Determining ^{241}Pu in environmental samples: case studies in alpine soils

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^{241}Pu / ^{241}Pu/^{239,240}Pu / *Alpine soils* /
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Summary. A procedure was developed for determining ^{241}Pu activity in environmental samples. This beta emitter isotope of plutonium was measured by ultra low level liquid scintillation, after several separation and purification steps that involved the use of a highly selective extraction chromatographic resin (Eichrom-TEVA). Due to the lack of reference material for ^{241}Pu, the method was nevertheless validated using four IAEA reference sediments with information values for ^{241}Pu. Next, the method was used to determine the ^{241}Pu activity in alpine soils of Switzerland and France. The ^{241}Pu/^{239,240}Pu and ^{238}Pu/^{239,240}Pu activity ratios confirmed that Pu contamination in the tested alpine soils originated mainly from global fallout from nuclear weapon tests conducted in the fifties and sixties. Estimation of the date of the contamination, using the ^{241}Pu/^{241}Am age-dating method, further confirmed this origin. However, the ^{241}Pu/^{241}Am dating method was limited to samples where Pu-Am fractionation was insignificant. If any, the contribution of the Chernobyl accident is negligible.

1. Introduction

Plutonium (Pu) found in the environment comes from fallout from past nuclear weapon tests (NWT), accidents in nuclear facilities (*e.g.* Chernobyl NPP) as well as normal discharges from reprocessing plants [1]. Over the last few decades, major attention has been paid to the alpha-emitting Pu radioisotopes (^{238}Pu, ^{239}Pu and ^{240}Pu) which are characterized by high radio-toxicity and long physical and biological half-lives. However, in the short term, the largest contribution to the total Pu radioactivity level in the environment comes from the beta-emitting ^{241}Pu. Although ^{241}Pu is radiologically not very important (low energy beta-emitter with a short half-life of 14.33 a), it decays to ^{241}Am which is highly radio-toxic (alpha-emitter, with a relatively long half-life of 432.6 a). ^{241}Am subsequently decays to ^{237}Np, which is also an alpha-emitter with an extremely long half life of 2.14 million years. Therefore, establishing a procedure for the accurate determination of ^{241}Pu is of particular interest, especially as it relates to generating a precise estimation of the long-term radiation dose to the population.

Moreover, the ^{241}Pu/^{239,240}Pu activity ratio is a fingerprint which reveals the origin of Pu contamination. For example, NWT fallout was characterized by a ^{241}Pu/^{239,240}Pu activity ratio of about 12–16 for the latitudes 40–50° North in 1963 [1–3]. For Chernobyl deposition, in contrast, the ^{241}Pu activity was higher by a factor of around 70–100 than that of ^{239,240}Pu at the time of the accident [1, 3–7]. Weapons grade plutonium, which is another important source of Pu in the environment, is characterized by a much lower ^{241}Pu/^{239,240}Pu activity ratio of about 0.5–4 [8–10]. This is why the simultaneous determination of ^{241}Pu and the alpha-emitter Pu radioisotopes is a useful tool for tracing sources of Pu in the environment.

However, as will be explained further below, the determination of ^{241}Pu has high radioanalytical requirements that have impeded a widespread quantification of this radioisotope in environmental samples. ^{241}Pu is a beta-emitter of very low energy ($E_{\max} = 20.8\,\mathrm{keV}$) and short half-life of 14.33 a; therefore state-of-the-art counting systems are required for determining the trace levels typically found in the environment. Over the last few decades, direct and indirect methods have been developed for its determination. The indirect methods are mainly based on the ^{241}Am built up in Pu originally electrodeposited on stainless steel discs [3]. This method is hindered by a lack of accuracy in comparison to direct methods because of a high uncertainty and high detection limit [5], and it also requires a lengthy storage of the samples before the analysis [5, 7]. Among the direct methods, low-level liquid scintillation counting (LSC) is most commonly used for quantifying ^{241}Pu [11–15]. New generations of LSC systems discriminate α and β events based on the differences in the de-excitation times of the triplet and singlet states in the solvent caused by high-energy α-particles and β particles respectively. This permits the measurement of the low-energy β particles of ^{241}Pu in the presence of the other Pu α-emitters. Recently, atom counting of ^{241}Pu by ICP-MS has also been possible in environmental samples [16–20]. However, a major drawback of ICP-MS is the high detection limit of 2–4 Bq/kg [17, 20] compared to LSC which has detection limits as low as 0.1 Bq/kg (this work).

Moreover, there is a lack of reference materials with a certified activity value for ^{241}Pu. For this reason, vali-

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dating the radioanalytical method is currently difficult. The best approach is to use environmental reference materials with information values for ^{241}Pu. Furthermore, a certified reference solution of ^{241}Pu is not readily available in the laboratories for the efficiency calibration of the LSC systems. To overcome this problem, some authors derive the counting efficiency of ^{241}Pu from a ^{3}H efficiency curve (*e.g.* CIEMAT/NIST efficiency tracing method [21]). Finally, as most environmental samples have low levels of ^{241}Pu, a high degree of radiochemical purification is required in order to eliminate interferences from other environmental radionuclides. This has been successfully achieved by separation and purification steps involving the use of ion chromatography or liquid–liquid extraction methods [5, 12, 13].

The first aim of this work was to develop a procedure for determining ^{241}Pu activity in environmental samples, and to quantify ^{241}Pu in alpine soils of France and Switzerland (Fig. 1). A two-step approach is presented in which alpha spectrometry is used for determining the alpha emitting Pu radionuclides (^{239,240}Pu, ^{238}Pu) and LSC for the beta emitting ^{241}Pu. Electrodeposited Pu alpha sources, already prepared within the framework of previous studies of alpine soils, were re-used in the proposed radiochemical procedure and their content of ^{241}Pu measured. The activity of ^{239,240}Pu, ^{238}Pu and ^{241}Am in the Alpine soils of France and Switzerland have been published elsewhere [22, 23].

