Nuclear Instruments and Methods in Physics Research B 294 (2013) 160–164

Contents lists available at SciVerse ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

AMS of the Minor Plutonium Isotopes

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ARTICLE INFO

Article history:
Received 2 June 2011
Received in revised form 25 June 2012
Available online 24 July 2012

Keywords:
Minor plutonium isotopes
Plutonium dating
Environmental plutonium
AMS

ABSTRACT

VERA, the Vienna Environmental Research Accelerator, is especially equipped for the measurement of actinides, and performs a growing number of measurements on environmental samples. While AMS is not the optimum method for each particular plutonium isotope, the possibility to measure ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu and ^{244}Pu on the same AMS sputter target is a great simplification. We have obtained a first result on the global fallout value of $^{244}Pu/^{239}Pu = (5.7 \pm 1.0) \times 10^{-5}$ based on soil samples from Salzburg prefecture, Austria. Furthermore, we suggest using the $^{242}Pu/^{240}Pu$ ratio as an estimate of the initial $^{241}Pu/^{239}Pu$ ratio, which allows dating of the time of irradiation based solely on Pu isotopes. We have checked the validity of this estimate using literature data, simulations, and environmental samples from soil from the Salzburg prefecture (Austria), from the shut down Garigliano Nuclear Power Plant (Sessa Aurunca, Italy) and from the Irish Sea near the Sellafield nuclear facility. The maximum deviation of the estimated dates from the expected ages is 6 years, while relative dating of material from the same source seems to be possible with a precision of less than 2 years. Additional information carried by the minor plutonium isotopes may allow further improvements of the precision of the method.

1. Introduction

Isotopic signatures of environmental plutonium are generally used to assess the origin of the material. While decay counting is restricted to ^{238}Pu, $^{239+240}$Pu, and ^{241}Pu, all mass spectrometric methods can in principle detect the isotopes ^{239}Pu ($T_{1/2}$ = 24.1 ka), ^{240}Pu (6.65 ka), ^{241}Pu (14.4 a), ^{242}Pu (373 ka), and ^{244}Pu (80.8 Ma). However, there are several publications available concerning isotopic concentrations of the minor plutonium isotopes ^{241}Pu, ^{242}Pu, and ^{244}Pu in environmental samples. [1] has assessed the global distribution of ^{241}Pu and ^{242}Pu, while [2] uses ^{241}Pu to distinguish Chernobyl plutonium from global fallout.

In [3] we have shown how the isotopic vector of Pu (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu) can be measured by combining the respective best suited method for each isotope. Due to the strong interference of ^{238}U in mass spectrometers, ^{238}Pu can generally be measured with alpha-spectrometry only. Also, while the combined activity of ^{239}Pu and ^{240}Pu can be determined efficiently by decay counting, their similar α-energies are not readily separated, thus a mass spectrometer is usually required to determine the isotopic ratio $^{240}Pu/^{239}Pu$. The short half-life of ^{241}Pu renders β-decay counting by LSC (Liquid Scintillation Counting) the most efficient method. For the long lived isotopes ^{242}Pu and ^{244}Pu only mass spectrometric methods are suitable. Among the mass spectrometric methods, AMS provides the most sensitive measurements [4], probably since in most cases the limit is imposed by background from ^{238}U rather than by detection efficiency. The destruction of molecules by stripping and the combination of several spectrometers, permits AMS to suppress background better than other methods.

If only AMS is used, ^{238}Pu cannot be measured, and a lower efficiency is achieved for ^{241}Pu. However, since no additional sample processing is required, the measurement of ^{241}Pu can be done at very little additional effort if the concentration of Pu in the sample is high enough.

During the last few years, we have carried out several studies on environmental Pu [5–7]. In most cases, the measurement of the $^{240}Pu/^{239}Pu$ ratio was the main interest. However, if we encountered samples with sufficiently high count rates for these isotopes, we additionally performed measurements of the minor Pu isotopes ^{241}Pu, ^{242}Pu, and in some cases even ^{244}Pu.

