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Determination of ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu at femtogram and attogram levels – evidence for the migration of fallout plutonium in an ombrotrophic peat bog profile

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The isotopic composition of plutonium (^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu) was investigated in a ~0.5 m long peat core from an ombrotrophic bog (Black Forest, Germany) using clean room procedures and accelerator mass spectrometry (AMS). This sophisticated analytical approach was ultimately needed to detect reliably the Pu concentrations present in the peat samples at femtogram (fg) and attogram (ag) levels. The mean ^{240}Pu/^{239}Pu isotopic ratio of 0.19 ± 0.02 ($N = 32$) in the peat layers, representing approximately the last 80 years, was in good agreement with the accepted value of 0.18 for the global fallout in the Northern Hemisphere. This finding is largely supported by the corresponding and rather constant ^{241}Pu/^{239}Pu (0.0012 ± 0.0005) and ^{242}Pu/^{239}Pu (0.004 ± 0.001) ratios. Since the Pu isotopic composition characteristic of the global fallout was also identified in peat samples pre-dating the period of atmospheric atom bomb testing (AD 1956–AD 1980), migration of Pu within the peat profile is clearly indicated. These results highlight, for the first time, the mobility of Pu in a peat bog with implications for the migration of Pu in other acidic, organic rich environments such as forest soils and other wetland types. These findings constitute a direct observation of the behaviour of Pu at fg and ag levels in the environment. The AMS measurements of Pu concentrations (referring to a corresponding activity of $^{240+239}$Pu from 0.07 mBq g^{-1} to 5 mBq g^{-1}) essentially confirm our *a priori* estimates based on existing ^{241}Am and ^{137}Cs data in the investigated peat core and agree well with the global fallout levels from the literature. Exclusively employing the Pu isotope ratios established for the peat samples, the date of the Pu irradiation (AD 1956, correctable to AD 1964) was calculated and subsequently compared to the ^{210}Pb age of the peat layers; this comparison provided an additional hint that global fallout derived Pu is not fixed in the peat column, but has migrated downwards along the peat profile to layers preceding the nuclear age.

Environmental impact

Plutonium represents a high radiological hazard for the environment and mankind. Assessing plutonium contamination and its exposure pathways to humans requires the knowledge of its behaviour in natural systems. Among these, peatlands, which cover 5% of the Earth's surface, are critical ecosystems due to their capability to accumulate a broad range of heavy metals. Our study constitutes the first direct observation of the mobility of plutonium in an ombrotrophic peat bog. With an ultra-sensitive analytical approach, the detection of global fallout derived plutonium at femtogram and attogram levels in the peat samples was accomplished. Our study demonstrates that the ultra-trace isotopic analysis of plutonium is a powerful tool for assessing the origin of plutonium contamination and its mobility in the environment.

Introduction

The assessment of nuclear contamination in ecosystems and its possible exposure pathways to human beings requires the analysis of sources and migration patterns of radionuclides in a wide range of natural systems. Among these, peatlands, which account for *ca.* 5% of the Earth's land area, should be rather retentive, given their capability of accumulating a broad range of potentially harmful elements, such as Hg, Pb, and As.[1]

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A major concern with respect to radioactive contamination of the environment is related to contamination from radionuclides with long half-lives and high radiotoxicity, such as those of plutonium (Pu) isotopes. ^{239}Pu ($t_{1/2} = 24.1$ ka) is produced in nuclear explosions as well as in nuclear reactors by neutron capture on ^{238}U followed by the β decays of the short lived ^{239}U and ^{239}Np. The heavier Pu isotopes, ^{240}Pu ($t_{1/2} = 6.65$ ka), ^{241}Pu ($t_{1/2} = 14.4$ a), and ^{242}Pu ($t_{1/2} = 373$ ka) are built up by successive neutron capture starting from ^{239}Pu. Thus, the isotopic composition of Pu reflects the irradiation history of the nuclear material. In fact, the isotopic ratios ^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu can be used as a reliable indicator of the contamination source.[2–4] For example, characteristic ^{240}Pu/^{239}Pu isotopic ratios in the global fallout and in Chernobyl fuel particles are in the ranges of 0.17–0.19 and 0.45–0.52, respectively.[5] Far away from highly contaminated sites, Pu is present in the environment at trace levels, on the order of 0.1 mBq g^{-1}, mainly from weapon test fallout with additional local contributions, *e.g.*, Chernobyl fallout. Due to the long half lives and the low concentration of Pu isotopes in the ambient environment, radiometric methods are less helpful than the far more sensitive mass spectrometric methods; among these, accelerator mass spectrometry (AMS) is presently the analytical technique which provides the highest sensitivity for Pu measurements (detection limit $\sim 2 \times 10^5$ atoms per sample),[6] allowing the determination of Pu at fg levels.[7]

