



Origin and age of an ongoing radioactive contamination of soils near La Hague reprocessing plant based on $^{239+240}\text{Pu}/^{238}\text{Pu}$ and $^{241}\text{Am}/^{241}\text{Pu}$ current ratios and ^{90}Sr and Ln(III) soil contents



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HIGHLIGHTS

- Determination of elevated actinides and ^{90}Sr activities near the La Hague nuclear reprocessing plant.
- Isotopic ratios show that the contamination is coming from old burnt fuel.
- The ^{241}Am - ^{241}Pu dating method yields a contamination date close to 1983.
- Elevated levels of cold light Ln (III) confirm the presence of old burnt fuel.
- The La Hague reprocessing plant operator decided to remove the contamination.

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ABSTRACT

Nuclear reprocessing plants are sources of environmental contamination by gaseous or liquid discharges. Numerous radionuclides are of concern, with actinides and ^{90}Sr being the most radiotoxic. Environmental radioactivity survey programs mostly use γ -spectrometry to track contaminations because γ -spectrometry is very cost effective and can be carried out on raw samples. On the other hand, the determination of β - or α -emitting radionuclides in environmental samples requires rather sophisticated analytical methods, and are thus dedicated to specific goals. However, measuring radionuclides such as Pu, Am, and Sr often provides more information about the presence of a current or prior contamination and on its origin, based on the isotopic composition of the samples. We found that the analysis of ^{241}Pu , $^{239+240}\text{Pu}$, ^{241}Am , and ^{90}Sr of a few selected soil samples taken near the nuclear reprocessing plant of La Hague, France, revealed the presence of a previous environmental contamination originating from several incidents in La Hague site involving atmospheric transfer and leaks in flooded waste pits. The ^{241}Am - ^{241}Pu dating method indicated a contamination period prior to 1983. The presence of elevated levels of light non-radioactive lanthanides and yttrium in the soil samples confirmed the involvement of cold fuel. Our results demonstrate how long-lived actinides are likely to reveal a long-term contamination of the environment by spent fuel. Our study indicates that there is a requirement to use more sophisticated tools than γ -spectrometry when surveying the environments surrounding industrial plants for nuclear power and nuclear reprocessing with a potential for the accidental release of radioactivity into the environment.

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1. Introduction

Nuclear reprocessing plants are facilities that treat nuclear-burnt fuel in order to: re-use some of the radionuclides for new fuel rods (Dancausse et al., 2008) (e.g. MOx fuel), separate long-lived radionuclides from short-lived radionuclides, and shape

wastes for intermediate or long-term storage (Pradel, 1997; Baron et al., 2019). Reprocessing operations are very hazardous for both workers and the environment, and the dedicated procedures are supervised by the national authorities. Nuclear reprocessing plants release specific radionuclides with activities limited by international recommendations and national laws. These emissions of radioactivity happen mostly under gaseous or liquid effluent forms. The two main reprocessing plants in Europe are situated very close to the Irish Sea (Sellafield) or the English Channel (La Hague) in order to benefit from the dilution effect produced by marine currents and heavy tides (du Bois and Dumas, 2005). The former has now shifted away from fuel reprocessing to a decommissioning phase of operation while the latter is still in operation.

Significant activities of radionuclides are measured in the Northern Atlantic and the North Sea for several radionuclides released by Sellafield and La Hague. In this respect, ^{137}Cs , ^{129}I , and ^{236}U from the two sites are used to trace routes of the waters from the Irish Sea and the English Channel to the Northern Atlantic Ocean (Perianez et al., 2016; Christl et al., 2017). Gaseous emissions of $^{14}\text{CO}_2$ and $^3\text{H}_2\text{O}$ are usually observed in the vegetation in the close vicinity of the reprocessing plants (Limer et al., 2015; Maro et al., 2017) and non-reactive species, such as ^{85}Kr , $^{129}\text{I}_2$, and $^{127}\text{I}_2$, can be detected much farther (Connan et al., 2014; Daraoui et al., 2016; Bollhofer et al., 2019). Ordinarily, the environments directly beside the plants and the biosphere compartments (grass, soils, and sediments) are investigated using environmental surveys for γ -emitters because this method is most cost effective. γ -Spectrometry is undeniably informative, but mostly reveals contamination by isotopes such as ^{137}Cs , which is not specific to the plant activities. If a contamination is recent, γ -spectrometry may detect ^{134}Cs , ^{133}Ba , ^{60}Co , $^{110\text{m}}\text{Ag}$, and ^{22}Na , some radio lanthanides, and ^{131}I (mostly in aerosols). If the contamination is substantial, γ -spectrometry may reveal the presence of ^{241}Am . However, U and transuranium actinides (TRU) or β -emitters fission products such as ^{90}Sr will remain undetected (Baron et al., 2019). In addition, the use of large quantities of ligands (trialkyl phosphine oxide (TPO), tri-*n*-butyl phosphate (TBP), 2-ethylhexylphosphonic-acid mono-2-ethylhexylester (PC-88 A), octyl (phenyl)-N,N-isobutylcarbamoylmethylphosphine oxide (CMPO)) as well as solvents (dodecane, kerosene, nitric acid) in the reprocessing of nuclear fuel will add chemical complexity to the discharges. In this respect, the mobility of the lanthanides and the actinides in the biosphere, otherwise considered very low, can be significantly increased (Keiling and Marx, 1991; Wang et al., 2019).