A second aim of this study was the determination of the source or origin of the Pu contamination in the Alpine soils of France and Switzerland. The soil is the primary receptor of atmospheric radioactive fallout and, because of the strong binding interaction with soil particles, the isotopes are little fractionated [24, 25]. Therefore, the activity ratios ^{241}Pu/^{239,240}Pu and ^{238}Pu/^{239,240}Pu in soil samples were used to determine the origin (source) of Pu in the alpine sites. Furthermore, the ^{241}Pu/^{241}Am activity ratios were used to determine the age of the Pu contamination, which is also an important data for distinguishing Pu sources. The applicability of the ^{241}Pu/^{241}Am age-dating method was tested in reference materials which have well-known Pu contamination dates.

2. Materials and methods

2.1 Reagents and radioisotope tracers

All reagents used in the experiments were of analytical grade (Fluka, Buchs, Switzerland). ^{242}Pu and ^{243}Am tracer solutions, provided by the D.I. Mendeleev Institute for Metrology (VNIIM), were used to spike the samples. The highly-selective extraction chromatography resins TEVA, DGA and TRU were provided by Triskem International (Bruz, France) and the ion exchange chromatography resin AG 1 × 8 by BIO-RAD Laboratories (Switzerland).

2.2 Study sites

Two alpine regions of Switzerland and France were selected for this study based mainly on two facts: firstly, the regions were relatively highly affected by the radioactive fallout in comparison with other low altitude regions; and secondly, they have been intensively investigated for other fallout radioisotopes [22, 23, 26–28].

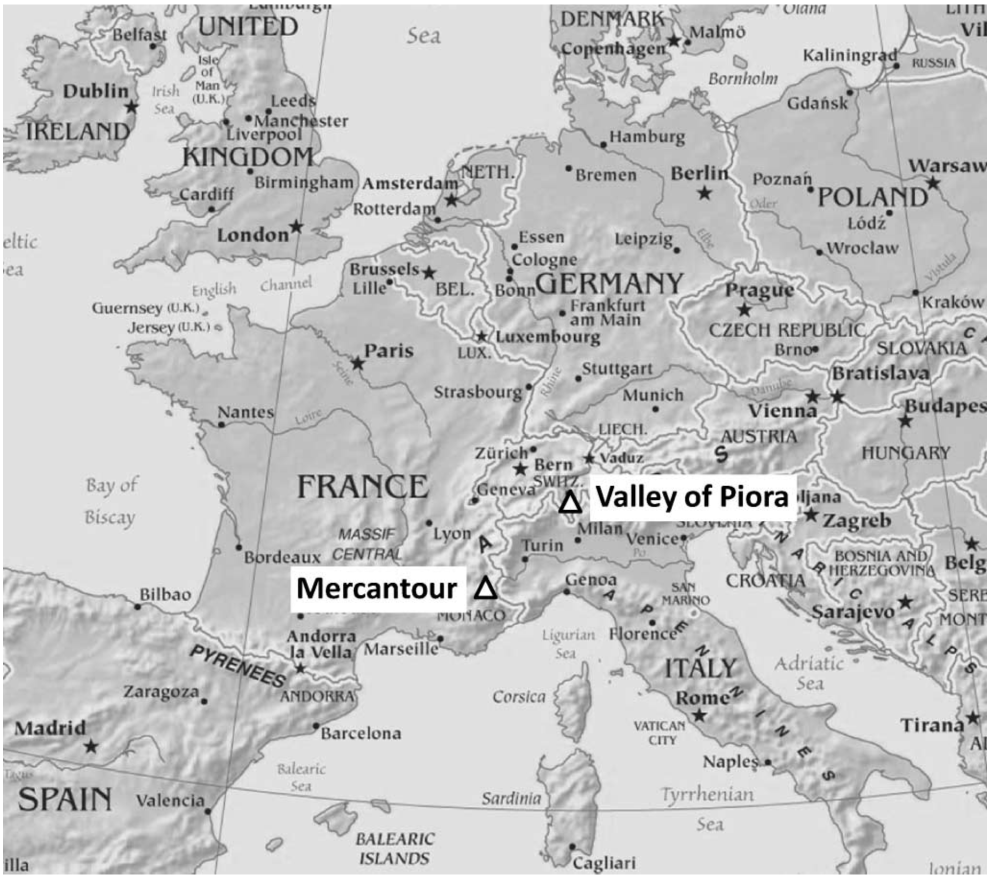

Fig. 1. Location of the study sites of Piora (Switzerland), and Mercantour (France).

The first study site is located in the Valley of Piora, which is a landlocked alpine valley of the Gotthard Massif in Southern Switzerland (Fig. 1). Annual precipitation averages approximately 1400 mm, and the mean temperature is 0 °C (MeteoSwiss, 2009). Snowfall amounts to up to 70% of the yearly precipitation. Snow depth often exceeds 4 m in January and February, and snow cover usually lasts until the end of May or mid-June depending on orientation, slope and wind exposure. Glacial deposits, moraines, landslides and accumulations of dolomite 'sand' have resulted in a mosaic of different soils. In the present study, a meadow, a wetland and a peat soil were investigated. The main characteristics of these soils have been described in other studies [23, 28].

The second site investigated is located in the Mercantour Massif, in the southern part of the Western Alps in France (Fig. 1). The area is a peat land located at an altitude of about 2200 m, with a total surface of nearly 10 000 m^2. In the region, the mean annual precipitation varies between 1000 to 1500 mm, with about one third in the form of snow [26]. The soils have been well-characterized in terms of their chemical and physical properties [22, 27]. A typical feature of these soils is their high content of organic matter, which amounts to up to 78% of the total weight at some depths. The soil texture is fine with a higher content of clays and silts compared to sands.

In the framework of previous studies, the soil samples for radioisotope analyses were collected from undisturbed areas of Mercantour (between 2002 and 2004 [22]), and the Valley of Piora (between 2006 and 2008 [23, 28]). The soil cores, up to 35–40 cm depth, were sectioned horizontally at intervals of 2 to 5 cm. The samples were dried at 105 °C and sieved at 2 mm. Then, they were crushed and ashed at 550 °C for 48 h. The samples were well homogenized, and then subsamples of several grams were taken for the radiochemical analysis.