In this work, Pu isotopes were determined in an undisturbed peat core from the Wildseemoor, an ombrotrophic bog in the Black Forest (SW Germany). This area of Europe was little affected by Chernobyl fallout, as the dispersion of the particle-form reactor debris was largely limited to the zone within 100 km from the accident.[8] Nevertheless, the Chernobyl contribution cannot be excluded *a priori*, since there is evidence of Chernobyl-derived Pu contamination beyond this zone; for example, a strong indication of mixing between Chernobyl and global fallout sources of Pu and Np was found in archived lichens (1986–1988) from Sweden.[9] Also, a pronounced Chernobyl contribution in soil from north-eastern Poland was identified, whereas global fallout Pu in forest soils and peat bogs of southern Poland was detected.[3] In an extensive study on Pu in several environmental matrices in the territory of Poland, the fallout pattern of Pu was reconstructed and the maximum inventory of the Chernobyl-derived Pu was found in the far north-east of the country.[10]

The investigated peat core was collected as part of a previous research project carried out at the University of Heidelberg,[11] when it was dated using the ^{210}Pb method. In addition, limited data on ^{241}Am and ^{137}Cs activities in the peat samples were obtained by gamma spectrometry.

In the present study, estimation of the Pu levels in the peat core was based on these existing ^{241}Am and ^{137}Cs data. Then for the direct measurements of the minute amounts of Pu expected in these samples, an efficient separation procedure for the extraction of Pu from peat samples was developed and AMS was chosen for the determination of the Pu isotopic composition. The isotopic ratios ^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu were analysed along the peat profile to identify the contamination source and migration pattern of this radionuclide. The measurement of the isotopic vector of Pu (^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu) allows the use of the ^{242}Pu/^{240}Pu isotopic ratio as an estimate of the initial ^{241}Pu/^{239}Pu isotopic ratio; in this way, it was possible to date the time of irradiation solely on the basis of Pu isotopes.[4] The Pu age obtained in this way was then compared to the age of the corresponding peat layer from the ^{210}Pb method.[11]

Experimental

Estimation of plutonium levels from ^{241}Am and ^{137}Cs

From the existing data on ^{241}Am and ^{137}Cs activities,[11] it is possible to obtain an estimate of the ^{239}Pu concentration in the peat core and, under the hypothesis of a solely global fallout origin, of the corresponding activity of $^{239+240}$Pu. ^{241}Am ($t_{1/2} =$ 430 a) is produced by the beta decay of its parent ^{241}Pu. The number of atoms of ^{241}Pu, $N_{^{241}\mathrm{Pu}}(t_0)$, which from the time of deposition produced the number of ^{241}Am $N_{^{241}\mathrm{Am}}(t)$, under the hypothesis of negligible deposition of ^{241}Am, is calculated as described previously:[12]

$$N_{^{241}\mathrm{Pu}}(t_0) = N_{^{241}\mathrm{Am}}(t)\left[\left(\lambda_{^{241}\mathrm{Am}} - \lambda_{^{241}\mathrm{Pu}}\right)/\lambda_{^{241}\mathrm{Pu}}\right]\left[1/\left(\mathrm{e}^{-\lambda_{^{241}\mathrm{Pu}}t} - \mathrm{e}^{-\lambda_{^{241}\mathrm{Am}}t}\right)\right] \tag{1}$$

where $t = 55$ years under the hypothesis of global fallout origin, and $\lambda_{^{241}\mathrm{Am}}$ and $\lambda_{^{241}\mathrm{Pu}}$ are the decay constants of ^{241}Am and ^{241}Pu, respectively.

The number of ^{239}Pu atoms is estimated from the decay corrected ^{241}Pu/^{239}Pu isotopic ratio from the global fallout:[6,13]

$$N_{^{239}\mathrm{Pu}} = N_{^{241}\mathrm{Pu}}/0.05 \tag{2}$$

The $^{240+239}$Pu activity, $A_{^{240+239}\mathrm{Pu}}$, can be subsequently obtained from the global fallout ^{240}Pu/^{239}Pu isotopic ratio, which is 0.18:[2]

$$A_{^{240+239}\mathrm{Pu}} = N_{^{239}\mathrm{Pu}}\left[\left(0.18\lambda_{^{240}\mathrm{Pu}}\right) + \lambda_{^{239}\mathrm{Pu}}\right] \tag{3}$$

