half-lives of the isotopes and the utility of using the isotopic ratios to distinguish non-global fallout sources might make $^{239+240}$Pu the preferred tracer for soil redistribution by wind studies for the decades to come.

Michelotti et al. (2013) used historical data and available modelling tools to evaluate how dynamic models might be utilized to better predict transport rates of plutonium with soil and sediment to distant, downwind locations from the Los Alamos National Laboratory, which is

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[2] www.modern.umweltgeo.unibas.ch.

Table 3
Comparative summary of the two main anthropogenic soil radiotracers ^{137}Cs and $^{239+240}$Pu. OM: organic matter; NPP: nuclear power plant; ICP-MS: inductively coupled plasma mass spectrometry; AMS: accelerator mass spectrometry; FRN: fallout radionuclides.

	^{137}Cs	$^{239+240}$Pu
Elemental characteristic	Alkali metal	Actinide metal
Origin(s)	Anthropogenic (nuclear weapon tests fallout and NPP accidents release)	Anthropogenic (nuclear weapon tests fallout only with the exception of areas in close proximity to nuclear accident sites)
$T_{1/2}$ (radioactive half-life)	30 years	24,110 and 6,561 years for ^{239}Pu and ^{240}Pu respectively
Radiation emission	Gamma emitter (662 keV)	Alphas emitters Alpha energies of ^{239}Pu and ^{240}Pu (5.157 and 5.168 MeV, respectively)
Laboratory determination	Gamma-ray spectrometry	Alpha-particle spectrometry; mass spectrometry, mainly ICP-MS and AMS
In-situ measurement	Possible using field-portable gamma-ray detector	Not possible
Soil mobility	Limited and reduced in fertile soil, strong binding to fine soil particles and/or OM	Slightly higher than for the other existing FRNs
Plant uptake	Soil-plant transfer reduced in fertile soils	Negligible plant uptake as compared to all other FRNs
Current investigated areas with this tracer	Worldwide application since 4 decades	Tested and then validated since < 1 decade in only a couples of countries (Table 1)
Scales of investigation	Plot to region	Field
Fallout occurrence and soil deposit	Worldwide with higher deposit in northern hemisphere	Worldwide with higher deposit in northern hemisphere

part of the US Department of Energy and where residual radioactivity remains in local soils from past operations. Considering thousand-year time periods, their results suggested that using static model parameters for simulating aeolian transport predicts significantly lower transport and more proximate deposition rates when environmental disturbances are considered (Michelotti et al., 2013).

The conclusion from these few preliminary wind erosion studies suggests that risk assessments should account for wind-driven as well as water-driven transport, and that such risks over an extended period of time need to account for environmental disturbances such as vegetation changes or fires (Michelotti et al., 2013; Van Pelt and Ketterer, 2013).

6.2. *Similarities and differences of $^{239+240}$Pu and ^{137}Cs as soil redistribution tracer*

One of the most widely used and validated approaches to evaluate soil redistribution rates is the analysis of ^{137}Cs, which originated mostly from the nuclear weapon testing programs in the 1950's and 1960's and from NPP accidents such as Chernobyl ((Mabit et al., 2008, 2013), Table 3). In contrast to plutonium, the natural abundance isotope of Caesium (^{133}Cs), which is an alkali metal (atomic number 55), is stable (note that there is one natural radiogenic trace isotope, ^{135}Cs). For the use as soil redistribution tracer, man-made ^{137}Cs and, in a very few studies, ^{134}Cs have been used (see (Mabit et al., 2013)). Like Pu, ^{137}Cs is strongly absorbed to fine soil particles and transported mainly by physical processes such as soil redistribution (Ketterer et al., 2004a, 2011; Everett et al., 2008).

On a global basis, above-ground nuclear weapons testing fallout is the dominant contributor to plutonium and caesium in the environment, and the distribution of this 1950's–1960's fallout is very similar for these two anthropogenic FRN. In terms of the number of atoms dispersed, the nuclear tests yielded more than six times as many atoms of $^{239+240}$Pu as ^{137}Cs (Everett et al., 2008). In terms of radioactivity, however, ^{137}Cs released by nuclear testing had an activity that was nearly two orders of magnitude higher than plutonium ((UNSCEAR, 2000); note that the latter is due to the considerably shorter half-life of ^{137}Cs as compared to $^{239+240}$Pu isotopes, which results in a higher radioactivity). Furthermore, Pu, in contrast to ^{137}Cs, is contained in the non-volatile fraction of nuclear fuel debris released from reactors during accidents such as the 1986 Chernobyl accident. Thus, the contribution of nuclear accidents to ^{137}Cs contamination is considerably higher and much wider spread as compared to Pu (see Section 2). The latter results in relatively high heterogeneity of reference site inventories for ^{137}Cs (as compared to Pu), which do not always meet the required criteria of < 30% coefficient of variance (IAEA, 2014a). If the evaluated contribution of Chernobyl to the overall fallout input is above 80%, then the year 1986 should be selected as the starting and main fallout input in the available ^{137}Cs-conversion models.

The different sorption behaviour of $^{239+240}$Pu compared to ^{137}Cs and the resulting differences in depth distribution have important implications for its use as tracer, especially regarding the conversion of measured FRN inventory changes into soil redistribution rates (see Section 5.2). While $^{239+240}$Pu activity in soils generally has a peak concentration slightly below the surface, an exponential decline with depth is more common for ^{137}Cs (see Sections 4.2 and 6.2 (Xu et al., 2013; Alewell et al., 2014)). This different depth distribution in soils is partly due to the fact that $^{239+240}$Pu is associated with organic matter and sesquioxides in addition to clay particles whereas ^{137}Cs is known to be mostly bound to the fine mineral clay fraction (Lujaniene et al., 2002; Qiao et al., 2012; Meusburger et al., 2016; Xu et al., 2017). Consequently, a relatively higher proportion of $^{239+240}$Pu is exchangeable and might migrate downward in soils (Schimmack et al., 2001; Meusburger et al., 2016). For example (Hirose et al., 2017) reported that in Mongolia and central-eastern Japan, the migration tendency of three major environmental radionuclides in surface soils is in the following order: $^{90}\text{Sr} \gg {}^{239+240}\text{Pu} > {}^{137}\text{Cs}$. The authors concluded that Pu is more mobile than Cs due to chemical erosion processes and has a deeper downward migration.

During physical erosion processes, a higher preferential transport with fine particles has been noted for ^{137}Cs as compared to $^{239+240}$Pu (Xu et al., 2017; Meusburger et al., 2016), which might be explained by the preferential binding of ^{137}Cs to clay particles while $^{239+240}$Pu with its association to organic matter and oxides will be attached to larger grain sizes. As such, a greater relative influence of the particle size correction factor might be expected for ^{137}Cs related soil redistribution assessments. It is important to point-out that the particle size correction factor would be needed for the conversion of FRN inventories to soil redistribution rates if FRN sorb preferentially to smaller particle and these smaller particles are preferentially transported. However, as particle size correction factors are complex to establish, most studies just assume a factor equal to 1.

Compared to ^{137}Cs, the migration of $^{239+240}$Pu into the soil is enhanced particularly if changes in pH and/or decomposition of organic matter occur (Ryan et al., 1998). A second explanation might be

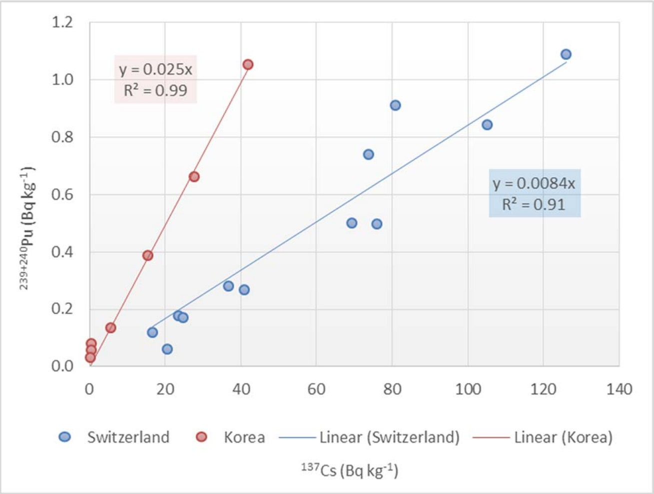

Fig. 2. Examples of correlation between $^{239\,+\,240}$Pu and ^{137}Cs content in soils of two Swiss Alpine grasslands (data from Alewell et al. (2014)) and one catchment from the Republic of Korea (data from Meusburger et al. (2016)).

the low expected uptake of plutonium by plant as compared to ^{137}Cs and thus no relocation to the soil surface (see discussion above and (Nisbet et al., 1993; Akleyev et al., 2000; Froehlich et al., 2016)).