2.3 Separation of Pu and Am for alpha spectrometry: previous studies

The radiochemical separation of Pu and Am and their measurements by alpha spectrometry were described in Solovitch-Vella *et al.* [22] and Luisier *et al.* [29]. Briefly, all the samples were digested using high-pressure microwave digestion. For the separation and purification of Pu and Am, two different radiochemical methods were applied. The first one combined the ion exchange resin AG 1 × 8 and the extraction chromatography resins TEVA and TRU (Mercantour samples [22]). The second method was based on the use of the extraction chromatographic resins TEVA and DGA (The Valley of Piora samples [29]). The alpha sources were prepared by electrodeposition on stainless steel plates using the method described by Bajo and Eikenberg [30]. High-resolution alpha spectrometry was performed on an alpha spectrometer with PIPS detectors (Alpha Analyst, Canberra Electronique, Savagny-le-Temple, France). The Pu and Am alpha sources were measured up to 10^6 s and the spectra were analyzed using GENIE2000. From the alpha-spectra, the activities of ^{239,240}Pu, ^{238}Pu and ^{241}Am, and the yields of the radiochemical separations were determined. The activity of ^{239,240}Pu, ^{238}Pu and ^{241}Am in the Alpine soils of France and Switzerland have been published elsewhere [22, 23].

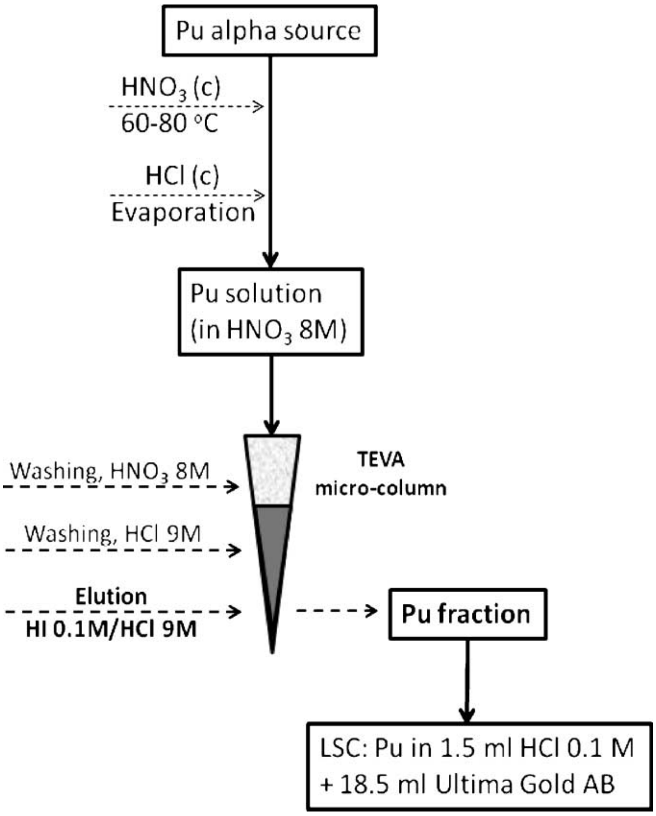

Fig. 2. Flow chart of a part of the radiochemical procedure proposed in this paper: dissolution of the Pu alpha source, and purification of the Pu fraction for LSC.

2.4 Dissolution of the Pu alpha sources

The Pu alpha source, electrodeposited on a stainless steel disc, was leached for 1 h with 10 ml of hot HNO_3 (65%). The solution was evaporated to dryness and the residue was re-dissolved in HCl (32%) in order to dissolve any insoluble particle left from the metal plate. The solution was evaporated to dryness, and the residue was taken in a few ml of HNO_3 (65%). The solution was once again evaporated to dryness and re-dissolved in 8 M HNO_3. The Pu fraction was then purified using extraction chromatography in a homemade small column (pipette tips) prepared with 100 mg of TEVA resin (Fig. 2). This step is crucial for eliminating potential quenchers like Ni or Fe that have been leached from the disc. Pu was retained on the column after an oxidation state adjustment with $NaNO_2$, while iron and other elements passed through it. The Pu was eluted with a solution of 0.1 M HI–9 M HCl, and the fraction evaporated to dryness. The residue was taken in 0.5 ml of 0.1 M HCl, and transferred to a standard 20 ml polyethylene liquid scintillation counter vial (Zinsser). The beaker was washed twice with 0.5 ml of 0.1 M HCl, and the wash solutions added to the vial. 18.5 ml of the scintillation cocktail Ultima Gold AB (Packard, Perkin Elmer) was added and the vial was well shaken before the measurement was taken. The laboratory work required for preparing a batch of six ^{241}Pu samples for LSC, starting from the electrodeposited Pu sources, can be carried out in a few hours. The samples were measured by LSC as explained further below.

2.5 Liquid scintillation counting

LSC was performed in an ultra low level liquid scintillation spectrometer Wallac Quantulus 1220 (PerkinElmer Inc., Finland). This spectrometer distinguishes events originating from alpha and beta decays using a pulse shape analyzer (PSA). A sealed source of ^{152}Eu (37 kBq) is used to determine an external standard quench parameter SQP(E). The LSC Quantulus 1220 was calibrated for the low beta energies of ^{241}Pu using the CIEMAT/NIST method [21]. This method is a standard approach for beta-emitting isotopes, where ^{3}H (half-life: 12.31 a, $E_{\max\beta} = 18.6$ keV) is used as an indicator of the performance of the LSC. The counting efficiency of ^{3}H was determined by measuring a set of quenched ^{3}H standard solutions prepared in the same geometry used for the ^{241}Pu samples. The efficiency of ^{3}H *vs.* the quench parameter SQP(E) curve was determined (Fig. 3). Then, the efficiency of ^{241}Pu ($\varepsilon_{^{241}\mathrm{Pu}}$) was derived from the efficiency of ^{3}H ($\varepsilon_{^{3}\mathrm{H}}$) using the following formula, obtained from the CIEMAT/NIST code CN2004 [21]:

$$\begin{aligned}\varepsilon_{^{241}\mathrm{Pu}} &= 0.299 + 0.8912\varepsilon_{^{3}\mathrm{H}} - 0.0002553\varepsilon_{^{3}\mathrm{H}}^{2} \\ &\quad - 0.00000751\varepsilon_{^{3}\mathrm{H}}^{3} + 0.000000169\varepsilon_{^{3}\mathrm{H}}^{4}\end{aligned}$$