Near the Sellafield nuclear processing plant, the tide-washed pastures bordering the Irish Sea contain significantly higher activities of ^{137}Cs and actinides compared to the terrestrial environment, indicating an association of the discharges with the sediments (Howard et al., 1996; Sanchez et al., 1998). While the contribution of discharges to the English Channel and North Sea from La Hague reprocessing plant is relatively well documented (Boust et al., 1996; Beks, 2000; du Bois and Dumas, 2005; Fievet et al., 2006; Farcy et al., 2007; Christl et al., 2017), this is not quite the case for the terrestrial environment. The French Nuclear Safety Technical Support Organization (IRSN) publishes online series of measurements in the terrestrial environment (including water and milk samples) around La Hague reprocessing plant (www.mesure-radioactivite.fr, in French and English) for several radionuclides, including Pu and Am, but no specific study dealing with the potential contamination of the soils near the plant by radionuclides such as actinides and ^{90}Sr existed before 2016 (IRSN, 2017a).

A number of recent technological advances has improved the measurement of actinides (U, Pu, Am), including the development of solid phase extraction supports, such as the Eichrom's resins TRU, TEVA and DGA developed by Horwitz et al. (2005), and progress in

α -spectrometry using semi-conductor PIPS detectors or in mass spectrometry methods. Even accelerator mass spectrometers (AMS) are now available for determining ultra-low level of actinides (Christl et al., 2013; Cusnir et al., 2017). Automatic fluxers or pressurized microwave digesters are currently available for dissolving radionuclides from the matrix before chemical separation. This means that determining actinides in matrices such as soil and sediments is currently much less challenging than previously reported. Thus, any radioactivity survey program should now incorporate the benefit of determining actinides when monitoring the environment close to a nuclear power plant or nuclear reprocessing plant, as well as during the process of dismantlement and waste disposal.

For this study, we were able to determine the source and age of an ongoing contamination of soils near La Hague nuclear reprocessing plant by using a few selected soil samples and the determination of ^{238}Pu ($T_{1/2} = 87.7$ y), $^{239+240}\text{Pu}$ ($^{239}\text{T}_{1/2} = 24'110$ y; $^{240}\text{T}_{1/2} = 6561$ y), ^{241}Am ($T_{1/2} = 432.2$ y) by α -spectrometry, ^{241}Pu ($T_{1/2} = 14.4$ y) by liquid scintillation counting, and ^{90}Sr ($T_{1/2} = 28.8$ y) by low-level proportional counting. We dated the origin of the contamination to the 1980's at most recent based on the ^{241}Am - ^{241}Pu dating method. The results of our study motivated the French Nuclear Safety Authority and TSO (Technical Safety Organizations such as ASN and IRSN) to reinforce the monitoring program surrounding La Hague reprocessing plant (IRSN, 2017b, c) and the operator to plan a cleaning procedure through the removal of part of the contaminated soil (IRSN, 2017a).

2. Material and methods

2.1. Sampling strategy

The French NGO ACRO monitors environmental radioactivity with local inhabitants. Its Citizen Observatory of Radioactivity in the Environment (CORE) monitors the impact of nuclear plants in Normandy and along the Loire River. ACRO's laboratory is certified by the French nuclear safety authorities for several radioactivity determination methods. All data produced in this program are published online (www.acro.eu.org) and uploaded into the French national database (www.mesure-radioactivite.fr).

In early 2016, samples collected by ACRO at La Hague in a small river flowing to the west of the nuclear reprocessing plant, the Ru des Landes, revealed the presence of several artificial radioelements that are usually only found in trace amounts: ^{60}Co , ^{129}I , ^{137}Cs , and ^{241}Am . Samples collected later showed that the contamination was spread to a pasture and the stream from its source, suggesting both atmospheric and phreatic transfers. In order to deepen the initial observations and assess the extent of the pollution around the Ru des Landes River, a broader sampling campaign was carried out by ACRO on 17 October and November 16, 2016.

A total of 35 samples were collected for analysis at the ACRO laboratory using gamma-ray spectrometry (31 soils, 3 sediments and 1 moss, Table SI-1). For this study, we focused on selected soil samples which have shown elevated level of ^{241}Am by γ -spectrometry. The sampling strategy was aimed at assessing the spatial extent of contamination around the source materialized by a concrete drinking trough (RDLO). Sampling was thus carried out randomly from the road which delimited the north of the plant down along the stream watershed. The type of land also guided the collection sites (wet meadow with the presence of a small wood).

2.2. Sampling site

The location of the sampling site is displayed on Fig. 1. It consists of a pasture, wetlands, and a stream located to the northwest of the

reprocessing plant, close to a former depository of radioactive waste in earthen trenches and concrete silos (see Fig. 1 for a diagram of the sampling positions). The size of investigated area is about 50 m × 100 m around the source of the stream, about 80 m from the north boundary of the reprocessing plant. The soil samples were collected with a spade shovel. Each sample was about 15 cm wide and 20 cm deep. Once extracted, several horizons were identified—up to 4 when it was possible, then cut out and placed in a separate plastic bag.

2.3. γ -spectrometry

Gamma spectroscopy was performed at ACRO's laboratory in compliance with ISO 18589–2:2015 and ISO 18589–3:2015 standards. Soil samples were broken up and cleared of stones and remaining plant parts (tufts of grass, roots, etc.). The sorted sample was then weighed and placed in an oven at 60 °C until a constant dry mass was obtained. The dry sample was then crushed, sieved (<2 mm), and homogenized. A representative aliquot was packaged in a cylindrical plastic container (effective volume 61 ml, diameter 75 mm, and height 18 mm), suitable for counting in gamma spectrometry.