Findings from activity ratios of ^{137}Cs to $^{239\,+\,240}$Pu at eroded sites (higher ratio compared to the global fallout) and at depositional sites (smaller ratio) in a headwater catchment of Lake Soyang (Republic of Korea) pointed to preferential transport of ^{137}Cs and offered a unique approach to determine in situ particle size correction factors that can be applied when both ^{137}Cs and $^{239\,+\,240}$Pu have the same fallout origin (Meusburger et al., 2016). Compared to the global fallout ratio, erosion sites are depleted in ^{137}Cs and sedimentation sites are slightly enriched, which was interpreted as a result of a more pronounced preferential transport of ^{137}Cs, which binds predominantly to fine soil particles (Meusburger et al., 2016; Xu et al., 2017). Implementing these particle size correction factors in the conversion of ^{137}Cs inventories to soil erosion rates resulted in comparable estimates of soil loss when using the ^{137}Cs or the $^{239\,+\,240}$Pu methods (Meusburger et al., 2016). The latter finding is not necessarily in contradiction to the higher mobility of Pu within the soil profile, as obviously Pu is more prone to colloidal transport while ^{137}Cs moves associated with fine soil particles.

In spite of the different chemical processes responsible for attachment and partial differences in vertical and lateral mobility, Cs and Pu show a linear correlation in many terrestrial ecosystems ((Huh and Su, 2004; Meusburger et al., 2016; Smith et al., 2016; Xu et al., 2017) see Fig. 2 for example). This indicates that (i) both elements are sufficiently tightly bound to soil particles, (ii) there is an overall relative resistance for those two elements to be leached out of the soil profile, (iii) attachment during the transportation process is stable (Muller et al., 1978; Everett et al., 2008) and (iv) that both are suitable tracers for soil redistribution assessment if concentrations in soils are high enough to allow proper measurement accuracy and if the heterogeneity of the overall fallout deposition - established through the inventory variability at the reference site(s) - results in a CV below 30% (see Section 5.1).

7. Conclusions and outlook

Due to its long half-life and almost unique fallout origin, $^{239\,+\,240}$Pu offers great potential to trace soil redistribution over long-term periods. One of the major advantages of $^{239\,+\,240}$Pu as soil redistribution tracer is certainly the initial fallout of this FRN not being significantly influenced by the NPP accidental releases (with the exception of regions situated in the close vicinity of the accident sites). The latter results in a relatively low heterogeneity of reference sites compared to ^{137}Cs, especially in European areas substantially affected by Chernobyl. With the development of the new FRN inventory conversion model MODERN, one milestone has been reached, as the limitation of past existing conversion models to convert $^{239\,+\,240}$Pu inventory changes into soil redistribution rates has been overcome.

As the $^{239\,+\,240}$Pu based soil redistribution assessment in agroecosystems is still in its infancy in comparison to the use of ^{137}Cs with less than a dozen of applied studies published in peer-reviewed journals until now, we would like to encourage the FRN scientific community to evaluate soil redistribution through testing $^{239\,+\,240}$Pu isotopes under various environmental conditions. The validation of its use against other more mature radio-isotopic techniques such as ^{137}Cs and/or ^{210}Pb$_{ex}$ was successful so far (Alewell et al., 2014; Meusburger et al., 2016; Xu et al., 2017) and should be promoted in the future. Furthermore, future studies should be encouraged to increase scientific investigation comparing soil redistribution rates derived from $^{239\,+\,240}$Pu isotopes versus other conventional/traditional approaches such as the measurements of catchment sediment yields and/or redistribution plot studies under natural or artificial rainfall simulations.

The FRN scientific community used the gamma-ray spectrometry radioanalytical technique since decades for the measurements of ^{137}Cs, ^{7}Be, and, to some extent, of ^{210}Pb$_{ex}$. Measurement of $^{239\,+\,240}$Pu isotopes in soil samples can be carried out by radiometric or mass spectrometric techniques with a higher accuracy as compared to the measurement of ^{210}Pb$_{ex}$ using gamma-ray spectrometry. Alpha-particle spectrometry is suitable for the measurement of $^{239\,+\,240}$Pu, but suffers from long counting times for the measurement process. Progress on the mass spectrometric techniques associated to their higher availability in laboratories worldwide, in particular regarding the ICP-MS techniques, and their fast measurement process and high sample throughput, add to the advantages of the $^{239\,+\,240}$Pu technique allowing intensive sampling and measurement campaigns across ecosystems.

One restriction of the approach to assess soil redistribution with the $^{239\,+\,240}$Pu tracer technique might be the limitation to a temporal integration over the past 5–6 decades (e.g. long-term soil redistribution assessment). To obtain medium- to short-term soil redistribution rate estimates resampling approaches have been proposed and already applied successfully for other FRNs (e.g., (Porto et al., 2014, 2016; Arata et al., 2017)). This field of research would certainly be an important future realm to be explored also for plutonium.

A further branch of research which needs more investigation is certainly the post-fallout behaviour of Pu isotopes in various soils including investigations of preferential adsorption/desorption mechanisms of the various oxidation states and the dependency on environmental conditions. This might shed more light onto the environmental mobility of Pu which is still under discussion within the related scientific community. More scientific and robust evidence of the conservative behaviour of Pu in various soil matrices is needed as potential oxidation of “stable” Pu(IV) could occur through interactions with minerals, complexants, humic substances, bacteria, and then modify significantly its transport and mobilization. In addition, more studies regarding the preferential adsorption of $^{239\,+\,240}$Pu by fine particles as well as the preferential transportation of these fine particles during erosion (or vice versa the preferential sedimentation of coarser particles with relatively lower $^{239\,+\,240}$Pu content) is needed to implement realistic particle size correction factors in conversion models during $^{239\,+\,240}$Pu inventory conversion to soil distribution rates. Last but not least to use $^{239\,+\,240}$Pu as a rigorous tool to quantify soil redistribution processes, further refinement and advancement of conversion models such as MODERN will be needed to increase accuracy of soil redistribution estimates from of $^{239\,+\,240}$Pu inventory measurements.

As shown throughout this review, recent advances in soil erosion research suggest that $^{239\,+\,240}$Pu will belong to the next generation of tracers as compared to the more mature FRN techniques. With the declining levels of ^{137}Cs worldwide (especially in the southern hemisphere) and because of their long half-lives which will ensure their usage for a long time period, Pu isotopes (i.e. ^{239}Pu and ^{240}Pu) have all the needed prerequisite and advantages to become one of the next anthropogenic soil radiotracers of importance to investigate and significantly improve our knowledge on agroecosystems sustainability and resilience to climate and land use change.

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References

Aggarwal, S.K., 2016. Alpha-particle spectrometry for the determination of alpha emitting isotopes in nuclear, environmental and biological samples: past, present and future. Anal. Methods 8, 5353–5371. http://dx.doi.org/10.1039/c6ay00920d.

Akleyev, A.V., Kostyuchenko, V.A., Peremyslova, L.M., Baturin, V.A., Popova, I.Y., 2000. Radioecological impacts of the Techa River contamination. Health Phys. 79, 36–47. http://dx.doi.org/10.1097/00004032-200007000-00008.

Alewell, C., Meusburger, K., Juretzko, G., Mabit, L., Ketterer, M.E., 2014. Suitability of 239 + 240PU and Cs-137 as tracers for soil erosion assessment in mountain grasslands. Chemosphere 103, 274–280. http://dx.doi.org/10.1016/j.chemosphere.2013.12.016.