The counting efficiency of ^{241}Pu varies between 30 and 43%, in the expected range of values of the quenching parameter SQP(E) (Fig. 3). The ^{241}Pu curve is then used to determine the counting efficiency in each sample.

The CPMs in the regions of ^{241}Pu and of the alpha-emitters were determined from the LSC sample spectrum, and the background correction was applied. Then, knowing that the detection of alpha particles in the LSC cocktail has approximately 100% efficiency (±1%), the total alpha activity in the source was used as a tracer to determine the radiochemical yield of the procedure. Finally, the activity concentration of ^{241}Pu in the sample ($A_{^{241}\mathrm{Pu}}$; in Bq per kg of dry mass) was calculated as:

$$A_{^{241}\mathrm{Pu}} = \frac{\mathrm{CPM}(^{241}\mathrm{Pu})\,A_{\alpha\text{-total}}}{\mathrm{CPM}_{\mathrm{alphas}}\,\varepsilon_{^{241}\mathrm{Pu}}\,m}$$

where CPM(^{241}Pu) is the counts per minute in the ^{241}Pu region of interest – ROI (channels 60–220), $\mathrm{CPM}_{\mathrm{alphas}}$ is the counts per minute of ^{242}Pu, ^{239,240}Pu and ^{238}Pu in the alpha ROI (channels 600–800), $\varepsilon_{^{241}\mathrm{Pu}}$ is the counting efficiency of ^{241}Pu calculated by the CIEMAT/NIST method, and m is the mass of dry sample used for the analysis (kg of dry weight). $A_{\alpha\text{-total}}$ is the total activity of the alpha Pu radioisotopes (^{239,240}Pu, ^{238}Pu and ^{242}Pu) in the initial sample, and was calculated from the alpha spectra.

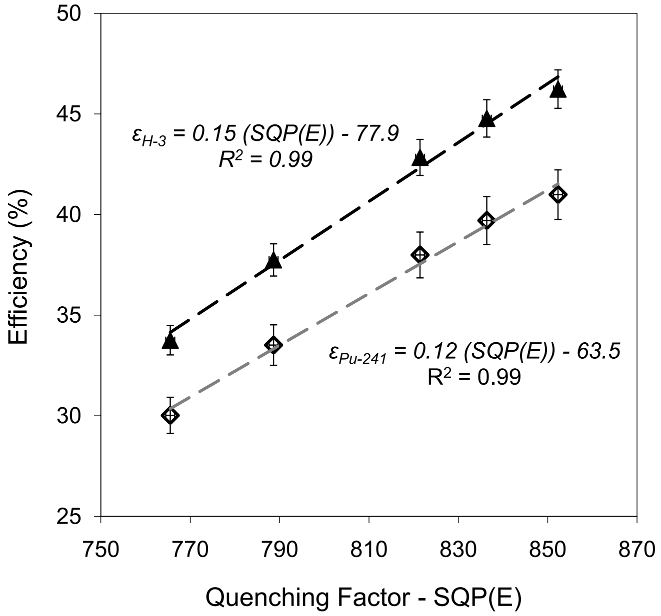

Fig. 3. Counting efficiencies of ^{3}H ($\varepsilon_{^{3}\mathrm{H}}$) and ^{241}Pu ($\varepsilon_{^{241}\mathrm{Pu}}$) *vs.* the quenching parameter SQP(E).

It should be added that the standard tracer solution of ^{242}Pu contains traces of ^{241}Pu; therefore the ^{241}Pu activities were also corrected for this additional contribution. The magnitude of this contamination was quantified by measuring the temporal increase of the ^{241}Am activity within the standard solution. An activity value of 44 (±2) mBq of ^{241}Pu per ml of standard solution of ^{242}Pu was estimated.

According to Currie's law [31], an average counting efficiency of 42% and a counting time of 360 min leads to a minimum detectable activity of 9 mBq for ^{241}Pu. In the present study, the range of minimum detectable activity concentrations (MDA) for ^{241}Pu varied between 0.1 and 1.1 Bq/kg. The MDA varies mainly due to the different sample weights (between 0.001 and 0.090 kg) used for the analysis. The combined uncertainty of the activity value was calculated according to recommended procedures [32]. The uncertainty of the activity is expressed as 2σ.

2.6 Validation of the radiochemical method

Four IAEA reference materials, with information values for ^{241}Pu, were used to validate the radiochemical method. The reference materials are sediments collected at: a) the Bothnian Sea, in the Baltic (IAEA-300); b) the Mururoa Atoll (IAEA-368), which is a former French nuclear weapons testing site in the Pacific Ocean; c) the Enewetak Atoll, in the Marshall Islands (IAEA-367), a former US nuclear weapons test site in the Central Pacific Ocean; and d) the Fangataufa lagoon, in the Fangataufa Atoll of the French Polynesia (IAEA-384).