The analyses were carried out using two gamma spectrometry measurement chains equipped with ultra-pure germanium detectors, respectively type N (Ortec detector, 32% efficiency) and type P (BSI detector, 50% efficiency), each mounted on a vertical cryostat, inside a 10 cm lead shield and equipped with a digital acquisition system (DSPEC, Ortec and ORION, Itech Instruments). The energy range taken as a reference was from 20 to 2000 keV. The reference efficiency of the detectors was determined using multi-radionuclide liquid sources and standardized materials with a range of similar densities supplied by the IAEA ((RGU1, RGTH1, IAEA135, IAEA365, SOIL6). Due to the small thickness of the packaging geometry used, no self-absorption correction was performed.

2.4. Plutonium and americium analyses

$^{239+240}\text{Pu}$, ^{238}Pu , and ^{241}Am were determined according to previously published procedures (Luisier et al., 2009; Alvarado et al., 2011). However, the leaching procedure was modified to take into account the smaller amounts of samples needed to reach the necessary sensitivity and the potential presence of refractory material (e.g. plutonium oxides). Briefly, 2.5 g of ash of soil sample was spiked with ^{242}Pu and ^{243}Am (25 mBq each) and mixed with

7.5 g of a mixture of $\text{Li}_2\text{B}_4\text{O}_7:\text{LiBO}_2$ 50:50 (Claisse, St-Foy, Canada) and 30 mg of LiBr. The mixture was introduced into a platinum crucible and melted for 15 min, using a Claisse M_4 fluxer (Claisse, St-Foy, Canada). The Claisse M_4 fluxer automatically produces an acidic (HNO_3 1 M) solution. This solution was acidified to 6 M by adding concentrated HNO_3 and the excess boric acid and silica was precipitated overnight by adding 1 ml of 0.2 M PEG 2000 (polyethylene glycol) solution. After centrifugation, the actinides were co-precipitated on alkaline-earth cation oxalates and the oxalates oxidized in concentrated HNO_3 at 200 °C under a pressure of 50 bars for 15 min in a pressurized microwave apparatus (Milestone Ultracalve IV). Actinides were co-precipitated on a small amount (5 mg Fe) of iron hydroxides and Pu(IV) extracted on TEVA resin (cartridge, 2 ml) and Am(III) on DGA resin (cartridge, 2 ml). Pu was purified on a small column (120 mg) of TEVA resin and Am was purified from lanthanides on a small column (120 mg) of TEVA resin using the thiocyanate method. Pu and Am fractions were electroplated on stainless steel disks in sulfate medium at pH 1.9 at 1.2 A (about 10 V) according to the method described by Bajo et al. (Bajo and Eikenberg, 1999). The disks were counted in an alpha spectrometer (Canberra Alpha Analyst) with PIPS detectors (450 mm^2) for a duration of 250'000 s and the spectra analyzed with APEX software (Mirion Technologies, Canberra, France).

2.5. Analysis of ^{241}Pu

The determination of ^{241}Pu was carried out according to the procedure describe in Corcho-Alvarado et al. (2011). Briefly, after counting plutonium alpha emitters, the disk was leached with HNO_3 and HCl. Pu was purified on a TEVA micro-column (120 mg). After elution of Pu with 0.1 M HI-9 M HCl and evaporation, Pu was taken in 2 × 0.5 ml 0.5 M HCl and transferred into a polyethylene flask containing 20 ml of Ultima Gold (Packard, PerkinElmer) and counted in a liquid scintillation counter (Wallac Quantulus 1220, PerkinElmer, Finland). The spectrometer distinguishes beta (^{241}Pu) and alpha events ($^{242}\text{Pu}+^{238}\text{Pu}+^{239+240}\text{Pu}$), thus the alpha events were used for calculating the overall radiochemical yield, taking into account the previous radiochemical yield of Pu from alpha spectrometry.

2.6. Analysis of ^{90}Sr

^{90}Sr was determined by measuring its daughter product, ^{90}Y , at secular equilibrium. 1.0 g of ashes of soil sample was mixed with