Alvarado, J.A.C., Steinmann, P., Estier, S., Bochud, F., Haldimann, M., Froidevaux, P., 2014. Anthropogenic radionuclides in atmospheric air over Switzerland during the last few decades. Nat. Commun. 5. http://dx.doi.org/10.1038/ncomms4030.

Arata, L., Alewell, C., Frenkel, E., A'Campo-Neuen, A., Iurian, A.R., Ketterer, M.E., Mabit, L., Meusburger, K., 2016a. MOdelling deposition and erosion rates with RadioNuclides (MODERN) - part 2: a comparison of different models to convert Pu239 + 240 inventories into soil redistribution rates at unploughed sites. J. Environ. Radioact. 162, 97–106. http://dx.doi.org/10.1016/j.jenvrad.2016.05.009.

Arata, L., Meusburger, K., Frenkel, E., A'Campo-Neuen, A., Iurian, A.R., Ketterer, M.E., Mabit, L., Alewell, C., 2016b. MOdelling deposition and erosion rates with RadioNuclides (MODERN) - part 1: a new conversion model to derive soil redistribution rates from inventories of fallout radionuclides. J. Environ. Radioact. 162, 45–55. http://dx.doi.org/10.1016/j.jenvrad.2016.05.008.

Arata, L., Meusburger, K., Bürge, A., Zehringer, M., Ketterer, M.E., Mabit, L., Alewell, C., 2017. Decision support for the selection of reference sites using 137Cs as soil erosion tracer. SOIL (accepted).

ATSDR, 2010. Toxicological Profile for Plutonium. Agency for Toxic Substances and Disease Registry. Department of Health and Human Services, Public Health Service, Atlanta, GA: U.S.

Auerswald, K., Fiener, P., Gomez, J.A., Govers, G., Quinton, J.N., Strauss, P., 2015. Comment on "Rainfall erosivity in Europe" by Panagos et al. (Sci. Total Environ., 511, 801–814, 2015). Sci. Total Environ. 532, 849–852. http://dx.doi.org/10.1016/j.scitotenv.2015.05.019.

Ayranov, M., Krahenbuhl, U., Sahli, H., Rollin, S., Burger, M., 2005. Radiochemical separation of actinides from environmental samples for determination with DF-ICP-MS and alpha spectrometry. Radiochim. Acta 93, 249–257. http://dx.doi.org/10.1524/ract.93.5.249.64278.

Bisinger, T., Hippler, S., Michel, R., Wacker, L., Synal, H.A., 2010. Determination of plutonium from different sources in environmental samples using alpha-spectrometry and AMS. Nucl. Instrum. Methods Phys. Res., Sect. B 268, 1269–1272. http://dx.doi.org/10.1016/j.nimb.2009.10.150.

Blume, H.-P., Brümmer, G.W., Fleige, H., Horn, R., Kandeler, E., Kögel-Knabner, I., Kretzschmar, R., Stahr, K., Wilke, B.-M., 2016. Scheffer/Schachtschabel Soil Science. 1-618 Springer-Verlag, Berlin Heidelberg.

Borrelli, P., Robinson, D.A., Fleische, r.L.R., Lugato, E., Alewell, C., Meusburger, K., Modugno, S., Ballabio, C., Schütt, B., Van Oost, L., Montanarella, L., Panagos, P., 2017. Quo vadis soil erosion? Global impacts of 21st century land use change. Nat. Commun (submitted).

Bossew, P., Lettner, H., Hubmer, A., Erlinger, C., Gastberger, A., 2007. Activity ratios of Cs-137, Sr-90 and Pu239 + 240 in environmental samples. J. Environ. Radioact. 97, 5–19. http://dx.doi.org/10.1016/j.jenvrad.2007.02.008.

Boulyga, S.F., Becker, J.S., 2002. Isotopic analysis of uranium and plutonium using ICP-MS and estimation of burn-up of spent uranium in contaminated environmental samples. J. Anal. At. Spectrom. 17, 1143–1147. http://dx.doi.org/10.1039/b202196j.

Bryan, N.D., Jones, D.L.M., Keepax, R.E., Farrelly, D.H., Abrahamsen, L.G., Pitois, A., Ivanov, P., Warwick, P., Evans, N., 2007. The role of humic non-exchangeable binding in the promotion of metal ion transport in groundwaters in the environment. J. Environ. Monit. 9, 329–347. http://dx.doi.org/10.1039/b701891f.

Bunzl, K., Kracke, W., Schimmack, W., 1992. Vertical migration of Pu-239 + Pu-240, Am-241 and Cesium-137 fallout in a forest soil under spruce. Analyst 117, 469–474. http://dx.doi.org/10.1039/an9921700469.

Cao, L., Ishii, N., Zheng, J., Kagami, M., Pan, S., Tagami, K., Uchida, S., 2017. Vertical distributions of Pu and radiocesium isotopes in sediments from Lake Inba after the Fukushima Daiichi nuclear power plant accident: source identification and accumulation. Appl. Geochem. 78, 287–294. http://dx.doi.org/10.1016/j.apgeochem.2017.01.012.

Cerdan, O., Govers, G., Le Bissonnais, Y., Van Oost, K., Poesen, J., Saby, N., Gobin, A., Vacca, A., Quinton, J., Auerswald, K., Klik, A., Kwaad, F., Raclot, D., Ionita, I., Rejman, J., Rousseva, S., Muxart, T., Roxo, M.J., Dostal, T., 2010. Rates and spatial variations of soil erosion in Europe: a study based on erosion plot data. Geomorphology 122, 167–177. http://dx.doi.org/10.1016/j.geomorph.2010.06.011.

Chamizo, E., Garcia-Leon, M., Synal, H.A., Suter, M., Wacker, L., 2006. Determination of the Pu-240/Pu-239 atomic ratio in soils from Palomares (Spain) by low-energy accelerator mass spectrometry. Nucl. Instrum. Methods Phys. Res., Sect. B 249, 768–771. http://dx.doi.org/10.1016/j.nimb.2006.03.136.

Chiappini, R., Pointurier, F., Millies-Lacroix, J.C., Lepetit, G., Hemet, P., 1999. Pu-240/Pu-239 isotopic ratios and Pu239 + 240 total measurements in surface and deep waters around Mururoa and Fangataufa atolls compared with Rangiroa atoll (French Polynesia). Sci. Total Environ. 238, 269–276.

Choppin, G.R., 1992. The role of natural organics in radionuclide migration in natural aquifer systems. Radiochim. Acta 58-9, 113–120.

Choppin, G.R., 2006. Actinide speciation in the environment. Mar. Chem. 99, 83–92.

Cizdziel, J.V., Ketterer, M.E., Farmer, D., Faller, S.H., Hodge, V.F., 2008. Pu-239, Pu-240, Pu-241 fingerprinting of plutonium in western US soils using ICPMS: solution and laser ablation measurements. Anal. Bioanal. Chem. 390, 521–530. http://dx.doi.org/10.1007/s00216-007-1741-x.

Cordell, D., Drangert, J.O., White, S., 2009. The story of phosphorus: global food security and food for thought. Glob. Environ. Chang. 19, 292–305. http://dx.doi.org/10.1016/j.gloenvcha.2008.10.009.

Dirican, A., Sahin, M., 2016. Comparison of acid leaching and fusion techniques to determine uranium in soil samples by alpha spectrometry. Appl. Radiat. Isot. 109, 189–192. http://dx.doi.org/10.1016/j.apradiso.2015.11.066.

DOE, 1980. Ecological relationships of plutonium in southwest ecosystems. In: Hanson, W. (Ed.), Transuranic Elements in the Environment. Technical Information Center, U.S. Department of Energy, Springfield, VA (DOE/TIC-22800).

Eikenberg, J., Bajo, S., Hitz, J., Wyer, L., 2001. Environmental radionuclide analyses around nuclear installations in Northern Switzerland. In: Proceedings of the 47th Annual Radiochemical Measurement Conference Honolulu, HI, pp. 1–6.

Elser, J., Bennett, E., 2011. A broken biogeochemical cycle. Nature 478, 29–31.