2.7 ^{241}Am/^{241}Pu age-dating method

^{241}Pu decays to ^{241}Am with a half-life of 14.35 a, and the ^{241}Pu/^{241}Am activity ratio changes predictably as a function of time. For this reason, ^{241}Pu has been used in combination with ^{241}Am as an age-dating tool for environmental samples [33–35]. The initial amount of ^{241}Am in the compartment is assumed to be zero, and the fractionation between the mother and daughter radionuclides negligible. The age of the Pu contamination can then be calculated from the decay equations governing the time-dependent activities of ^{241}Pu and ^{241}Am in the soil layer as:

$$\begin{aligned}A_{\mathrm{ge\,(a)}} &= \left(\frac{1}{\left(\lambda_{^{241}\mathrm{Pu}} - \lambda_{^{241}\mathrm{Am}}\right)}\right) \\ &\quad \times \ln\left(1 + \left(\frac{A_{^{241}\mathrm{Am}}\left(\lambda_{^{241}\mathrm{Pu}} - \lambda_{^{241}\mathrm{Am}}\right)}{A_{^{241}\mathrm{Pu}}\lambda_{^{241}\mathrm{Am}}}\right)\right)\end{aligned}$$

Table 1. ^{241}Pu and ^{241}Am activity concentrations (Bq per kg of dry mass) measured in the reference materials. The recommended or information activity value of ^{241}Pu and ^{241}Am are also shown. The activity values were corrected for the corresponding reference date (Ref. dates, column 1) of the material. The recovery of the dissolution of the Pu alpha source and the purification of the Pu fraction (Partial), and the overall recovery (Overall) for the whole procedure including the preparation of the Pu alpha source for alpha spectrometry, are also shown. The estimated ^{241}Am/^{241}Pu contamination date and the reported dates of the Pu contamination are given in the last two columns of the table. The numbers of replicates are also given (column 3). All given uncertainties are 2σ.

Sample (Ref. date)	Origin	No.	Recovery (%)		Activity measured (Bq/kg)		Reference activity (Bq/kg)		^{241}Am/^{241}Pu contamination date	Reported date of the contamination
			Partial	Overall	^{241}Am	^{241}Pu	^{241}Am	^{241}Pu		
IAEA-300 (1.1.1993)	Bothnian Sea	2	69	61	1.4 ± 0.4	15 ± 3	1.38^{b} (1.2–1.5)	20 ± 5^{a}	1968 ± 7	1955–1986
IAEA-368 (1.1.1990)	Mururoa Atoll	2	65	42	1.5 ± 0.2	19 ± 4	1.3^{b}	$17\text{–}70^{a}$	1968 ± 7	1966–1974
IAEA-367 (1.1.1990)	Enewetak Atoll	2	62	56	27 ± 4	198 ± 37	26.4^{a} (24–28)	174 ± 16^{a}	1958 ± 8	1948–1958
IAEA-384 (1.8.1996)	Fangataufa Atoll	1	63	53	9.4 ± 0.4	63 ± 8	7.1^{b} (6.7–7.4)	56 ± 5^{a}	1961 ± 8	1966–1970

a: Information value;
b: Recommended value.

where λ is the decay constant for ^{241}Pu ($0.04837\ \text{yr}^{-1}$) and ^{241}Am ($0.0016\ \text{yr}^{-1}$), A is the measured activity of ^{241}Pu and ^{241}Am, respectively.

The ^{241}Pu/^{241}Am age-dating method is useful for indentifying single Pu sources. However, in regions affected by multiple sources of Pu (ex. NWTs, Chernobyl accident, *etc.*) or by several inputs of the same source of Pu (ex. the weapon tests at the Mururoa atoll carried out between 1966 and 1996); the method provides a weighted mean of the ages of all the Pu components.

3. Results and discussion

3.1 Analysis of reference materials

The results of the Pu and Am analyses of the four reference materials are presented in Table 1. The radiochemical recoveries obtained for the dissolution of the Pu alpha sources and purification of the Pu fractions varied between 62 and 69% (Table 1). The overall recoveries, including the preparation of the Pu sources for alpha spectrometry, varied between 42 and 61% (Table 1). The quenching of the ^{241}Pu sources was extremely low (SQP(E): 840–860), which resulted in an average counting efficiency of ^{241}Pu as high as 42%. This means that good quality LSC sources were prepared using the proposed radiochemical procedure.

The overall means of the measured activity concentrations of ^{241}Pu in the reference materials are in good agreement with the information values (Table 1). In the case of the reference material IAEA-368, the information value of ^{241}Pu is based on the results of two laboratories. Our results approach the lower value of 17 ± 1 Bq/kg reported by one laboratory. Activity values of 11 ± 3 and 12 ± 5 Bq/kg of ^{241}Pu were recently measured by SF-ICP-MS for this sample [36]. This demonstrates that the overall radiochemical procedure presented here was accurate.

The sources and dates of the Pu contamination in the regions of origin of the reference materials are relatively well-known. Therefore, the contamination dates of these samples were estimated using the ^{241}Pu/^{241}Am age-dating method in order to investigate its applicability. The estimated contamination dates of the reference materials suitably correspond to the expected weighted mean dates of the contamination (Table 1). For example, the estimated contamination date of 1968 (±7 a) for the Bothnian sediments (IAEA-300) represents a weighted mean date of the two main sources of Pu in the sediments, which are the NWTs with a maximum peak in 1963 and the Chernobyl accident in 1986 [37]. For the Enewetak atoll (IAEA-367), in the Marshall Islands, the calculated contamination date of 1958 (±8 a) is well within the period between 1948 and 1958, when this region was affected by the nuclear-weapon tests conducted by the United States.

For the IAEA-368, the estimated contamination date of 1968 (±7 a) is also in complete agreement with the period from 1966 to 1974 when France carried out atmospheric nuclear weapons tests in the Mururoa Atoll. In the case of the reference material IAEA-384, from the Fangataufa Atoll, the estimated contamination date of 1961 (±8) conforms to the fact that in this Atoll the atmospheric weapons tests were conducted between 1966 and 1970, including the largest test in the French Polynesia in 1968.

3.2 ^{241}Pu in alpine soils

The ^{241}Pu activity concentrations in thirty-two soil samples from two alpine regions in France and Switzerland are given in Tables 2 and 3. All the uncertainties are expressed as 2σ. In the case of profile 1 of the Mercantour wetland, the results are the average of two different measurements (Table 3). In order to compare the investigated sites, the activity concentrations and activity ratios were decay corrected to 1 June 2009. The date of the Pu contamination, calculated by the ^{241}Am/^{241}Pu age-dating method, is also given for each sample.