Dating with plutonium can be done very precisely by using the ratio $^{241}Am/^{241}Pu$ (e.g. [8]). The parent nuclide ^{241}Pu ($T_{1/2}$ = 14.4 yr) and the daughter ^{241}Am are different chemical elements and thus this ratio yields the date of either the irradiation or that of the last chemical separation. While this is a useful method for applications in the scope of nuclear safeguards, chemical fractionation occurring while the sample resides in the environment compromises its use for environmental studies. Without the presence of the daughter isotope ^{241}Am in the sample, the age since the irradiation

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http://dx.doi.org/10.1016/j.nimb.2012.06.017

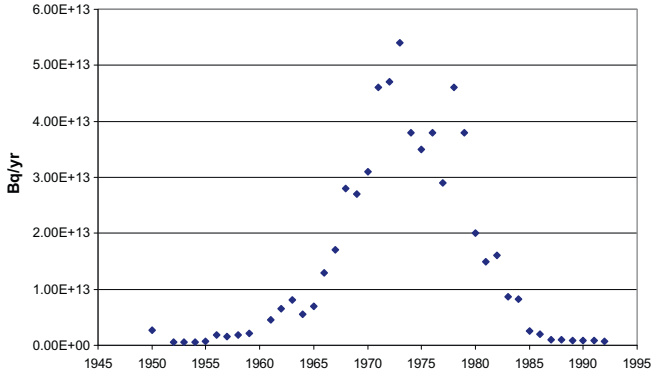

Fig. 1. Discharges of ^{241}Pu from Sellafiled into the Irish Sea. Data are taken from [15].

can be assessed only if the initial isotopic abundance of ^{241}Pu is known. This abundance, however, depends strongly on the production process, and thus is generally ambiguous. We propose to use the isotopic ratios of the other plutonium isotopes to estimate the initial ^{241}Pu content. To check the accuracy of this estimate, we have applied the method to measured literature values for a thermonuclear weapons test [9], and for the Chernobyl accident where we adopt the numbers obtained by [10] given by [2]. Additionally, we have simulated thermal neutron irradiation of ^{238}U. To demonstrate the practical applicability, we have measured environmental samples of different origin.

^{244}Pu is especially well suited to differentiate between plutonium from nuclear weapons and reactors [11]. The short lived nuclide ^{243}Pu ($T_{1/2}$ = 5 h) decays in a reactor before ^{244}Pu is produced, which results in ^{244}Cm being the isotope of mass 244 produced in a reactor. In a nuclear explosion, however, in which all nuclear reactions happen on a time scale of microseconds, ^{244}Pu can be produced directly via neutron captures on plutonium isotopes, and also by captures on uranium and subsequent β-decays after the explosion.

Little has been published so far on ^{244}Pu in environmental samples. Results have been published for the thermonuclear weapons test "Ivy Mike" (^{244}Pu/^{239}Pu = $(11.8 \pm 0.7) \times 10^{-4}$) [9] and for the low-yield test "Barbel" (^{244}Pu/^{239}Pu = $(2.3 \pm 0.4) \times 10^{-3}$) [12]. Local weapons test fallout in Bikini atoll sediments and soils has been measured with AMS recently by [11], yielding ^{244}Pu/^{239}Pu ratios between 2.8×10^{-4} and 5.7×10^{-4}. In the outer layer of a deep-sea manganese nodule a ^{244}Pu/^{239}Pu ratio of approximately 1×10^{-3} has been observed (taken from Fig. 3 of [13]), which the authors attribute to a global fallout.

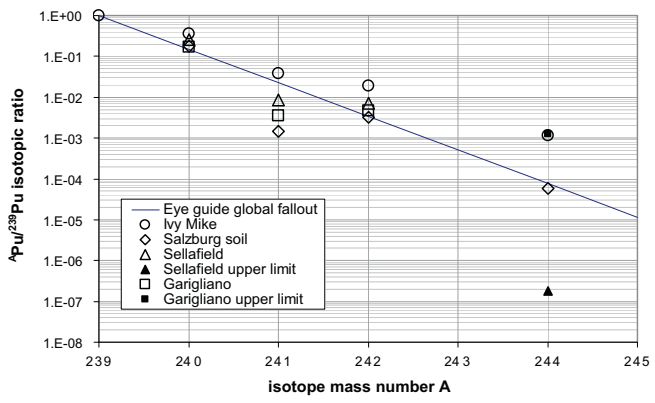

Fig. 2. Isotopic ratios relative to ^{239}Pu measured for the various types of samples in this work.