Evans, R., Boardman, J., 2016a. A reply to Panagos et al., 2016 (Environmental science & policy 59 (2016) 53–57). Environ. Sci. Pol. 60, 63–68. http://dx.doi.org/10.1016/j.envsci.2016.03.004.

Evans, R., Boardman, J., 2016b. The new assessment of soil loss by water erosion in Europe. Panagos P. et al., 2015 Environmental Science & Policy 54, 438–447—a response. Environ. Sci. Pol. 58, 11–15. http://dx.doi.org/10.1016/j.envsci.2015.12.013.

Everett, S.E., Tims, S.G., Hancock, G.J., Bartley, R., Fifield, L.K., 2008. Comparison of Pu and ^{137}Cs as tracers of soil and sediment transport in a terrestrial environment. J. Environ. Radioact. 383–393.

Evrard, O., Pointurier, F., Onda, Y., Chartin, C., Hubert, A., Lepage, H., Pottin, A.C., Lefevre, I., Bonte, P., Laceby, J.P., Ayrault, S., 2014. Novel insights into Fukushima nuclear accident from isotopic evidence of plutonium spread along coastal rivers. Environ. Sci. Technol. 48, 9334–9340. http://dx.doi.org/10.1021/es501890n.

FAO, ITPS, 2015. Status of the world's soil resources (SWSR) - main report. In: Food and Agriculture Organization of the United Nations and Intergovernmental Technical Panel on Soils Rome, Italy, (1–650 pp.).

Fiener, P., Auerswald, K., 2016. Comment on "The new assessment of soil loss by water erosion in Europe" by Panagos et al. (Environmental Science & Policy 54 (2015) 438–447). Environ. Sci. Pol. 57, 140–142. http://dx.doi.org/10.1016/j.envsci.2015.12.012.

Foster, G.R., Hakonson, T.E., 1987. Erosional Losses of Fallout Plutonium, Symposium on Environmental Research for Actinide Elements. Marine Inst.; Pacific Northwest Lab., Richland, WA (USA); Sapelo Island (USA); Georgia University, pp. 7–11 (Nov 1984).

Froehlich, M.B., Dietze, M.M.A., Tims, S.G., Fifield, L.K., 2016. A comparison of fallout 236U and 239Pu uptake by Australian vegetation. J. Environ. Radioact. 151 (Part 3), 558–562. http://dx.doi.org/10.1016/j.jenvrad.2015.06.021.

Gilbert, N., 2009. Environment: the disappearing nutrient. Nature 461, 716–718. http://dx.doi.org/10.1038/461716a.

Hancock, G.J., Leslie, C., Everett, S.E., Tims, S.G., Brunskill, G.J., Haese, R., 2011. Plutonium as a chronomarker in Australian and New Zealand sediments: a comparison with Cs-137. J. Environ. Radioact. 102, 919–929. http://dx.doi.org/10.1016/j.jenvrad.2009.09.008.

Hancock, G.J., Tims, S.G., Fifield, L.K., Webster, I.T., 2014. The release and persistence of radioactive anthropogenic nuclides. In: Waters, C.N., Zalasiewicz, J.A., Williams, M., Ellis, M., Snelling, A.M. (Eds.), Stratigraphical Basis for the Anthropocene. Geological Society Special Publication, Geological Soc Publishing House, Bath, pp. 265–281.

Hardy, E.P., Krey, P.W., Volchok, H.L., 1973. Global inventory and distribution of fallout plutonium. Nature 241, 444–445.

Harley, J.H., 1980. Plutonium in the environment - a review. J. Radiat. Res. 21, 6–7.

Hirose, K., 2012. 2011 Fukushima Dai-ichi nuclear power plant accident: summary of regional radioactive deposition monitoring results. J. Environ. Radioact. 111, 13–17. http://dx.doi.org/10.1016/j.jenvrad.2011.09.003.

Hirose, K., Kikawada, Y., Igarashi, Y., Fujiwara, H., Jugder, D., Matsumoto, Y., Oi, T., Nomura, M., 2017. Plutonium, Cs-137 and uranium isotopes in Mongolian surface soils. J. Environ. Radioact. 166, 97–103. http://dx.doi.org/10.1016/j.jenvrad.2016.01.007.

Hoo, W.T., Fifield, L.K., Tims, S.G., Fujioka, T., Mueller, N., 2011. Using fallout plutonium as a probe for erosion assessment. J. Environ. Radioact. 102, 937–942. http://dx.doi.org/10.1016/j.jenvrad.2010.06.010.

Hou, X.L., Roos, P., 2008. Critical comparison of radiometric and mass spectrometric methods for the determination of radionuclides in environmental, biological and nuclear waste samples. Anal. Chim. Acta 608, 105–139. http://dx.doi.org/10.1016/j.aca.2007.12.012.

Hu, Q.H., Weng, J.Q., Wang, J.S., 2010. Sources of anthropogenic radionuclides in the environment: a review. J. Environ. Radioact. 101, 426–437. http://dx.doi.org/10.1016/j.jenvrad.2008.08.004.

Huh, C.A., Su, C.C., 2004. Distribution of fallout radionuclides (Be-7, Cs-137, Pb-210 and Pu-239,Pu-240) in soils of Taiwan. J. Environ. Radioact. 77, 87–100. http://dx.doi.org/10.1016/j.jenvrad.2004.03.002.

IAEA, 2009. A Procedure for the Rapid Determination of Pu Isotopes and Am-241 in Soil and Sediment Samples by Alpha Spectrometry, Vienna, Austria. International Atomic Energy Agency, Vienna, Austria.

IAEA, 2011. Radioactive Particles in the Environment: Sources, Particle Characterization and Analytical Techniques, IAEA-TECDOC-1663. International Atomic Energy Agency, Vienna, Austria.

IAEA, 2014a. Guidelines for Using Fallout Radionuclides to Assess Erosion and Effectiveness of Soil Conservation Strategies. International Atomic Energy Agency, Vienna, Austria (1–213 pp.).

IAEA, 2014b. A Procedure for the Sequential Determination of Radionculides in Environmental Samples: Liquid Scintillation Counting and Alpha Spectrometry for 90Sr, 241Am and Pu Radioisotopes, Vienna, Austria. International Atomic Energy Agency, Vienna, Austria.

Iurian, A.R., Mabit, L., Cosma, C., 2014. Uncertainty related to input parameters of Cs-137 soil redistribution model for undisturbed fields. J. Environ. Radioact. 136, 112–120. http://dx.doi.org/10.1016/j.jenvrad.2014.05.013.

Iurian, A.R., Phaneuf, M.O., Mabit, L., 2015. Mobility and bioavailability of radionuclides in soils. In: Walther, C., Gupta, D.K. (Eds.), Radionuclides in the Environment: Influence of Chemical Speciation and Plant Uptake on Radionuclide Migration. Springer, pp. 37–59.

Iurian, A.R., Pitois, A., Kis-Benedek, G., Migliori, A., Padilla-Alvarez, R., Ceccatelli, A., 2016. Assessment of measurement result uncertainty in determination of Pb-210 with the focus on matrix composition effect in gamma-ray spectrometry. Appl. Radiat. Isot. 109, 61–69. http://dx.doi.org/10.1016/j.apradiso.2015.11.067.

Joshi, S.R., Shukla, B.S., 1991. The role of the water soil distribution coefficient in the watershed transport of environmental radionuclides. Earth Planet. Sci. Lett. 105, 314–318. http://dx.doi.org/10.1016/0012-821x(91)90139-9.

Jurecic, S., Benedik, L., Planinsek, P., Necemer, M., Kump, P., Pihlar, B., 2014. Analysis of uranium in the insoluble residues after decomposition of soil samples-by various techniques. Appl. Radiat. Isot. 87, 61–65. http://dx.doi.org/10.1016/j.apradiso.2013.11.077.

Kato, H., Onda, Y., Teramage, M., 2012. Depth distribution of Cs-137, Cs-134, and I-131 in soil profile after Fukushima Dai-ichi nuclear power plant accident. J. Environ. Radioact. 111, 59–64. http://dx.doi.org/10.1016/j.jenvrad.2011.10.003.