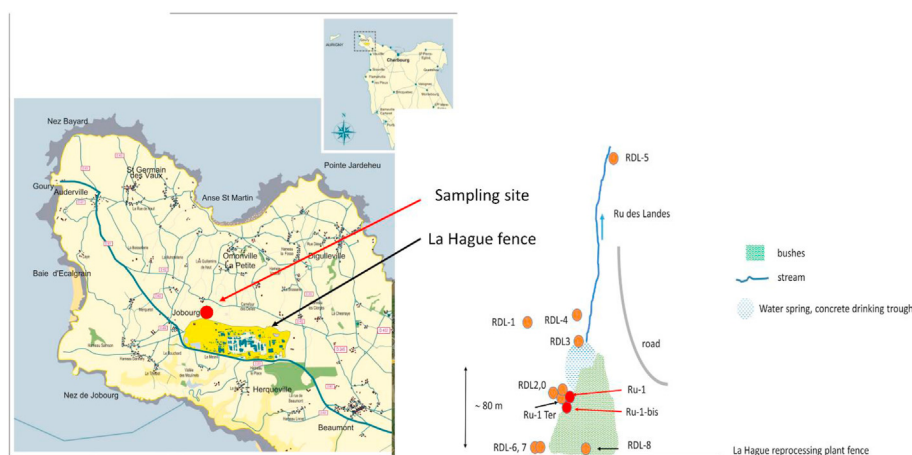


Fig. 1. North Cotentin (Normandy) with the location of the la Hague reprocessing plant. Brown points represent the soil sampling sites, with red points more specifically analyzed in this study. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3.0 g of $\text{Li}_2\text{B}_4\text{O}_7:\text{LiBO}_2$ 50:50 and 15 mg of LiBr. 10 mg of Y^{3+} carrier (as YCl_3 solution) was added and the mixture was fused in a Claisse M4 fluxer. After precipitating the excess boric acid and silica using 1 ml of 0.2 M PEG 2000, alkaline-earth cations and Y^{3+} were precipitated as oxalates. After wet ashing of the oxalates in a pressurized microwave apparatus (Milestone UltraClave IV), the pH of the solution was adjusted to 3 with concentrated NH_4OH . Y^{3+} was extracted on a homemade resin specific for yttrium (Chauvin et al., 2006; Froidevaux et al., 2006), and then eluted in 20 ml 1 M HCl and 50 ml of H_2O . Adding oxalic acid to this solution yielded yttrium oxalate, which was filtered off on a Millipore (GSWOP 02400) filter. The yttrium source was counted in a low-level proportional counter 30 times in blocks of 4 h (Tennelec LB4100w). The purity of the ^{90}Y source was checked by calculating the half-life from the counting blocks. $T_{1/2}$ must be between 60 and 68 h for ^{90}Y source to be declared pure enough. The overall chemical yield was determined on Y after ashing of the source by using ICP-OES (PerkinElmer Ultima 3300 DV).

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

The method has been described in detail in Corcho-Alvarado et al. (2011). The ^{241}Am - ^{241}Pu age dating method is based on the decrease of ^{241}Pu to ^{241}Am with $T_{1/2}$ of 14.35 y, as presented in Equation (1). The ^{241}Am initial activity must be set to zero, with no fractionation of the daughter from the precursor during the assessed time. Leakage from spent fuel may respect those assertions, but some exceptions will be discussed later (see Results and Discussion part below).

$$\text{Age} = \left(\frac{1}{\lambda_{\text{Pu-241}} - \lambda_{\text{Am-241}}} \right) \cdot \ln \left[1 + \frac{A_{\text{Am-241}} (\lambda_{\text{Pu-241}} - \lambda_{\text{Am-241}})}{A_{\text{Pu-241}} \cdot \lambda_{\text{Am-241}}} \right] \quad (\text{eq. 1})$$

with $\lambda_x = \ln(2)/T_{1/2}$, and A_x the activity of either ^{241}Pu or ^{241}Am .

2.8. Determination of rare earth elements (REE) in soil samples

3.0 g of soil ashes were mixed with 7.5 g of a mixture of $\text{Li}_2\text{B}_4\text{O}_7:\text{LiBO}_2$ 50:50 (Claisse, St-Foy, Canada) and 30 mg of LiBr. The mixture was transferred into a platinum crucible and fused for 15 min using a Claisse M4 fluxer. After precipitating the excess boric acid and silica using 1 ml of 0.2 M PEG 2000, followed by centrifugation, and the necessary dilution steps, an aliquot was analyzed for REE by ICP-OES (PerkinElmer Ultima 3300 DV). Calibrations were carried out using TraceSelect standards from Fluka (Switzerland).

2.9. Quality control

The validation of the ^{90}Sr determination on soil/sediment samples was made by participating in the IRSN 142 S R 300 inter-laboratory comparison (2016, bias: 4.7%). The validation of ^{238}Pu , $^{239+240}\text{Pu}$, and ^{241}Am determination was made by participating in several PROCORAD inter-laboratory comparison exercises (fecal ashes 2018, bias: $^{239+240}\text{Pu}$: +0.4%; ^{238}Pu : +0.5%; ^{241}Am : +1.9%; fecal ashes 2016, bias: $^{239+240}\text{Pu}$: 0%; ^{238}Pu : +5.2%; ^{241}Am : +0.5 and 2.0%) and the Proficiency Test: IAEA-CU-2009-03 ($^{239+240}\text{Pu}$ and ^{238}Pu , bias: 0%). In addition, several references materials are measured periodically to insure the quality control of the methods: e.g. IAEA-soil-6: Pu: 1.06 (R:1.04); ^{90}Sr : 29.8–32.2 (R:30.4).

3. Results and discussion

3.1. Radionuclides activities

The results of the analysis of selected soils samples for γ -, β -, and α -emitters are presented in Tables 1 and 2. Initial γ -spectrometry measurements revealed the presence of several γ -emitters such as ^{137}Cs , ^{129}I , ^{60}Co , and ^{241}Am (Table 1 and Table SI-1). The presence of ^{241}Am led to further search of other α -emitter such as Pu, and fission products such as ^{90}Sr . Results showed that the ^{241}Am activities as determined by γ -spectrometry are close to the ones obtained by α -spectrometry, with a 20% excess. In Ru-1 Bis site sample, the presence of ^{137}Cs at 26 Bq/kg dry weight (dw) is not excessive, taking into account the contributions of the nuclear bomb tests fallout and the Chernobyl accident. A similar conclusion extends to litter of the Ru-1 Ter site, but not at a further depth, where ^{137}Cs activities above 200 Bq/kg were determined. The determination of ^{129}I and ^{60}Co at trace levels in some samples were also good indicators of a potential contamination coming from La Hague reprocessing plant. Nevertheless, the low level of ^{60}Co contamination, a short half-life ($T_{1/2} = 5.27$ y) radionuclide, compared to ^{137}Cs ($T_{1/2} = 30.17$ y) was a first indicator of the possibility of a prior contamination or a more recent contamination with cooled fuel.