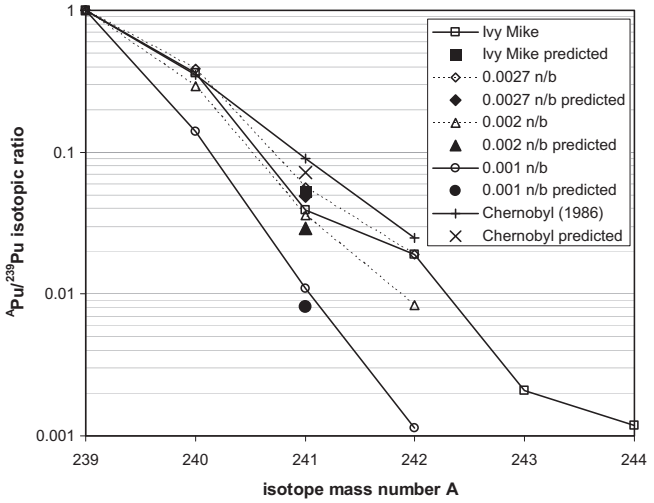

Fig. 3. Literature values and simulated thermal irradiation, immediately after production. The filled symbols near mass 241 show the initial ^{241}Pu/^{239}Pu ratio as predicted from ^{242}Pu/^{239}Pu by Eq. (1).

2. Samples

Samples were obtained from three different projects. In [5] depth profiles of ^{239}Pu and ^{240}Pu (among others) were obtained from the region of Nassfeld (Salzburg, Austria). While ^{137}Cs and ^{90}Sr in this region stem from the reactor accident in Chernobyl, ^{238}Pu/$^{239(240)}$Pu and ^{241}Am/$^{239(240)}$Pu activity ratios as well as the ^{239}Pu/^{240}Pu isotope ratio determined by AMS identified global fallout as the source of plutonium. The samples used for this work (T2F and T2G in [5]) were collected on the mountain pasture "Naßfeld-alm" at an altitude of 2530 m ASL, at 47.018 N, 13.012 E on August 25th, 1999. The chemical separation of the samples (separating ^{241}Am from ^{241}Pu) was carried out in summer 2006, the AMS measurement in August 2006. The minor plutonium isotope ratios have already been presented in Fig. 4 of [14].

The discharge history of Pu from Sellafield is well documented [15]. Though releases extended from 1952–1992, the peak discharge occurred between 1970 and 1980 (Fig. 1). A marine sediment core was collected in 1993 at 54.416 N, 3.563 W by the research vessel Gauss, Federal Maritime and Hydrographic Agency, Germany. This core was investigated for a number of isotopes in [16] and recently for Pu isotopes and ^{236}U with AMS at VERA [7]. Generally, the chronology of the 48 cm long core is unclear, since

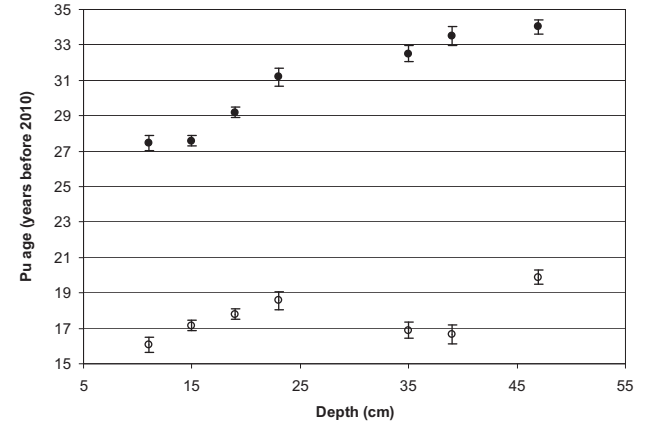

Fig. 4. Age-depth relation for the Sellafield core with (filled points) and without (hollow points) the information from ^{242}Pu.

mixing of the sediment is suggested by the oceanographic situation of the sampling site and hence [7] expects an "average integral ratio" of the discharges in the core; despite this, clearly discriminated peaks in the $^{239(40)}$Pu, ^{238}Pu, and ^{241}Pu are observed in [16]. For the present work, the AMS sputter targets prepared for [7] were re-measured for ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu and ^{244}Pu. The chemical sample preparation was performed in November 2009, while the AMS re-measurement was done in December 2011. For some of the samples, ^{240}Pu/^{239}Pu and ^{242}Pu/^{239}Pu data have already been given in [7], however the data in the present manuscript stems from the new measurement.