Kelley, J.M., Bond, L.A., Beasley, T.M., 1999. Global distribution of Pu isotopes and 237Np. Sci. Total Environ. 237–238, 483–500. http://dx.doi.org/10.1016/s0048-9697(99)00160-6.

Ketterer, M.E., Szechenyi, S.C., 2008. Determination of plutonium and other transuranic elements by inductively coupled plasma mass spectrometry: a historical perspective and new frontiers in the environmental sciences. Spectrochim. Acta B At. Spectrosc. 63, 719–737. http://dx.doi.org/10.1016/j.sab.2008.04.018.

Ketterer, M.E., Watson, B.R., Matisoff, G., Wilson, C.G., 2002. Rapid dating of recent aquatic sediments using Pu activities and Pu-240/Pu-239 as determined by quadrupole inductively coupled plasma mass spectrometry. Environ. Sci. Technol. 36, 1307–1311. http://dx.doi.org/10.1021/es010826g.

Ketterer, M.E., Hafer, K.M., Jones, V.J., Appleby, P.G., 2004a. Rapid dating of recent sediments in Loch Ness: inductively coupled plasma mass spectrometric measurements of global fallout plutonium. Sci. Total Environ. 322, 221–229. http://dx.doi.org/10.1016/j.scitotenv.2003.09.016.

Ketterer, M.E., Hafer, K.M., Link, C.L., Kolwaite, D., Wilson, J., Mietelski, J.W., 2004b. Resolving global versus local/regional Pu sources in the environment using sector ICP-MS. J. Anal. At. Spectrom. 19, 241–245. http://dx.doi.org/10.1039/b302903d.

Ketterer, M.E., Hafer, K.M., Mietelski, J.W., 2004c. Resolving Chernobyl vs. global fallout contributions in soils from Poland using Plutonium atom ratios measured by inductively coupled plasma mass spectrometry. J. Environ. Radioact. 73, 183–201. http://dx.doi.org/10.1016/j.jenvrad.2003.09.001.

Ketterer, M.E., Zheng, J., Yamada, M., 2011. applications of transuranics as tracers and chronometers in the environment. In: Baskaran, M. (Ed.), Handbook of Environmental Isotope Geochemistry. vols. 1 and 2 Springer-Verlag, Berlin (395–417 pp.).

Kim, C.S., Kim, C.K., Martin, P., Sansone, U., 2007. Determination of Pu isotope concentrations and isotope ratio by inductively coupled plasma mass spectrometry: a review of analytical methodology. J. Anal. At. Spectrom. 22, 827–841. http://dx.doi.org/10.1039/b617568f.

Kirchner, G., 2013. Establishing reference inventories of Cs-137 for soil erosion studies: methodological aspects. Geoderma 211, 107–115. http://dx.doi.org/10.1016/j.geoderma.2013.07.011.

Kirchner, G., Bossew, P., De Cort, M., 2012. Radioactivity from Fukushima Dai-ichi in air over Europe; part 2: what can it tell us about the accident? J. Environ. Radioact. 114, 35–40. http://dx.doi.org/10.1016/j.jenvrad.2011.12.016.

Koning, N.B.J., Van Ittersum, M.K., Becx, G.A., Van Boekel, M., Brandenburg, W.A., Van den Broek, J.A., Goudriaan, J., Van Hofwegen, G., Jongeneel, R.A., Schiere, J.B., Smies, M., 2008. Long-term global availability of food: continued abundance or new scarcity? NJAS-Wagen. J. Life Sci. 55, 229–292.

Koo, Y.-H., Yang, Y.-S., Song, K.-W., 2014. Radioactivity release from the Fukushima accident and its consequences: a review. Prog. Nucl. Energy 74, 61–70. http://dx.doi.org/10.1016/j.pnucene.2014.02.013.

Kwong, L.L.W., Gastaud, J., La Rosa, J., Lee, S.H., Povinec, P.P., Wyse, E., 2004. Determination of Pu-241 in marine samples using co-precipitation with rare earth fluoride and liquid scintillation spectrometry. J. Radioanal. Nucl. Chem. 261, 283–289.

Lal, R., Tims, S.G., Fifield, L.K., Wasson, R.J., Howe, D., 2013. Applicability of Pu-239 as a tracer for soil erosion in the wet-dry tropics of northern Australia. Nucl. Instrum. Methods Phys. Res., Sect. B 294, 577–583. http://dx.doi.org/10.1016/j.nimb.2012.07.041.

Lal, R., Fifield, L.K., Tims, S.G., Wasson, R.J., Howe, D., 2015. Using Pu-239 as a tracer for fine sediment sources in the Daly River, Northern Australia. In: Simenel, C., Frohlich, M., Lee, B.Q., Schauries, D. (Eds.), Heavy Ion Accelerator Symposium 2014. EPJ Web of Conferences, E D P Sciences, Cedex A.

Le, M.H., Buddenbaum, J.E., Burns, R.E., Shonka, J.J., Gaffney, S.H., Donovan, E.P., Flack, S.M., Widner, T.E., 2011. An independent review and prioritization of past radionuclide and chemical releases from the Los Alamos National Laboratory - implications for future dose reconstruction studies. J. Environ. Monit. 13, 2735–2747. http://dx.doi.org/10.1039/c1em10374a.

Lee, M.H., Lee, C.W., 1999. Determination of Cs-137, Sr-90 and fallout Pu in the volcanic soil of Korea. J. Radioanal. Nucl. Chem. 239, 471–476. http://dx.doi.org/10.1007/bf02349053.

Lin, W., Chen, L., Yu, W., Ma, H., Zeng, Z., Lin, J., Zeng, S., 2015. Radioactivity impacts of the Fukushima nuclear accident on the atmosphere. Atmos. Environ. 102, 311–322. http://dx.doi.org/10.1016/j.atmosenv.2014.11.047.

Lin, W.H., Chen, L.Q., Yu, W., Ma, H., Zeng, Z., Zeng, S., 2016. Radioactive source terms for the Fukushima nuclear accident. Sci. China Earth Sci. 59, 214–222. http://dx.doi.org/10.1007/s11430-015-5112-8.

Lind, O.C., Oughton, D.H., Salbu, B., Skipperud, L., Sickel, M.A., Brown, J.E., Fifield, L.K., Tims, S.G., 2006. Transport of low (240)Pu/(239)Pu atom ratio plutonium-species in the Ob and Yenisey Rivers to the Kara Sea. Earth Planet. Sci. Lett. 251, 33–43. http://dx.doi.org/10.1016/j.epsl.2006.08.023.

Litaor, M.I., Ibrahim, S.A., 1996. Plutonium association with selected solid phases in soils of Rocky Flats, Colorado, using sequential extraction technique. J. Environ. Qual. 25, 1144–1152. http://dx.doi.org/10.2134/jeq1996.00472425002500050030x.

Lokas, E., Mietelski, J.W., Ketterer, M.E., Kleszcz, K., Wachniew, P., Michalska, S., Miecznik, M., 2013. Sources and vertical distribution of Cs-137, Pu-238, Pu239 + 240 and Am-241 in peat profiles from southwest Spitsbergen. Appl. Geochem. 28, 100–108. http://dx.doi.org/10.1016/j.apgeochem.2012.10.027.

Loughran, R.J., Pennock, D.J., Walling, D.E., 2002. Spatial distribution of caesium-137. In: Handbook for the Assessment of Soil Erosion and Sedimentation Using Environmental Radionuclides. Springer (97–109 pp.).

Lujaniene, G., Plukis, A., Kimtys, E., Remeikis, V., Jankunaite, D., Ogorodnikov, B.I., 2002. Study of Cs-137, Sr-90, Pu-239,Pu-240, Pu-238 and Am-241 behavior in the Chernobyl soil. J. Radioanal. Nucl. Chem. 251, 59–68. http://dx.doi.org/10.1023/a:1015185011201.

Mabit, L., Benmansour, M., Walling, D.E., 2008. Comparative advantages and limitations of the fallout radionuclides Cs-137, Pb-210(ex) and Be-7 for assessing soil erosion and sedimentation. J. Environ. Radioact. 99, 1799–1807. http://dx.doi.org/10.1016/j.jenvrad.2008.08.009.