Thus, α -spectrometry was used to determine the activities of Pu isotopes and ^{241}Am . Because $^{239+240}\text{Pu}$ isotopes was found in large amounts (>114 Bq/kg dw), liquid scintillation counting was further used to determine ^{241}Pu β -activities. In addition, the presence of ^{90}Sr , a nuclear fission product, above 100 Bq/kg dw was a second indication that the contamination originates from nuclear fuel or nuclear wastes (see Table 2). Nevertheless, the ^{90}Sr contamination might not have the same origin as Pu and Am because Sr being an alkaline-earth cation, it is much more mobile than cations of higher charge density such as actinides in the environment.

3.2. Plutonium activity ratios

Results of the Pu determination are presented in Table 2 and Fig. 2a and b. ^{238}Pu and ^{241}Pu activities are perfectly correlated to the $^{239+240}\text{Pu}$ activities, showing a same origin for all the Pu isotopes. Pu isotopic ratios are good indicators of the origin of an environmental radioactive contamination. This is mostly due to the type of reactor, the neutron flux, the fuel enrichment and the burn up yield of the fuel, (Joe et al., 2012; Lantz et al., 2015; Konegger-Kappel and Prohaska, 2016). When Pu isotopes originate from the fallout of the atmospheric nuclear bomb tests of the 60's (NBT) and the burn up of the SNAP-9A satellite, the $^{238}\text{Pu}/^{239+240}\text{Pu}$ isotopic ratio is close to 0.03 in the northern hemisphere (UNSCEAR, 2000). For instance, in Switzerland, data from 58 soils collected between 2015 and 2019 whose ^{238}Pu was detected above the detection limit show an average $^{238}\text{Pu}/^{239+240}\text{Pu}$ activity ratio of 0.030 ± 0.008 ($n = 58$, see for instance (Froidevaux, 2016)). For the same sample of soils, the average $^{241}\text{Am}/^{239+240}\text{Pu}$ activity ratio was 0.436 ± 0.086 ($n = 115$). When mass spectrometry methods are

Table 1

Activity of soil samples for several γ -emitters radionuclides, in Bq/kg dw. Uncertainties for $k = 2$.

| Sample n° | depth (cm) | ^{137}Cs | ^{129}I | ^{60}Co | ^{241}Am |
|-----------|------------|-------------------|------------------|------------------|-------------------|
| Ru-1Bis | 0–5 | 25.8 ± 3.1 | 20.8 ± 3.0 | <3.1 | 109 ± 13 |
| Ru-1 Ter | Litter | 12.1 ± 2.1 | 27.2 ± 4.0 | 5.8 ± 1.3 | 198 ± 19 |
| Ru-1 Ter | 0–10 | 215 ± 15 | 20.5 ± 2.7 | <6 | 160 ± 15 |
| Ru-1 Ter | 10–15 | 142 ± 12 | 8.3 ± 1.7 | <4 | 82 ± 10 |
| Ru-1 Ter | 15–20 | 65 ± 5 | 16.1 ± 2.7 | <3 | 88 ± 8 |

Table 2
Activity of soil samples for several β and α -emitters, in Bq/kg dw. Uncertainties for $k = 2$.

| Sample n° | depth (cm) | $^{239+240}\text{Pu}$ | ^{238}Pu | ^{241}Pu | ^{241}Am | ^{90}Sr |
|-----------|------------|-----------------------|-------------------|-------------------|-------------------|------------------|
| Ru-1Bis | 0–5 | 114 ± 9 | 9.4 ± 0.8 | 266 ± 24 | 91.5 ± 8.4 | 212 ± 17 |
| Ru-1 Ter | Lit | 212 ± 15 | 17.1 ± 1.3 | 537 ± 48 | 166 ± 13 | 170 ± 14 |
| Ru-1 Ter | 0–10 | 492 ± 34 | 39 ± 3 | 1377 ± 122 | 108 ± 10 | 122 ± 10 |
| Ru-1 Ter | 10–15 | 196 ± 14 | 15.6 ± 1.2 | 501 ± 45 | 64 ± 5 | 104 ± 9 |
| Ru-1 Ter | 15–20 | 241 ± 19 | 20 ± 2 | 609 ± 54 | 78 ± 6 | 89 ± 7 |