Table 2. ^{241}Pu and ^{241}Am activity concentrations (Bq/kg of dry mass) measured in the alpine soils of the Valley of Piora, Switzerland. The ^{241}Pu/^{239,240}Pu, ^{238}Pu/^{239,240}Pu and ^{241}Am/^{239,240}Pu activity ratios shown in this table were calculated using ^{239,240}Pu, ^{238}Pu and ^{241}Am data taken from Luisier *et al.* [28] and Chawla *et al.* [23]. All the activities and ratios were corrected for 01.06.2009. The contamination dates, obtained by the ^{241}Am/^{241}Pu dating method, are reported in the last column. All given uncertainties are 2σ.

Soil description	Depth (cm)	^{241}Pu (Bq/kg)	^{241}Am (Bq/kg)	^{241}Pu/^{239,240}Pu	^{238}Pu/^{239,240}Pu	^{241}Am/^{239,240}Pu	Contamination date
Meadow	3–9	1.2 ± 0.2	0.7 ± 0.1	1.3 ± 0.2	0.022 ± 0.004	0.40 ± 0.04	1949 ± 12
	9–15	0.5 ± 0.1	0.27 ± 0.02	0.8 ± 0.1	0.015 ± 0.006	0.42 ± 0.05	1944 ± 14
Wetland[a]	0–5	4.0 ± 0.4	1.5 ± 0.2	1.1 ± 0.2	0.037 ± 0.006	0.43 ± 0.03	1957 ± 8
	5–10	21 ± 3	6.8 ± 0.6	1.3 ± 0.2	0.026 ± 0.002	0.44 ± 0.02	1960 ± 8
	10–16	9 ± 1	3.6 ± 0.3	1.1 ± 0.2	0.022 ± 0.004	0.43 ± 0.03	1956 ± 9
Peat	0–5	4.4 ± 0.6	1.7 ± 0.1	1.2 ± 0.2	0.034 ± 0.002	0.46 ± 0.03	1958 ± 8
	5–10	4.7 ± 0.6	1.6 ± 0.2	1.0 ± 0.2	0.029 ± 0.004	0.36 ± 0.03	1959 ± 9
Peat	0–4	8 ± 1		1.4 ± 0.2	0.027 ± 0.002		
Wetland	0–5	5.1 ± 0.7	1.5 ± 0.2	1.5 ± 0.2	0.034 ± 0.004	0.46 ± 0.03	1962 ± 8
Wetland	0–5	1.8 ± 0.2		1.6 ± 0.2	0.032 ± 0.006		
	5–9	1.6 ± 0.2		1.3 ± 0.2	0.022 ± 0.004		
NWT (2009)				1.3–1.7[b]			1963 (maximum)
Chernobyl fallout				> 27[b]			1986

a: Profile used for the estimation of the total surface deposition;
b: Expected activity ratios on the 1 June 2009.

Table 3. ^{241}Pu activity concentrations (Bq/kg of dry mass) measured in the alpine soils of the Valley of Mercantour, in France. The ^{241}Pu/^{239,240}Pu, ^{238}Pu/^{239,240}Pu and ^{241}Am/^{239,240}Pu activity ratios shown in this table are calculated using ^{239,240}Pu, ^{238}Pu and ^{241}Am data taken from Solovitch-Vella *et al.* [22] and unpublished data. All the activities and ratios are corrected for 01.06.2009. The contamination dates, obtained by the ^{241}Am/^{241}Pu dating method, are reported in the last column. All given uncertainties are 2σ.

Soil description	Depth (cm)	^{241}Pu (Bq/kg)	^{241}Am (Bq/kg)	^{241}Pu/^{239,240}Pu	^{238}Pu/^{239,240}Pu	^{241}Am/^{239,240}Pu	Contamination date
Wetland Profile 1	0–3	1.9 ± 0.4	0.22 ± 0.03	2.3 ± 0.4	0.048 ± 0.014	0.29 ± 0.02	1982 ± 7
	3–6	1.7 ± 0.3	0.38 ± 0.05	1.8 ± 0.4	0.027 ± 0.006	0.39 ± 0.03	1969 ± 10
	6–10	10 ± 2	1.8 ± 0.1	1.7 ± 0.4	0.021 ± 0.002	0.31 ± 0.02	1973 ± 7
	10–12	3.3 ± 0.6	0.7 ± 0.3	1.6 ± 0.3	0.017 ± 0.002	0.32 ± 0.07	1969 ± 18
	12–15	0.9 ± 0.2	0.18 ± 0.09	1.4 ± 0.3	0.023 ± 0.006	0.33 ± 0.04	1970 ± 22
	15–19	1.2 ± 0.2	0.2 ± 0.2	1.2 ± 0.3	0.016 ± 0.006	0.40 ± 0.05	1971 ± 28
	21–25	6 ± 1	0.9 ± 0.1	1.7 ± 0.4	0.023 ± 0.004	0.28 ± 0.02	1976 ± 7
	25–30	5.7 ± 0.8	0.33 ± 0.05	1.8 ± 0.3	0.019 ± 0.002	0.10 ± 0.01	1998 ± 2
	30–42	1.6 ± 0.2	0.06 ± 0.01	1.7 ± 0.3	0.020 ± 0.004	0.07 ± 0.01	2007 ± 1
Wetland	2–5	53 ± 7	11.6 ± 0.4	1.5 ± 0.2	0.023 ± 0.002	0.33 ± 0.01	1969 ± 5
	0–2	18 ± 2	4.0 ± 0.2	1.6 ± 0.2	0.027 ± 0.002	0.34 ± 0.01	1969 ± 5
	2–5	6 ± 1	1.6 ± 0.1	1.7 ± 0.2	0.021 ± 0.002	0.45 ± 0.02	1965 ± 6
	0–5	2.8 ± 0.4	0.56 ± 0.04	1.9 ± 0.3	0.015 ± 0.006	0.34 ± 0.03	1971 ± 6
	0–5	17 ± 2	4.8 ± 0.2	1.4 ± 0.2	0.021 ± 0.002	0.39 ± 0.02	1963 ± 6
	0–5	30 ± 4	6.4 ± 0.2	1.8 ± 0.3	0.024 ± 0.004	0.38 ± 0.02	1970 ± 6
Wetland Profile 2[a]	0–2	16 ± 2	3.2 ± 0.2	1.9 ± 0.3	0.027 ± 0.002	0.38 ± 0.01	1971 ± 5
	2–4	8 ± 1	1.7 ± 0.1	1.6 ± 0.2	0.029 ± 0.004	0.36 ± 0.02	1969 ± 5
	4–6	6 ± 1	1.6 ± 0.1	1.7 ± 0.2	0.049 ± 0.006	0.48 ± 0.02	1964 ± 6
	6–8	1.4 ± 0.2	0.32 ± 0.02	2.2 ± 0.3	0.023 ± 0.008	0.50 ± 0.03	1969 ± 6
	8–10	0.8 ± 0.1	0.09 ± 0.01	3.0 ± 0.5	0.021 ± 0.014	0.34 ± 0.03	1983 ± 5
	10–15	0.8 ± 0.1	0.04 ± 0.01	1.1 ± 0.2	0.027 ± 0.006	0.06 ± 0.01	2000 ± 2
NBT (2009)				1.3–1.7[b]			1963 (maximum)
Chernobyl fallout				> 27[b]			1986