The Garigliano nuclear power plant was situated at Sessa Aurunca near the Garigliano river in Campania, Italy. It consisted of a boiling water reactor with a thermal power of 506 MW, and was in operation from 1964 to 1978 [6], and is presently in the decommissioning phase. Though mainly operated with 2.3% enriched UO_2, mixed oxide fuel, consisting of UO_2 and PuO_2, was also used. During operation and decommissioning, liquid effluents were drained into a channel which connects the plant to the river. A core from the sediment inside the (now dry) drain channel (41.257 N; 13.832 E) and another one from the entry point of the channel into the river was collected in May 2006; Pu was separated in autumn 2006, and the AMS measurement was performed in August 2007. Based on the ^{239,240}Pu depth profiles, the highest activity sample from each core was used for this work.

3. Methods

In studies on the yield of heavy elements in thermonuclear explosions [12,17,9] a general exponential trend with increasing mass was observed. Similar trends are observed for irradiation in reactors. This trend can be understood under the simplifying assumption of an identical cross section for all involved (n,γ) reactions; the chance to produce a mass n masses above the initial nucleus is then the probability of absorbing exactly n neutrons, which is described by a Poison distribution [18]. As long as the neutron absorption probability is small, this can be approximated by an exponential distribution. Furthermore, the higher binding energy of even-even nuclei leads to a higher abundance of isotopes with even masses; a factor of 1.58 was observed for the "Ivy Mike" device [9]. Thus the initial ratio between mass 241 and 239 will be the same as that between mass 242 and 240:

$$\left(\frac{^{241}Pu}{^{239}Pu}\right)_0 = \left(\frac{^{242}Pu}{^{240}Pu}\right) \quad (1)$$

and thus we obtain the time T since irradiation

$$T = \frac{T_{1/2}}{\ln 2} \ln \frac{\left(\frac{^{241}Pu}{^{239}Pu}\right)}{\left(\frac{^{242}Pu}{^{240}Pu}\right)} \quad (2)$$

with $T_{1/2}$ = 14.4 yr the half-life of ^{241}Pu.

Despite the present-day availability of improved nuclear data for a more detailed simulation, calculation of the actual isotope yields is complicated by the fact that a constant neutron flux throughout the uranium or plutonium used in the devices cannot be assumed. The resultant distribution will generally exhibit a higher yield of the heavier masses (more frequently produced in the high flux spots) than indicated by the lighter masses.

Simulations are possible for simplified cases, especially for thermal neutrons, which corresponds roughly to the case of reactor production. Additionally, we assume that the duration of the irradiation is much shorter than the half life of ^{241}Pu. Both neutron capture and fission are taken into account, the corresponding cross sections were taken from the ENDF/B-VII.0 database [19]. The system of differential equations was solved numerically with Mathematica (Wolfram Research, Champaign, IL, USA) for different assumed burn-up levels.

The methods to extract the plutonium from the environmental samples varied between the different projects; the (dry) sample mass was 1 g for Sellafield, 2–12 g for Garigliano, and 20 g for Salzburg samples, respectively. Generally, the samples were leached, and plutonium was extracted with ion exchange. After co-precipitation with 1 to 3 mg iron, the sample was calcined to produce plutonium oxide embedded in an iron oxide matrix.

The AMS facility VERA is especially equipped for the measurement of heavy ions [14]. Uranium pilot beams are used for tuning the spectrometer, which is then scaled to the various Pu isotopes for the measurement. Slow sequencing is done between the isotopes. The switching times between the different isotopes is typically 15 s, therefore fast variations of the ion source output are not completely averaged out and contribute to the uncertainty of the measured isotopic ratios. PuO^- is extracted and injected into the accelerator. The high-energy beam analysers are designed to allow the transport of 5 + actinide ions at a terminal voltage of 3 MV. Oxygen is used as a stripper gas which results in a stripping yield of 5% for this charge state. For most previously published data a Time-of-Flight (ToF) detector with ~25% efficiency was used to further suppress potential background from ^{238}U; but we have never observed such background, so measurements can also be carried out without ToF, resulting in a theoretical detection efficiency of 4×10^{-4}. However, under typical sputter source conditions, for 10^{10} Pu atoms in the sputter target we obtain a count rate of ~30 s^{-1} (for PuO_2^- only 1/10 of this count rate is observed). Since the sputter targets last for many hours, the available accelerator beam time usually limits the detection efficiency. We hope that we can improve on this by reducing the amount of iron matrix used, which requires new handling procedures.