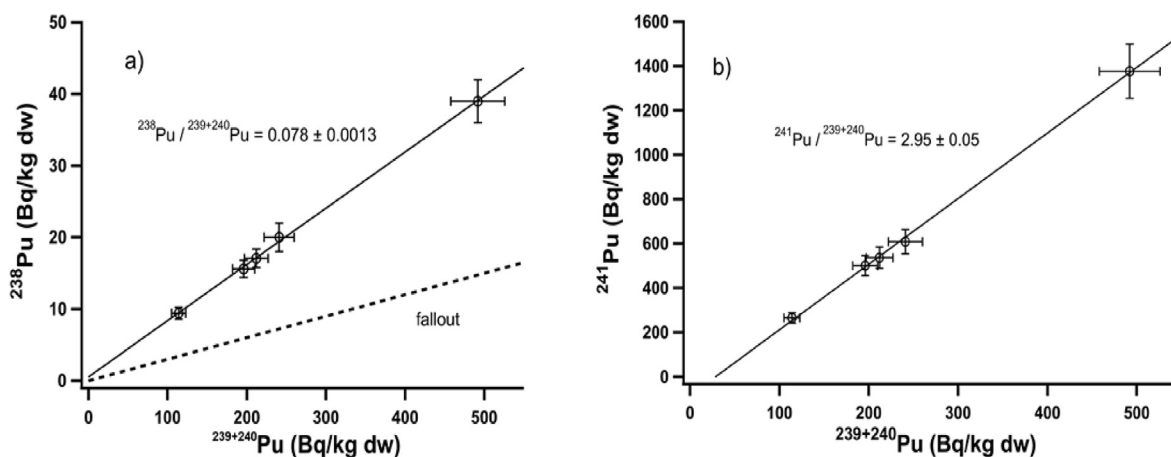


Fig. 2. a) ^{238}Pu (Bq/kg ms) in function of $^{239+240}\text{Pu}$ (Bq/kg dw). The dotted line indicates the dependency for the fallout of the 60's (NBT and SNAP-9A). B) ^{241}Pu (Bq/kg dw) in function of $^{239+240}\text{Pu}$ (Bq/kg ms).

available, the isotopic mass ratio $^{240}\text{Pu}/^{239}\text{Pu}$ is close to 0.18 for NBT fallout (Froidevaux and Haldimann, 2008; Froidevaux et al., 2010). Thus, activity ratios differing significantly from these values are suspicious. The $^{238}\text{Pu}/^{239+240}\text{Pu}$ activity ratio in this study was 0.0784 ± 0.0013 and differed significantly from the one of the NBT and SNAP-9A satellite (Fig. 2a). In addition, this points toward a low burn up fuel yield and a fuel with low enrichment in ^{235}U (Joe et al., 2012; Lantz et al., 2015; Nicolaou and Biegalski, 2018). For instance, in high burnup reactors, $^{238}\text{Pu}/^{239+240}\text{Pu}$ activity ratio is greater than 1 as determined experimentally and with the ORIGEN-2 code (Joe et al., 2012). In a study about the evolution of the $^{240}\text{Pu}/^{239}\text{Pu}$ in sediments collected in the vicinity of the Sellafield nuclear reprocessing plant, Lindahl et al. demonstrated the changing nature of operations at the Sellafield plant from weapons-grade Pu production to reprocessing spent nuclear fuel, with higher burn-up times in the late 1950s (Lindahl et al., 2011). Thus, the low ^{235}U enrichment and the low burnup of the fuel was a third indication that the contamination might involve previous events because the nuclear technology moved to higher enrichment and burnup later on.

The $^{241}\text{Pu}/^{239+240}\text{Pu}$ activity ratio is also a fingerprint which may reveal the origin of Pu contamination. In this study, the $^{241}\text{Pu}/^{239+240}\text{Pu}$ activity ratio was 2.95 ± 0.05 . In 1963, the NBT $^{241}\text{Pu}/^{239+240}\text{Pu}$ activity ratio was 12–16 at the latitude of 40° – 50° north. It was higher than 70–100 for the Chernobyl fallout at the time of the accident, while weapons grade plutonium is characterized by a much lower ratio, between 0.5 and 4 (UNSCEAR, 2000). The low value of the $^{241}\text{Pu}/^{239+240}\text{Pu}$ activity ratio in this study was a fourth indication that the contamination, or the content of the contamination, was ancient because the ^{241}Pu ($T_{1/2} = 14.4$ y) had time to significantly decrease. This might also indicate that weapons grade fuel was involved in the reprocessing waste.

3.3. ^{241}Am and $^{241}\text{Am}/^{241}\text{Pu}$ dating

Because ^{241}Am and ^{241}Pu were detected in all analyzed samples, the study was able to use Equation (1) to determine the age of the contamination, based on the assumption that ^{241}Am was not present at the time of the reprocessing and fuel dispersion into the environment. This hypothesis may not be fully correct, but Equation (1) nevertheless gives a satisfactory estimation of the time elapse since the fuel burning (Alvarado et al., 2011). For Ru-1 Bis sample (0–5 cm), the age was 51.4 y, which situates the contamination in the sixties (1965). This age does not address the possibility of ^{241}Am being already present in the fuel and the fact that ^{241}Am may be more (or less) mobile in soils than its parent ^{241}Pu . However, the PUREX process used in reprocessing plants usually separates Am from Pu. In addition, ^{241}Pu , the precursor of ^{241}Am , will start to accumulate during the burn-up of the fuel. Thus, if Am is not separated from Pu in the waste, the $^{241}\text{Am}/^{241}\text{Pu}$ age dating method will give at least information on the age of the fuel. In the Ru-1 Ter site, results show that significant activities of both ^{241}Pu and ^{241}Am were detected at a depth of 20 cm. This means that both actinides are leaking at further depths. Using a full profile (integrating all the soil layers where activities are detected) is a good way to reduce the bias caused by the varying mobility of the parent and daughter products. Thus, for Ru-1 Ter samples, it is necessary to consider the full depth profile (without the litter sample) and integrate the activities per unit surface (Bq/cm²) using the soil density and the thickness of the soil layer according to equation (2).

$$A_S \left[\frac{\text{Bq}}{\text{cm}^2} \right] = A_m \left[\frac{\text{Bq}}{\text{g}} \right] \cdot \rho \left[\frac{\text{g}}{\text{cm}^3} \right] \cdot \Delta h \text{ [cm]} \quad (\text{eq. 2})$$

with A_S , the activity by unit surface, A_m the mass activity, ρ the mass of soil per volume unit, and Δh the thickness of the soil layer (Table SI-1).