a: The profile 2 of the wetlands was used for the estimation of the total surface deposition;
b: Expected activity ratios on the 1 June 2009.

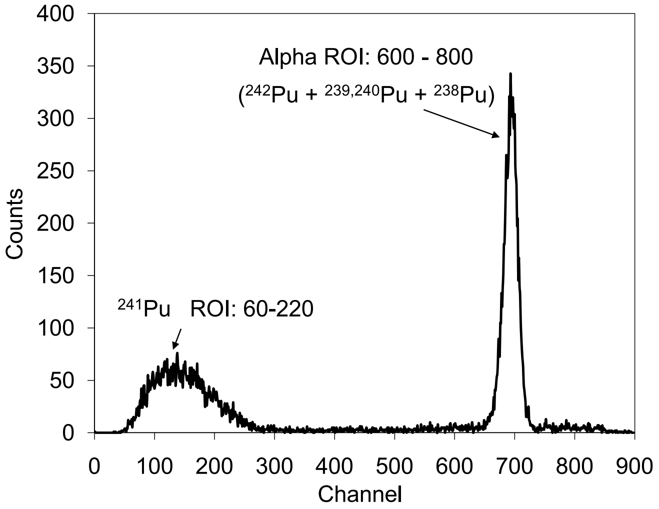

Fig. 4. Plutonium spectra of the sample IAEA-367, measured by LSC in the Quantulus 1220.

The ^{241}Pu activity concentrations in the alpine soils show depth profiles similar to the ones observed for other Pu radioisotopes (^{238}Pu, ^{239,240}Pu) and ^{241}Am in these sites [22, 23]. Maximums ^{241}Pu activity values are generally found in the upper 10 cm of the soil profiles (Tables 2 and 3).

The ^{241}Pu activity concentrations in the upper 10 cm of the alpine soils (1–53 Bq/kg, Tables 2 and 3) are significantly higher than the values detected in surface soils of low altitude regions [14, 15, 18, 38–40]. This tendency may be explained by the increased levels of radioactive fallout at high altitude due to a higher precipitation rate [27].

For example, lower ^{241}Pu activity concentrations of maximum 1 Bq/kg (decay corrected for 2009) were measured in surface soils of the lowland valleys in northern Switzerland [38]. Similarly, low ^{241}Pu values of maximum 2.5 Bq/kg were detected in surface soils of a low altitude valley in southern Switzerland [40]. Low ^{241}Pu activities have also been reported for other low altitude soils, for example, in Hungary [14, 15, 18] and in St. Petersburg, Russia [39]. The Pu in all these sites has been shown to come from the NWTs. However, increased levels of ^{241}Pu in low altitude soils have been reported for regions also affected by radioactive fallout from the Chernobyl accident, such as in Poland [5] and in Ukraine [41].

The surface deposition or total inventory of ^{241}Pu (Bq/m^2) was calculated by summing the product of each depth section's ^{241}Pu activity (Bq/kg), the soil bulk density (kg/m^3) and its thickness (m). Two profiles, one from the Valley of Piora (indicated in Table 2) and one from Mercantour (indicated in Table 3), were used for this calculation taken into account that the soil densities of these two wetlands were reported previously [22, 23]. The total inventories of ^{241}Pu in the Mercantour wetlands and the Valley of Piora were 160 and 230 Bq/m^2, respectively. These inventories are similar to the inventories of ^{241}Pu reported for other European regions located at high altitudes. For example, in a natural pasture in Romania located at 1600–1900 m above sea level, similar surface depositions of up to 300 Bq/m^2 (decay corrected for 2009) were reported for the ^{241}Pu fraction originated by the NWTs [13].