The $^{240+239}$Pu activity can also be estimated from the ^{137}Cs activity; the cumulative areal inventory of ^{137}Cs and $^{240+239}$Pu from the global fallout in soils from forest, grassland and arable land in Bavaria was reported[14] with an activity ratio of $^{240+239}$Pu/^{137}Cs $= 0.018 \pm 0.0024$; this ratio when decay-corrected to the end of 2009 gives:

$$A_{^{240+239}\mathrm{Pu}} = 0.03A_{^{137}\mathrm{Cs}} \tag{4}$$

Sample collection and previous measurements

The ombrotrophic peat core was collected in 2006 at Wildseemoor in the Black Forest (GPS-point N 48° 43′ 03″; E 08° 27′ 34″), the largest peat bog in Germany, following a well-established protocol for the collection, handling and preparation of peat samples for physical, chemical, mineralogical and isotopic analyses.[15]

The contribution of the vegetation to the inventories of ^{210}Pb is crucial to the accuracy of dating of peat cores.[16–18] In the analysed peat core, the aerial vegetation and the plant remains overlying the peat constituted a 5 cm thick layer above the peat surface. This overlying compartment of vegetation was collected and taken into account for the dating of the core. The frozen core was cut into ~1 cm slices using a stainless steel band saw. Aliquots of 1–2 grams of dry samples were measured for ^{210}Pb, ^{137}Cs and ^{241}Am employing a low background gamma spectrometer. The ^{210}Pb age of the individual samples was calculated using the unsupported ^{210}Pb data and applying the constant rate of the supply model.[19] The activities of ^{210}Pb in the peat core (0–69 cm depth) and the five layers of overlying vegetation (−5 to 0 cm depth) are reported in Fig. 1 together with the resulting age dates of the layers. Fig. 1 presents also the profiles of the ^{137}Cs and ^{241}Am activities. Further details on the collection and handling of the samples and gamma spectrometry measurements can be found elsewhere.[11]

Chemical separation of plutonium

In the current study, weighing and all further manipulation of peat samples prior to their dissolution were accomplished in Class 100 clean benches. The chemical separation of Pu from the digested peat samples was carried out in a metal-free, ultraclean environment (laboratory Class 100 and work benches Class 10) at the Institute for Geosciences, University of Heidelberg, Germany. All employed reagents were of ultra-pure quality. Nitric acid used was sub-boiled twice (DuoPUR, MLS, Leutkirch, Germany) in a clean air cabinet. High purity water (18.2 MΩ cm) from a MilliQ Element (Millipore) water supply system was used throughout. Before use, all materials in contact with the actual samples were cleaned thoroughly following well established procedures developed for the analysis of ultra-trace element concentrations in Arctic ice and snow.[20]

The five layers of overlying vegetation and the top three layers of peat were not available for Pu analysis, but a total of 32 peat samples, whose depths refer to the lower boundaries of the peat layers spanning from 6 down to 47 cm, were considered for the actual study. The 32 dried peat samples (1 g) were digested with 12 mL of concentrated nitric acid each, employing a microwave-assisted high-pressure autoclave (ultraCLAVE II, MLS, Leutkirch, Germany).[21,22] At this step, reference materials containing mainly ^{242}Pu or ^{244}Pu are usually added to the samples as tracers to allow the quantification of Pu concentrations. In this work, however, no such spikes were added to the peat samples, in order to allow the determination of ^{242}Pu and possibly ^{244}Pu in the samples.

Subsequently, the dissolved Pu in the digestion solutions was quantitatively converted to the oxidation state Pu(IV) through addition of sodium nitrate in 3 M nitric acid. The separation of Pu from the sample solution was achieved using a UTEVA® resin column. Pu was eluted from the column after reduction to Pu(III) by applying a solution of 0.2 M hydroxylammonium hydrochloride and 0.02 M ascorbic acid in 2 M nitric acid. After co-precipitation with iron hydroxide and conversion to iron oxide, the purified Pu fractions of the peat samples were transported to the VERA laboratory (Vienna); the samples were pressed into the sputtering cathodes suited to the 3 MV tandem accelerator facility at VERA and measured for ^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu isotopic ratios following well established experimental procedures.[4,6] In this way, a total of 32 peat samples, spanning a period from AD 1917 to AD 1992, as well as four chemistry blanks and three aliquots of an in-house reference material with a known ^{239}Pu concentration were analysed. The chemical separation of Pu from the peat samples was accomplished in May 2012 and the AMS measurements of Pu isotopes were performed shortly thereafter in June 2012.