Counting statistics were no limitation for the Sellafield marine core samples, since their concentration of radionuclides is exceptionally high; as already reported in [7], to avoid saturation of the detectors by the very high count rates we had to reduce the source output strongly, by running the cesium reservoir essentially at room temperature instead of the usual 150 °C. Therefore, these sputter targets appeared almost untouched after the measurement. All data was normalized to a pulser running at a fixed frequency to correct for any detector dead time that arose as a result of high counting rates.

Since all Pu isotopes are measured in the same ionization chamber, we assume the same ion optical transmission. The AMS device can in principle introduce large fractionation, since each isotope is essentially measured with a different tuning of the (relatively complex) mass spectrometer, and the tunings may differ in quality. Since we obtain our plutonium tunings by scaling from the ^{238}U pilot beam the heavier plutonium masses are more likely to suffer from ion optical losses. The resultant uncertainty is difficult to assess, since no plutonium standard with isotopic ratios suitable for AMS is available so far, which would allow to monitor and correct machine fractionation for every measurement. However, reference materials measured in the past suggest a typical precision better than 10%. To monitor whether the beam tuning degrades as a result of drift in the components, the ^{236}U/U ratio of our in-house uranium standard Vienna-KkU is measured using three sputter targets per turn of the sample wheel. It should be noted that systematic trends in the ion optical transmission of the different Pu isotopes will partly cancel out in the double-ratio used in Eq. (2).

We expect little fractionation during chemical sample preparation, and blank material allows any laboratory contamination to be traced.

The beam analysers will not distinguish between the in-growing ^{241}Am and the remaining ^{241}Pu. However, the time span between the separation of ^{241}Am and the AMS measurement is still

Table 1
Measured isotopic ratios of environmental plutonium. Uncertainties are counting statistics (1σ).

Sample name	Description	$^{240}Pu/^{239}Pu$	$^{241}Pu/^{239}Pu$	$^{242}Pu/^{239}Pu$	$^{244}Pu/^{239}Pu$	Pu age
T2F	Soil, Salzburg	0.184 ± 0.001	$(1.39 \pm 0.07) \times 10^{-3}$	$(3.19 \pm 0.11) \times 10^{-3}$	$(6.35 \pm 0.11) \times 10^{-5}$	52.4 ± 1.6
T2G	Soil, Salzburg	0.174 ± 0.002	$(1.48 \pm 0.11) \times 10^{-3}$	$(3.26 \pm 0.17) \times 10^{-3}$	$(5.09 \pm 0.16) \times 10^{-5}$	52.6 ± 2.5
D2_20_4	Garigliano, drain channel	0.167 ± 0.010	$(4.8 \pm 1.3) \times 10^{-3}$	$(6.6 \pm 1.5) \times 10^{-3}$	n.d.	43 ± 9
E2_21_16	Garigliano, river sediment	0.178 ± 0.009	$(2.2 \pm 0.8) \times 10^{-3}$	$(2.8 \pm 0.9) \times 10^{-3}$	n.d.	41 ± 13
St60e	Sellafield, 11 cm depth	0.226 ± 0.001	$(8.45 \pm 0.12) \times 10^{-3}$	$(7.19 \pm 0.11) \times 10^{-3}[(6.4 \pm 0.7) \times 10^{-3}]^*$	$<3.5 \times 10^{-6}$	27.5 ± 0.4 [25.1 ± 2.3]*
St60g	15 cm	0.228 ± 0.001	$(8.15 \pm 0.08) \times 10^{-3}$	$(7.04 \pm 0.07) \times 10^{-3}$	$<2.0 \times 10^{-6}$	27.6 ± 0.3
St60i	19 cm	0.226 ± 0.001	$(7.79 \pm 0.05) \times 10^{-3}$	$(7.22 \pm 0.07) \times 10^{-3}$	$<1.4 \times 10^{-6}$	29.2 ± 0.3
St60k	23 cm	0.218 ± 0.001	$(6.97 \pm 0.11) \times 10^{-3}$	$(6.85 \pm 0.11) \times 10^{-3}[(5.5 \pm 0.2) \times 10^{-3}]^*$	$<2.1 \times 10^{-6}$	31.2 ± 0.5 [26.6 ± 0.8]*
St60q	35 cm	0.197 ± 0.001	$(6.18 \pm 0.09) \times 10^{-3}$	$(5.86 \pm 0.09) \times 10^{-3}$	$<1.9 \times 10^{-6}$	32.5 ± 0.4
St60s	39 cm	0.192 ± 0.001	$(5.94 \pm 0.11) \times 10^{-3}$	$(5.75 \pm 0.10) \times 10^{-3}$	$<3.0 \times 10^{-6}$	33.5 ± 0.5
St60w	47 cm	0.183 ± 0.001	$(4.60 \pm 0.06) \times 10^{-3}$	$(4.35 \pm 0.06) \times 10^{-3}[(5.4 + 0.7) \times 10^{-3}]^*$	$<2.2 \times 10^{-6}$	34.0 ± 0.4 [38.5 ± 2.7]*