The alpine sites show ^{241}Pu/^{239,240}Pu activity ratio between 0.8 and 2.2 (Tables 2 and 3). Similar ^{241}Pu/^{239,240}Pu activity ratios of 1.6 ± 0.4 (reference date: 2008) have been detected in alpine soils of Coglio, in Ticino [40]. Comparable ^{241}Pu/^{239,240}Pu activity ratios of 1.6 ± 0.4 (reference date: 2001) were also reported for soil samples from the lowland valleys in northern Switzerland [38]. The ^{241}Pu/^{239,240}Pu activity ratios calculated for both study sites are indistinguishable from the activity ratios originated by the NWTs

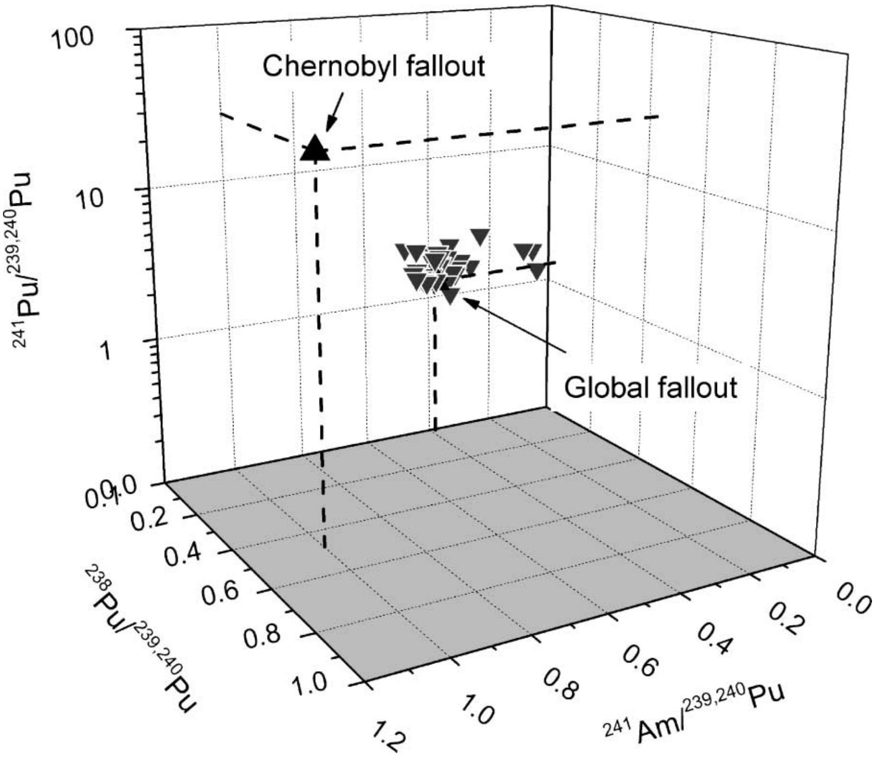

Fig. 5. The ^{241}Pu/^{239,240}Pu activity ratios *vs.* the ^{241}Am/^{239,240}Pu and ^{238}Pu/^{239,240}Pu activity ratios calculated for the alpine soils of France and Switzerland (▼). The ^{241}Pu/^{239,240}Pu, ^{238}Pu/^{239,240}Pu and ^{241}Am/^{239,240}Pu activity ratios depicted in this figure were calculated using ^{239,240}Pu, ^{238}Pu and ^{241}Am data taken from Solovitch-Vella *et al.* [22], Luisier *et al.* [28] and Chawla *et al.* [23]. The activity ratios of known contamination sources are also given for comparison (▲: Chernobyl accident and NWT). The values are decay corrected for the 01.06.2009. For the Chernobyl accident, a ^{241}Am/^{239,240}Pu ratio of 1 was assumed.

(Fig. 5), which currently range between 1.3 and 1.7 (Tables 2 and 3). An examination of the $^{238}Pu/^{239,240}Pu$ (0.02–0.04) and $^{241}Am/^{239,240}Pu$ (0.3–0.5) activity ratios further reinforces the theory that Pu in both alpine sites comes mainly from global fallout (Fig. 5). This result corresponds to previous studies that have concluded that Pu in both regions was originated by the NWT [22, 23, 27, 42].

In the soils of the Valley of Piora and at shallow depths in the Mercantour sites, the vertical distribution of ^{241}Pu is similar to those reported for $^{239,240}Pu$, ^{238}Pu and ^{241}Am (Tables 2 and 3) [22, 23]. The date of the Pu contamination, calculated by the $^{241}Am/^{241}Pu$ age-dating method, is between 1944 and 1973 (Tables 2 and 3). This result further confirms that the origin of the Pu radioisotopes was the radioactive fallout originated by the atmospheric NWT in the fifties and sixties. No indication of the presence of Pu from the Chernobyl accident was found in these samples, which agrees with previous studies of the Pu contamination in both regions [22, 23, 27, 42, 43].

At depth in the Mercantour wetlands, significant differences in the vertical distributions of Pu and Am have been reported by Solovitch-Vella *et al.* [22]. These differences were explained by the different migration mechanisms of both elements in the fully-saturated wetlands [22]. While Am is strongly retained in the organic rich layers of the wetlands (organic matter: 69 to 77% of the total weight), Pu seems to be slightly mobilized, potentially by the formation of colloids. Hence, a slight enrichment of Am with respect to Pu was observed at “intermediate” depths (high organic content) with a subsequent depletion of Am at deeper depths [22]. Therefore, the ages of the Pu contamination at depth deviate to younger ages below 35 a (Table 3). This result shows the limitation of the $^{241}Am/^{241}Pu$ age-dating method to compartments where the Pu-Am fractionation is negligible. For such cases, it would be advisable to calculate full depth profile ages.

4. Conclusions

A radiochemical procedure was developed for the determination of ^{241}Pu in environmental samples, based on the use of extraction chromatography resins. The new procedure was used to study the ^{241}Pu activity in alpine soils from two regions of France and Switzerland. The $^{241}Pu/^{239,240}Pu$, $^{238}Pu/^{239,240}Pu$ and $^{241}Am/^{239,240}Pu$ activity ratios provided unique information for determining the source of these actinides in the environment. The ratios showed clear evidence that the plutonium present in the soil originated from global fallout from nuclear weapons tests. The calculation of the elapsed time since the Pu contamination by the $^{241}Am/^{241}Pu$ age-dating method further confirmed this origin. However, this dating method was limited to samples where the Pu-Am pair had not suffered any fractionation. The $^{241}Pu/^{239,240}Pu$ activity ratios measured for the first time in these alpine soils can be accepted as background values in the assessment of the radiological situation in alpine regions.

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