Integration of As for the three soil layers (0–10, 10–15, 15–20 cm) gives an inventory of 7.98 Bq/cm² for ²⁴¹Pu and 0.809 Bq/cm² for ²⁴¹Am. Introducing the inventories into Equation (1) yields an age of 29.5 y, which situates the contamination to 1986. Adding the litter to the soil inventory yields an age of 32.6 y, which situates the contamination to 1983. This date might be approximate given the limitations presented above; nevertheless, it refers to a contamination that occurred several decades ago or to a more recent event involving old waste.

3.4. Lanthanides and yttrium content of the soil

The nuclear fission of ²³⁵U produces new nuclides with mass distribution expressed as fission yield centered on Z ~90 and Z ~140 (Bourg and Poinssot, 2017). Thus, lanthanides (Ln), and more specifically light Ln, are by-products of the nuclear fission with high yield, as well as strontium and yttrium (Z ~ 90) isotopes. Radioactive Ln usually have short (<1 y) to very short (minutes) half-lives and give rise to other Ln, mostly through β⁻ or β⁺ disintegration. For instance, light radioactive La isotopes disintegrate to Ce isotopes, some of them transforming to lighter La isotopes or Pr, which in turn disintegrate to Ce or Nd, depending on the mass. As a result, in cold nuclear fuel, light Ln are in excess compared to natural abundance (Bourg and Poinssot, 2017). Geological events such paleoweathering can be the source of rare earths (REE) enrichment or depletion in soils. In a study on rare REE in soil profiles of various ecosystems across Germany, Mihajlovic et al. found that of all the studied soils, Histosol have the lowest content in REE, with a significant depletion compared to the upper continental crust (UCC) (Mihajlovic et al., 2019). The soils investigated in this study are similar to histosol, with a high content in organic matter (from 70 to 82%, LOI) thus natural REE enrichment is not favored. The results of the determination of Ln and Y in soil samples are presented in Table 3.

Results show that light Ln predominate over heavier Ln in all the samples. In soil samples, the total Ln content is usually lower than 100 ppm and Y close to 10–20 ppm (He et al., 2005; Vukojevic et al., 2019). Here we show that the Ln content is much higher, in particular for La, Ce, Nd, and Y. Plotting the content of Y and Ln as a function of the Ce content demonstrates the fissionogenic origin of the light Ln, as displayed in Fig. 3. When the Ce content increases, Y, La, Nd, and, to a lesser extent Gd content, also increase. Oppositely, the content of heavier Ln, such as Eu–Lu, is not sensitive to the Ce content. In a study of Ln abundance in the uranium ore of the Oklo natural nuclear reactor, Hidaka et al. demonstrated that 32–80% of La, Ce, and Nd, and 14% of Gd was of fissionogenic origin, while this percentage was zero for the heavier Ln (Hidaka et al., 1988). Thus, it appears that the content of light Ln in our samples are mostly of fissionogenic origin and that the fuel has already cooled for a significant time (probably several decades).

3.5. Possible scenario of contamination

In October 2016 and January 2017, ACRO made public some of

Table 3
Content (ppm) in Ln and Y of the soils. Uncertainties (k = 2) are 5% for Y, La–Nd and 10% for Eu–Lu.

| Sample n° | depth (cm) | La | Ce | Nd | Eu | Gd | Tb | Ho | Lu | Y |
|-----------|------------|-----|-----|-----|----|----|----|----|----|-----|
| Ru-1Bis | 0–5 | 305 | 679 | 423 | 24 | 71 | 12 | 18 | 10 | 391 |
| Ru-1 Ter | Lit | 251 | 585 | 406 | 25 | 72 | 13 | 18 | 9 | 365 |
| Ru-1 Ter | 0–10 | 122 | 292 | 261 | 20 | 41 | 18 | 15 | 9 | 224 |
| Ru-1 Ter | 10–15 | 111 | 264 | 268 | 21 | 42 | 18 | 15 | 10 | 230 |
| Ru-1 Ter | 15–20 | 88 | 269 | 256 | 21 | 41 | 20 | 16 | 11 | 238 |