* $^{241}Pu/^{239}Pu$ ratios taken from [7], and Pu ages calculated from these ratios.

relevant. Am (most likely) has a different negative ion yield to Pu, which introduces an uncertainty into the mass 241 determination. We are not aware of any published ionization yield for Am, but [20] has investigated other monoxide ions of actinides: the relative negative-ion formation probability of ThO^-, UO^-, NpO^-, and PuO^- is approximately 1:3:5:7. As an example, we assume that Am does form negative monoxide ions even two times better than Pu, and that the measurement is carried out one year after chemical separation. Since 5% of ^{241}Pu will have decayed into ^{241}Am, the observed count rate for mass 241 will appear 5% higher, which corresponds to a 1 yr lower age. As another extreme example, if we assume that Am does not form any negative monoxide ions at all (which is definitively not the case, see [7]), the sample will appear one year older - as it actually is. Since no information is available on the actual ion yield of Am, which is moreover expected to vary with the matrix of the sputter target and with ion source conditions, we assume an additional uncertainty of 1 year for the age determination per year between separation and measurement.

4. Results and discussion

Fig. 2 and Table 1 shows the results measured in this work, in comparison to the numbers given for the "Ivy Mike" nuclear test in [9]. 43 counts of ^{244}Pu were successfully measured on Salzburg soil within 1.5 h. The resultant isotopic ratio for $^{244}Pu/^{239}Pu$ is $(5.7 \pm 1.0) \times 10^{-5}$. This value is significantly lower than the value given in [13]. A contribution of reactor material in our samples, in particular from the Chernobyl accident, could cause a lower ratio. However, a significant contribution from Chernobyl was excluded in [5]. Additionally, while a $^{241}Pu/^{239}Pu$ ratio of 2.7×10^{-2} is expected for Chernobyl debris in 2011, our measured ratio of $(1.43 \pm 0.06) \times 10^{-3}$ is more than one order of magnitude lower, and lies perfectly on the eye guide for global fallout (through masses 239 and 242 of Salzburg soil). We think that our value better represents the northern hemisphere global fallout ratio than that taken from [13]. A possible explanation for the higher ratio observed in the deep sea crust (VA13–2, 9°18′ N, 146°03′ W, 4830 m depth) would be influence from the various nuclear test sites in the south Pacific. We think this assumption is supported by the $^{240}Pu/^{239}Pu$ of ~0.25 observed in the nodule sample (also taken from Fig. 3 in [13]), while the accepted northern hemisphere global fallout average is 0.185 [1]; this value is also observed in our Salzburg soil samples.

The time since irradiation calculated using Eq. (2) for the measurements from literature and the simulations for thermal neutrons is shown in Table 2 and Fig. 3. Since all ratios were calculated for the time of production, or corrected for ^{241}Pu decay, an age of 0 is expected in all cases. While the Mike test appears 6 years older than expected, the simulated thermal neutron results appear too young, and the deviation grows with the assumed burnup. The Chernobyl data appears 5 years too young; a more accurate estimate is obtained if we assume production by thermal neutrons. In this case, we do not use Eq. (2), but fit the simulation to the measured $^{240}Pu/^{239}Pu$ ratio, which results in a total thermal neutron fluence of 0.0025 b^{-1}, and in an estimated age deviating by less than 2 years from the known calendar date of the Chernobyl explosion. This agreement is surprising, considering that the processes in the actual reactor deviated significantly from a simple thermal neutron irradiation.