Mabit, L., Meusburger, K., Fulajtar, E., Alewell, C., 2013. The usefulness of Cs-137 as a tracer for soil erosion assessment: a critical reply to Parsons and Foster (2011). Earth Sci. Rev. 127, 300–307. http://dx.doi.org/10.1016/j.earscirev.2013.05.008.

Mabit, L., Benmansour, M., Abril, J.M., Walling, D.E., Meusburger, K., Iurian, A.R., Bernard, C., Tarjan, S., Owens, P.N., Blake, W.H., Alewell, C., 2014. Fallout Pb-210 as a soil and sediment tracer in catchment sediment budget investigations: a review. Earth Sci. Rev. 138, 335–351. http://dx.doi.org/10.1016/j.earscirev.2014.06.007.

Masarik, J., 2010. Origin and distribution of radionuclides in the continental environment. In: Froehlich, K. (Ed.), Environmental Radionuclides: Tracers and Timers of Terrestrial Processes. Radioactivity in the Environmentpp. 1–25.

Matisoff, G., Whiting, P.J., 2011. Measuring Soil Erosion Rates Using Natural (Be-7, Pb-210) and Anthropogenic (Cs-137, Pu-239, Pu-240) Radionuclides. Springer-Verlag, Berlin, Berlin.

Matisoff, G., Ketterer, M.E., Rosén, K., Mietelski, J.W., Vitko, L.F., Persson, H., Lokas, E., 2011. Downward migration of Chernobyl-derived radionuclides in soils in Poland and Sweden. Appl. Geochem. 26, 105–115. http://dx.doi.org/10.1016/j.apgeochem.2010.11.007.

Meusburger, K., Mabit, L., Ketterer, M., Park, J.H., Sandor, T., Porto, P., Alewell, C., 2016. A multi-radionuclide approach to evaluate the suitability of Pu239 + 240 as soil erosion tracer. Sci. Total Environ. 566, 1489–1499. http://dx.doi.org/10.1016/j.scitotenv.2016.06.035.

Meusburger, K., Porto, P., Mabit, L., La Spada, C., Arata, L., Alewell, C., 2017. Excess lead-210 and plutonium-239 + 240: two suitable radiogenic soil erosion tracers for mountain grassland sites. Land Degrad. Dev (submitted).

Michel, H., Ketterer, M.E., Barci-Funel, G., 2007. ICP-MS analysis of plutonium activities and Pu-240/Pu-239 ratio in alpha spectrometry planchet deposits. J. Radioanal. Nucl. Chem. 273, 485–490. http://dx.doi.org/10.1007/s10967-007-6673-6.

Michelotti, E.A., Whicker, J.J., Eisele, W.F., Breshears, D.D., Kirchner, T.B., 2013. Modeling aeolian transport of soil-bound plutonium: considering infrequent but normal environmental disturbances is critical in estimating future dose. J. Environ. Radioact. 120, 73–80. http://dx.doi.org/10.1016/j.jenvrad.2013.01.011.

Mietelski, J.W., Was, B., 1995. Plutonium from Chernobyl in Poland. Appl. Radiat. Isot. 46, 1203–1211. http://dx.doi.org/10.1016/0969-8043(95)00162-7.

Mitchell, P.I., Vintro, L.L., Dahlgaard, H., Gasco, C., SanchezCabeza, J.A., 1997.

Perturbation in the Pu-240/Pu-239 global fallout ratio in local sediments following the nuclear accidents at Thule (Greenland) and Palomares (Spain). Sci. Total Environ. 202, 147–153. http://dx.doi.org/10.1016/s0048-9697(97)00111-3.

Moreno, J., LaRosa, J.J., Danesi, P.R., Burns, K., Vajda, N., Sinojmeri, M., 1998. Determination of 241Pu by LSC in combined procedure for Pu radionuclides, 241Am and 90Sr analysis in environmental samples. Radioact. Radiochem. 9, 35–44.

Muller, R.N., Sprugel, D.G., Kohn, B., 1978. Erosional transport and deposition of plutonium and cesium in 2 small midwestern watersheds. J. Environ. Qual. 7, 171–174.

Muramatsu, Y., Ruhm, W., Yoshida, S., Tagami, K., Uchida, S., Wirth, E., 2000. Concentrations of Pu-239 and Pu-240 and their isotopic ratios determined by ICP-MS in soils collected from the Chernobyl 30-km zone. Environ. Sci. Technol. 34, 2913–2917. http://dx.doi.org/10.1021/es0008968.

Nelson, D.M., Lovett, M.B., 1978. Oxidation state of plutonium in the Irish Sea. Nature 276, 599–601.

Neu, M.P., Ruggiero, C.E., Francis, A.J., 2002. Bioinorganic chemistry of plutonium and interactions of plutonium with microorganisms and plants. In: Hoffman, D. (Ed.), Advances in Plutonium Chemistry 1967–2000. American Nuclear Society la Grange Park Illinois and University Research alliance, Amarillo, Texas, pp. 169–211.

Nisbet, A.F., Salbu, B., Shaw, S., 1993. Association of radionuclides with different molecular-size fractions in soil solution - implications for plant uptake. J. Environ. Radioact. 18, 71–84. http://dx.doi.org/10.1016/0265-931x(93)90066-g.

Nishihara, K., Iwamoto, H., and Suyama, K.: Estimation of Fuel Compositions in Fukushima-Daiichi Nuclear Power Plant, JAEA-Data/Code 2012, http://jolissrch-inter.tokai-sc.jaea.go.jp/pdfdata/JAEA-Data-Code-2012-018.pdf (Date of access: 29/02/2016). 2012.

Orr, B., Schoppner, M., Tinker, R., Plastino, W., 2013. Detection of radioxenon in Darwin, Australia following the Fukushima Dai-ichi nuclear power plant accident. J. Environ. Radioact. 126, 40–44. http://dx.doi.org/10.1016/j.jenvrad.2013.07.002.

Osvath, I., Tarjan, S., Pitois, A., Groening, M., Osborn, D., 2016. IAEA's ALMERA network: supporting the quality of environmental radioactivity measurements. Appl. Radiat. Isot. 109, 90–95. http://dx.doi.org/10.1016/j.apradiso.2015.12.062.

Oughton, D.H., Fifield, L.K., Day, J.P., Cresswell, R.C., Skipperud, L., Di Tada, M.L., Salbu, B., Strand, P., Drozcho, E., Mokrov, Y., 2000. Plutonium from Mayak: measurement of isotope ratios and activities using accelerator mass spectrometry. Environ. Sci. Technol. 34, 1938–1945. http://dx.doi.org/10.1021/es990847z.

Paatero, J., Hameri, K., Jaakkola, T., Jantunen, M., Koivukoski, J., Saxen, R., 2010. Airborne and deposited radioactivity from the Chernobyl accident - a review of investigations in Finland. Boreal Environ. Res. 15, 19–33.

Panagos, P., Meusburger, K., Van Liedekerke, M., Alewell, C., Hiederer, R., Montanarella, L., 2014. Assessing soil erosion in Europe based on data collected through a European network. Soil Sci. Plant Nutr. 60, 15–29. http://dx.doi.org/10.1080/00380768.2013.835701.

Panagos, P., Borrelli, P., Poesen, J., Ballabio, C., Lugato, E., Meusburger, K., Montanarella, L., Alewell, C., 2015. The new assessment of soil loss by water erosion in Europe. Environ. Sci. Pol. 54, 438–447. http://dx.doi.org/10.1016/j.envsci.2015.08.012.

Panagos, P., Borrelli, P., Poesen, J., Meusburger, K., Ballabio, C., Lugato, E., Montanarella, L., Alewell, C., 2016a. Reply to "The new assessment of soil loss by water erosion in Europe. Panagos P. et al., 2015 Environ. Sci. Policy 54, 438–447-A response" by Evans and Boardman Environ. Sci. Policy 58, 11–15. Environ. Sci. Pol. 59, 53–57. http://dx.doi.org/10.1016/j.envsci.2016.02.010.