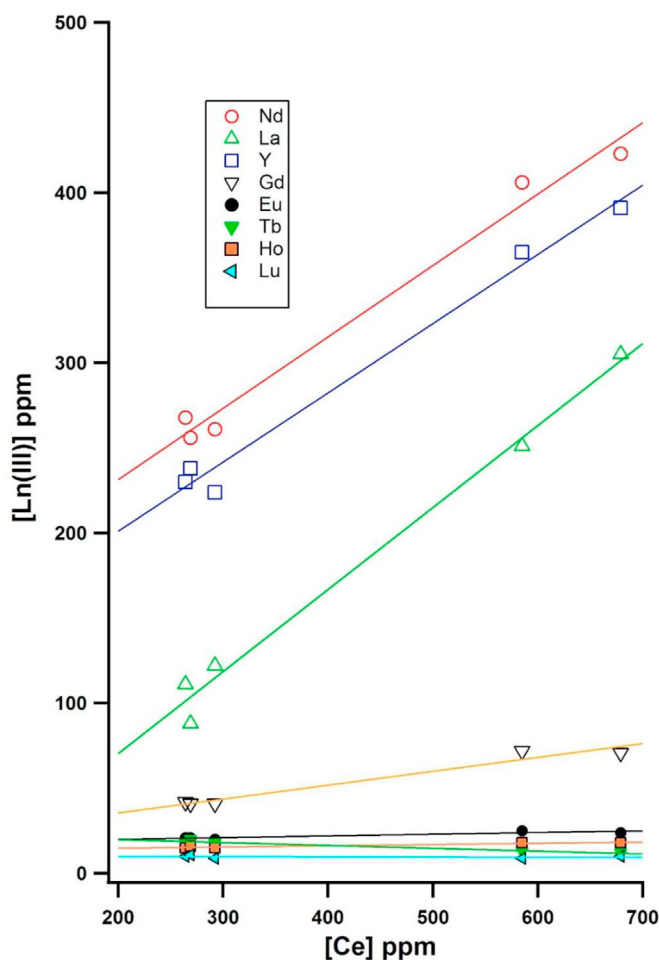


Fig. 3. Ln and Y content (ppm) in function of the Ce content (ppm) of the soils samples.

the collected data about the presence of several activation and fission products in the environment near La Hague nuclear reprocessing plant (ACRO, 2016, 2017). As a consequence, ASN (the French Nuclear Authority) mandated IRSN (French Institute of Nuclear Safety and Radiation Protection) to investigate the origin of the contamination. Based on IRSN documents released further, it appeared that a localized contamination had been known for several years, if not decades, and that IRSN carries out a survey program specific to this contamination (IRSN, 2017c). Further investigations by IRSN, in collaboration with the operator of the nuclear reprocessing plant (ORANO), revealed that several incidents during the 70's and beginning of 80's, involving the zone to the northwest of the reprocessing plant (ZNO), might have resulted in the contamination of the underground waters and soils in close proximity to the reprocessing plant. In particular, a fire that occurred on January 6, 1981 in a silo, located within the compounds of the reprocessing plant, at the North-West extremity of the site, containing waste from the natural uranium-graphite-gaz technology had involved the dispersion of ¹³⁷Cs and the flooding of the pit by the fire extinguisher. In addition, leakages from pits containing waste at the ZNO site might also be responsible for contaminating underground waters and soils. The extend of the contamination reported by IRSN and Orano is not well determined. However, the highest activities are found along the watershed of the Ru des Landes stream, especially in the surrounding of its source. Based on the low ²³⁸Pu/²³⁹⁺²⁴⁰Pu and low ²⁴¹Pu/²³⁹⁺²⁴⁰Pu ratios encountered in this study, it's plausible that natural uranium-graphite

waste was involved in the contamination.

As a consequence of this work and its own, IRSN recommended that the plant operator extend the specific search of radionuclides such as ^{90}Sr , Pu, and Am to the water table. IRSN also recommended evaluating the possibility of a continuous contamination through runoff from the ZNO to the surrounding environment. Finally, IRSN required the operator to include ^{90}Sr , and particularly ^{90}Sr in milk, in its reinforced monitoring plan. Eventually, the operator took the recent decision to remove the most contaminated soil layer close to the resurgence of the Ru des Landes River and to lower the water table upstream of the resurgence to avoid new contribution from artificial radionuclides to the site (IRSN, 2017a).

4. Conclusions

In this work, we show that the determination of several α and β -emitters in a few soil samples, in addition to the determination of γ -emitters, is much more informative than the determination of γ -emitters alone. This perspective enabled us to determine the source and age of a contamination in the vicinity of La Hague reprocessing plant. Because both α and β -emitter measurements are time- and resource- (human and material) consuming, they must be carried out on selected samples. In this respect, soil samples probably constitute the most interesting archive and should be preferred to other samples (grass, water), mostly because actinides are rather immobile in soil. Based on a survey of the literature, only a few laboratories carry out ^{241}Pu determination. Nevertheless, its measurement can be done using the source used for α -spectrometry, with only a few additional steps ((Alvarado et al., 2011) and Experimental Part). The only limitation to ^{241}Pu determination is the detection limit by LSC, because ^{241}Pu is a low-energy β -emitter ($E_{\text{max}} = 20.8$ keV), yielding a counting efficiency close to 30% only. The detection limit is consequently rather high, often in the range 0.1–1.1 Bq/kg dw (Alvarado et al., 2011). However, the determination of both ^{241}Pu and ^{241}Am gives interesting information about the age of the fuel involved in the contamination and greatly justifies the small amount of extra work involved, particularly when α -spectrometry yield $^{239+240}\text{Pu}$ activities above several Bq per kg of dry mass.

CRedit authorship contribution statement

Pierre-André Pittet, Investigation Mylène Josset, Conceptualization, Investigation, Writing David Boilley, Conceptualization, Investigation, Writing Antoine Bernollin, Conceptualization, Investigation, Guillaume Rougier, Investigation Pascal Froidevaux, Conceptualization, Investigation, Methodology, Ressources, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2020.129332>.

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