Table 1 also gives the results for the ages of the environmental samples. For the Salzburg soil, an age of 52.5 ± 1.5 yr is obtained, corresponding to the year 1954. This age is 8 yr before the maximum of the nuclear weapons tests in 1963, and the deviation is similar to that for the Ivy Mike test. If this trend holds for all material produced in nuclear explosions, a correction could be applied reducing the deviation. The Garigliano results suffer from a larger statistical uncertainty, due to lower Pu concentration in the samples. The age is 42 ± 8 yr, which corresponds to the year 1965, in agreement with expectations.

Our new $^{240}Pu/^{239}Pu$ data for the Sellafield core agrees with previous measurements on the same sputter targets presented in [7], while the three $^{242}Pu/^{239}Pu$ ratios given there have significantly

Table 2
Apparent plutonium age calculated for literature data and simulated irradiation with thermal neutrons.

Description	$^{240}Pu/^{239}Pu$	$^{241}Pu/^{239}Pu$	$^{242}Pu/^{239}Pu$	Apparent Pu age immediately after production (yr)
"Ivy Mike" weapons test [9]	0.363	0.039	0.019	6.2
Chernobyl debris [2]	0.35	0.09	0.025	−4.8
Thermal neutrons on ^{238}U, fluence 0.0027 b^{-1}	0.387	0.057	0.019	−3.0
Thermal neutrons on ^{238}U, fluence 0.002 b^{-1}	0.29	0.036	0.008	−4.5
Thermal neutrons on ^{238}U, fluence 0.001 b^{-1}	0.14	0.011	0.0011	−6.2

lower precision. However, one sample (St60 k) shows a deviation of about 25% from the previously published data, which is much more than allowed by counting statistics (see Table 1). We attribute this outlier to variations in the transmission of ^{242}Pu through the spectrometer, limiting the reproducibility of the present method. Since a deviation of 25%, corresponding to a dating error of about 5 years, is relevant for the present work, this emphasizes the need for an AMS standard which would allow to trace and correct for such variations.

Our Sellafield dataset is well suited to illustrate the advantage of using the ^{242}Pu information for dating. Fig. 4 shows a comparison of the ages obtained by using Eq. (2) compared to an estimate of the initial ^{241}Pu/^{239}Pu which is based only on ^{240}Pu/^{239}Pu:

$$\left(\frac{^{241}Pu}{^{239}Pu}\right)_0 = \left(\frac{^{240}Pu}{^{239}Pu}\right)^2 \quad (3)$$

While the age shift due to the neglected even–odd offset of this simpler method could probably be handled, the ^{242}Pu information establishes a monotonous age-depth curve for the sediment core, however the data covers only a short time span of seven years. The time range 1977 to 1984 falls well into the later part of the Sellafield discharges; however, if the age is calibrated against a simulated thermal neutron irradiation, a fluence of 0.0015 b^{-1} fits best, and leads on an estimated age correction of 5 years. This shifts the time span into the maximum of the Sellafield release history.

5. Conclusions

The conventional approach towards source assessment of an unknown material is to measure elemental concentrations and isotopic ratios, and to compare them with a database of all viable sources. This works also for environmental plutonium isotopes, and probably would lead to the same source assignments as the method proposed in this work. However, we think that the calculation of "predictive" values like burn-up, irradiation date, or production mode (i.e. reactor vs. explosion) makes the assessment more straightforward.

The measurement of ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu and ^{244}Pu allows for more precise assessment of the history and origin of environmental plutonium. We obtained the first results on the global fallout ratio of ^{244}Pu/^{239}Pu. Additionally we have shown that the use of ^{241}Pu and ^{242}Pu allows dating of the time of irradiation accurate to within 6 years, while our data on the Irish Sea sediment core suggest that relative dating of material from the same source is possible with a precision of less than 2 years. The information contained in the other plutonium isotopes may allow further improvement in the precision. When a reactor origin can be assumed, possibly based on the absence of ^{244}Pu, and by calibrating the data against simulated thermal neutron data with the same ^{240}Pu/^{239}Pu, an accuracy of 2 years is suggested by our data.

Acknowledgements

The work presented in this paper was partially performed in the frame of a European Commission-Joint Research Centre "In-Service Training" scheme at the JRC-IT. The authors thank Dr. H. Nies, IAEA-MEL (present affiliation), and the Federal Maritime and Hydrographic Agency, Hamburg (Germany), for the courtesy of providing the Irish Sea sediment samples. Financial support by the FWF Austrian Science Fund (project number P21403-N19) is gratefully acknowledged.

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