Panagos, P., Borrelli, P., Poesen, J., Meusburger, K., Ballabio, C., Lugato, E., Montanarella, L., Alewell, C., 2016b. Reply to the comment on "The new assessment of soil loss by water erosion in Europe" by Fiener & Auerswald. Environ. Sci. Pol. 57, 143–150. http://dx.doi.org/10.1016/j.envsci.2015.12.011.

Parsons, A.J., Foster, I.D.L., 2011. What can we learn about soil erosion from the use of 137Cs? Earth-Sci. Rev. 108, 13.

Penrose, W.R., Metta, D.N., Hylko, J.M., Rinckel, L.A., 1987. The reduction of plutonium (V) by aquatic sediments. J. Environ. Radioact. 5, 169–184. http://dx.doi.org/10.1016/0265-931X(87)90033-6.

Pentreath, R.J., 1995. The analysis of pu in environmental-samples - a brief historical-perspective. Appl. Radiat. Isot. 46, 1279–1285. http://dx.doi.org/10.1016/0969-8043(95)00171-9.

Perkins, R.W., Thomas, C.W., 1980. Worldwide fallout. In: Transuranic Elements in the Environment. In: Hanson, W.C. (Ed.), Tech. Inf. Center US Department of Energy, pp. 53–82.

Pitois, A., Osvath, I., Tarjan, S., Groening, M., Osborn, D., 2016. Role of the IAEA's ALMERA network in harmonization of analytical procedures applicable worldwide for radiological emergencies. Radiat. Prot. Environ. 39, 53–61. http://dx.doi.org/10.4103/0972-0464.190396.

Poreba, G.J., Bluszcz, A., 2008. Influence of the parameters of models used to calculate soil erosion based on Cs-137 tracer. Geochronometria 32, 21–27. http://dx.doi.org/10.2478/v10003-008-0026-5.

Porto, P., Walling, D.E., Alewell, C., Callegari, G., Mabit, L., Mallimo, N., Meusburger, K., Zehringer, M., 2014. Use of a Cs-137 re-sampling technique to investigate temporal changes in soil erosion and sediment mobilisation for a small forested catchment in southern Italy. J. Environ. Radioact. 138, 137–148. http://dx.doi.org/10.1016/j.jenvrad.2014.08.007.

Porto, P., Walling, D.E., Cogliandro, V., Callegari, G., 2016. Exploring the potential for using Pb-210(ex) measurements within a re-sampling approach to document recent changes in soil redistribution rates within a small catchment in southern Italy. J. Environ. Radioact. 164, 158–168. http://dx.doi.org/10.1016/j.jenvrad.2016.06.026.

Qiao, J.X., Hou, X.L., Miro, M., Roos, P., 2009. Determination of plutonium isotopes in waters and environmental solids: a review. Anal. Chim. Acta 652, 66–84. http://dx.doi.org/10.1016/j.aca.2009.03.010.

Qiao, J.X., Hou, X.L., Roos, P., Miro, M., 2011. Rapid isolation of plutonium in environmental solid samples using sequential injection anion exchange chromatography followed by detection with inductively coupled plasma mass spectrometry. Anal. Chim. Acta 685, 111–119. http://dx.doi.org/10.1016/j.aca.2010.10.029.

Qiao, J.X., Hansen, V., Hou, X.L., Aldahan, A., Possnert, G., 2012. Speciation analysis of I-129, Cs-137, Th-232, U-238, Pu-239 and Pu-240 in environmental soil and sediment. Appl. Radiat. Isot. 70, 1698–1708. http://dx.doi.org/10.1016/j.apradiso.2012.04.006.

Rollin, S., Sahli, H., Holzer, R., Astner, M., Burger, M., 2009. PU and NP analysis of soil and sediment samples with ICP-MS. Appl. Radiat. Isot. 67, 821–827. http://dx.doi.org/10.1016/j.apradiso.2009.01.041.

Rosner, G., Hotzl, H., Winkler, R., 1992. Determination of Pu-241 by low-level beta-proportional counting - application to Chernobyl fallout samples and comparison with the Am-241 buildup method. J. Radioanal. Nucl. Chem. Artic. 163, 225–233. http://dx.doi.org/10.1007/bf02034796.

Ryan, J.N., Illangasekare, T.H., Litaor, M.I., Shannon, R., 1998. Particle and plutonium mobilization in macroporous soils during rainfall simulations. Environ. Sci. Technol. 32, 476–482. http://dx.doi.org/10.1021/es970339u.

Sanders, C.J., Eyre, B.D., Santos, I.R., Machado, W., Luiz-Silva, W., Smoak, J.M., Breithaupt, J.L., Ketterer, M.E., Sanders, L., Marotta, H., Silva, E., 2014. Elevated rates of organic carbon, nitrogen, and phosphorus accumulation in a highly impacted mangrove wetland. Geophys. Res. Lett. 41, 2475–2480. http://dx.doi.org/10.1002/2014gl059789.

Sanders, C.J., Santos, I.R., Maher, D.T., Breithaupt, J.L., Smoak, J.M., Ketterer, M., Call, M., Sanders, L., Eyre, B.D., 2016. Examining (239) + (240)Pu, Pb-210 and historical events to determine carbon, nitrogen and phosphorus burial in mangrove sediments of Moreton Bay, Australia. J. Environ. Radioact. 151, 623–629. http://dx.doi.org/10.1016/j.jenvrad.2015.04.018.

Schimmack, W., Auerswald, K., Bunzl, K., 2001. Can Pu239 + 240 replace Cs-137 as an erosion tracer in agricultural landscapes contaminated with Chernobyl fallout? J. Environ. Radioact. 53, 41–57. http://dx.doi.org/10.1016/s0265-931x(00)00117-x.

Schimmak, W., Auerswald, K., Bunzl, K., 2002. Estimation of soild erosion and deposition rates at an agricultural site in Bavaria, Germany, as derived from fallout radiocesium and plutonium as tracers. Naturwissenschaften 89, 43–46.

Schwantes, J.M., Orton, C.R., Clark, R.A., 2012. Analysis of a nuclear accident: fission and activation product releases from the Fukushima Daiichi nuclear facility as remote indicators of source identification, extent of release, and state of damaged spent nuclear fuel. Environ. Sci. Technol. 46, 8621–8627. http://dx.doi.org/10.1021/es300556m.

Smith, B.S., Child, D.P., Fierro, D., Harrison, J.J., Heijnis, H., Hotchkis, M.A.C., Johansen, M.P., Marx, S., Payne, T.E., Zawadzki, A., 2016. Measurement of fallout radionuclides, Pu-239,Pu-240 and Cs-137, in soil and creek sediment: Sydney Basin, Australia. J. Environ. Radioact. 151, 579–586. http://dx.doi.org/10.1016/j.jenvrad.2015.06.015.

Steinhauser, G., 2014. Fukushima's forgotten radionuclides: a review of the understudied radioactive emissions. Environ. Sci. Technol. 48, 4649–4663. http://dx.doi.org/10.1021/es405654c.

Sutherland, R.A., 1996. Caesium-137 soil sampling and inventory variability in reference locations: a literature survey. Hydrol. Process. 10, 43–53.

Sutherland, R.A., 1998. The potential for reference site resampling in estimating sediment redistribution and assessing landscape stability by the caesium-137 method. Hydrol. Process. 12, 995–1007.

Taylor, D.M., 2001. Environmental plutonium - creation of the universe to twenty-first century mankind. In: Kudo, A. (Ed.), Plutonium in the Environment, (1–14 pp.).

Taylor, A., Blake, W.H., Smith, H.G., Mabit, L., Keith-Roach, M.J., 2013. Assumptions and challenges in the use of fallout beryllium-7 as a soil and sediment tracer in river basins. Earth Sci. Rev. 126, 85–95. http://dx.doi.org/10.1016/j.earscirev.2013.08.002.

Tims, S.G., Everett, S.E., Fifield, L.K., Hancock, G.J., Bartley, R., 2010a. Plutonium as a tracer of soil and sediment movement in the Herbert River, Australia. Nucl. Instrum. Methods Phys. Res., Sect. B 268, 1150–1154. http://dx.doi.org/10.1016/j.nimb.2009.10.121.

Tims, S.G., Pan, S.M., Zhang, R., Fifield, L.K., Wang, Y.P., Gao, J.H., 2010b. Plutonium AMS measurements in Yangtze River estuary sediment. Nucl. Instrum. Methods Phys. Res., Sect. B 268, 1155–1158. http://dx.doi.org/10.1016/j.nimb.2009.10.122.

Tims, S.G., Fifield, L.K., Hancock, G.J., Lal, R.R., Hoo, W.T., 2013. Plutonium isotope measurements from across continental Australia. Nucl. Instrum. Methods Phys. Res., Sect. B 294, 636–641. http://dx.doi.org/10.1016/j.nimb.2012.07.010.

Tims, S.G., Froehlich, M.B., Fifield, L.K., Wallner, A., De Cesare, M., 2016. 236U and 239,240Pu ratios from soils around an Australian nuclear weapons test site. J. Environ. Radioact. 151 (Part 3), 563–567. http://dx.doi.org/10.1016/j.jenvrad.2015.06.020.

Turner, M., Rudin, M., Cizdziel, J., Hodge, V., 2003. Excess plutonium in soil near the Nevada Test Site, USA. Environ. Pollut. 125, 193–203. http://dx.doi.org/10.1016/s0269-7491(03)00071-x.

UNSCEAR, 2000. Sources and Effects of Ionizing Radiation. United Nations Scientific Committee on the Effects of Atomic Radiation, New York (1–213 pp.).

Vajda, N., Kim, C.K., 2010. Determination of Pu isotopes by alpha spectrometry: a review of analytical methodology. J. Radioanal. Nucl. Chem. 283, 203–223. http://dx.doi.org/10.1007/s10967-009-0342-x.

Vajda, N., Kim, C.K., 2011. Determination of transuranium isotopes (Pu, Np, Am) by radiometric techniques: a review of analytical methodology. Anal. Chem. 83, 4688–4719. http://dx.doi.org/10.1021/ac2008288.

Van Pelt, R.S., Ketterer, M.E., 2013. Use of anthropogenic radioisotopes to estimate rates of soil redistribution by wind II: the potential for future use of 239 + 240Pu. Aeolian Res. 9, 103–110. http://dx.doi.org/10.1016/j.aeolia.2013.01.004.

Vanmaercke, M., Poesen, J., Verstraeten, G., de Vente, J., Ocakoglu, F., 2011. Sediment yield in Europe: spatial patterns and scale dependency. Geomorphology 130, 142–161. http://dx.doi.org/10.1016/j.geomorph.2011.03.010.

Varga, Z., Suranyi, G., Vajda, N., Stefanka, Z., 2007. Improved sample preparation method for environmental plutonium analysis by ICP-SFMS and alpha-spectrometry. J. Radioanal. Nucl. Chem. 274, 87–94. http://dx.doi.org/10.1007/s10967-006-6908-y.

Wakabayashi, S., Itoh, S., Kihou, N., Matsunami, H., Hachinohe, M., Hamamatsu, S., Takahashi, S., 2016. Influence of water management and fertilizer application on Cs-137 and Cs-133 uptake in paddy rice fields. J. Environ. Radioact. 157, 102–112. http://dx.doi.org/10.1016/j.jenvrad.2016.03.010.

Walling, D.E., 2006. Tracing versus monitoring: new challenges and opportunities in erosion and sediment delivery research. In: Owens, P.N., Collins, A.J. (Eds.), Soil Erosion and Sediment Redistribution in River Catchments. CABI, Wallingford.

Walling, D.E., 2012. The use of fallout radionuclides in the study of erosion and sedimentation. In: Meyers, R.A. (Ed.), Encyclopedia of Sustainability, Science and Technology. Springer Verlag, Berlin.

Walling, D.E., Quine, T.A., 1990. Calibration of Caesium-137 measurements to provide quantitative erosion rate data. Land Degrad. Rehabil. 2, 161–175.

Walling, D.E., He, Q., Blake, W., 1999. Use of ^{7}Be and ^{137}Cs measurements to document short- and medium-term rates of water-induced soil erosion on agricultural land. Water Resour. Res. 35, 3865–3874.

Walling, D.E., He, Q., Appleby, P.G., 2002. Conversion models for use in soil-erosion, soil-redistribution and sedimentation investigations. In: Zapata, F. (Ed.), Handbook for the Assessment of Soil Erosion and Sedimentation Using Environmental Radionuclides, pp. 111–164 (Kluwer, Dordrecht. Netherlands).

Walling, D.E., Y, Z., He, Q., 2014. Conversion models and related software. In: IAEA (Ed.), Guidelines for Using Fallout Radionuclides to Assess Erosion and Effectiveness of Soil Conservation Strategies. International Atomic Energy Agency, Vienna, pp. 125–148.

Xu, Y.H., Qiao, J.X., Hou, X.L., Pan, S.M., 2013. Plutonium in soils from Northeast China and its potential application for evaluation of soil erosion. Sci Rep 3, 8. http://dx.doi.org/10.1038/srep03506.

Xu, C., Athon, M., Ho, Y.F., Chang, H.S., Zhang, S.J., Kaplan, D.I., Schwehr, K.A., DiDonato, N., Hatcher, P.G., Santschi, P.H., 2014a. Plutonium immobilization and remobilization by soil mineral and organic matter in the far-field of the Savannah River Site, US. Environ. Sci. Technol. 48, 3186–3195. http://dx.doi.org/10.1021/es404951y.

Xu, Y., Qiao, J., Hou, X., Pan, S., Roos, P., 2014b. Determination of plutonium isotopes (238Pu, 239Pu, 240Pu, 241Pu) in environmental samples using radiochemical separation combined with radiometric and mass spectrometric measurements. Talanta 119, 590–595. http://dx.doi.org/10.1016/j.talanta.2013.11.061.

Xu, Y., Qiao, J., Pan, S., Hou, X., Roos, P., Cao, L., 2015. Plutonium as a tracer for soil erosion assessment in northeast China. Sci. Total Environ. 511, 176–185. http://dx.doi.org/10.1016/j.scitotenv.2014.12.006.

Xu, Y., Pan, S., Wu, M., Zhang, K., Hao, Y., 2017. Association of Plutonium isotopes with natural soil particles of different size and comparison with 137Cs. Sci. Total Environ. 581–582, 541–549. http://dx.doi.org/10.1016/j.scitotenv.2016.12.162.

Yamamoto, M., Sakaguchi, A., Ochiai, S., Takada, T., Hamataka, K., Murakami, T., Nagao, S., 2014. Isotopic Pu, Am and Cm signatures in environmental samples contaminated by the Fukushima Dai-ichi nuclear power plant accident. J. Environ. Radioact. 132, 31–46. http://dx.doi.org/10.1016/j.jenvrad.2014.01.013.

Zapata, F., 2003. The use of environmental radionuclides as tracers in soil erosion and sedimentation investigations: recent advances and future developments. Soil Tillage Res. 69, 3–13.

Zhang, K.X., Pan, S.M., Xu, Y.H., Cao, L.G., Hao, Y.P., Wu, M.M., Xu, W., Ren, S., 2016. Using Pu239 + 240 atmospheric deposition and a simplified mass-balance model to re-estimate the soil erosion rate: a case study of Liaodong Bay in China. J. Radioanal. Nucl. Chem. 307, 599–604. http://dx.doi.org/10.1007/s10967-015-4208-0.

Zheng, J., Tagami, K., Watanabe, Y., Uchida, S., Aono, T., Ishii, N., Yoshida, S., Kubota, Y., Fuma, S., Ihara, S., 2012. Isotopic evidence of plutonium release into the environment from the Fukushima DNPP accident. Sci Rep 2. http://dx.doi.org/10.1038/srep00304.

Zollinger, B., Alewell, C., Kneisel, C., Meusburger, K., Brandova, D., Kubik, P., Schaller, M., Ketterer, M., Egli, M., 2015. The effect of permafrost on time-split soil erosion using radionuclides (Cs-137, Pu239 + 240, meteoric Be-10) and stable isotopes (delta C-13) in the eastern Swiss Alps. J. Soils Sediments 15, 1400–1419. http://dx.doi.org/10.1007/s11368-014-0881-9.