Irradiation date of plutonium

The estimated date of the time of irradiation (t_i) of Pu was calculated according to a previous study:[4]

$$t_{\mathrm{i}} = \mathrm{In}\left[\left(^{242}\mathrm{Pu}/^{240}\mathrm{Pu}\right)/\left(^{241}\mathrm{Pu}/^{239}\mathrm{Pu}\right)\right]1/\lambda_{^{241}\mathrm{Pu}} \quad (5)$$

assuming that at the time of irradiation, t_0:

$$^{242}\mathrm{Pu}/^{240}\mathrm{Pu} = {}^{241}\mathrm{Pu}/^{239}\mathrm{Pu} \quad (6)$$

with $\lambda_{^{241}\mathrm{Pu}}$, the decay constant of ^{241}Pu.

Results and discussion

Estimation of plutonium levels from ^{241}Am and ^{137}Cs

As presented in Fig. 1, ^{241}Am was discontinuously detectable in the Wildseemoor peat core in the layers from 21 cm depth

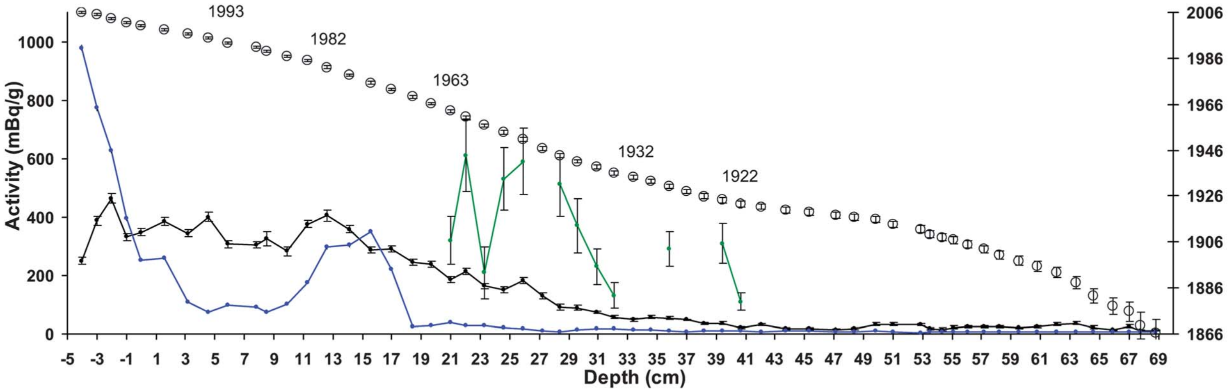

Fig. 1 The activities of ^{210}Pb (black dots) and the corresponding ages (empty circles) of the peat layers are shown as a function of depth; the activities of ^{137}Cs (blue dots) and ^{241}Am (green dots), where detected, are as well presented. The activities of ^{241}Am are multiplied by 100 in order to be better visible in the plotted area. Depths refer to the lower boundaries of the peat layers.

(AD 1961) down to 41 cm depth (AD 1922);[11] its activity ranged between ~1 and 6 mBq g^{-1} with an average value of ~3.5 mBq g^{-1}. This ^{241}Am activity corresponds to a concentration of ~3×10^{-14} g g^{-1}. In moss samples from a bog in the Eastern Italian Alps,[23] an ^{241}Am concentration of 2×10^{-14} g g^{-1} was detected, and attributed to the global fallout origin on the basis of the ^{240}Pu/^{239}Pu isotopic ratios measured in the same samples. Given the similarity between the ^{241}Am concentrations, this could be an indication of the global fallout origin of Pu also in the Wildseemoor peat samples.

The profile of ^{137}Cs, shown in Fig. 1, revealed a maximum of ~1000 mBq g^{-1} in the top layer of the living vegetation; the ^{137}Cs activity decreased continuously down to ~90 mBq g^{-1} between 5 and 8 cm depth (AD 1995 and AD 1989, respectively). A peak was found between 10 and 18 cm depth (AD 1987 and AD 1969, respectively) with the maximum of ~350 mBq g^{-1} at 16 cm depth (AD 1975). After this peak, the activity of ^{137}Cs decreased slowly from ~30 mBq g^{-1} down to ~10 mBq g^{-1} at 69 cm depth (AD 1867). In the analysed peat core, the Chernobyl peak (AD 1986) of ^{137}Cs appears to be moved downwards by 6 cm, while the global fallout peak (AD 1963) seems not to be preserved and ^{137}Cs is detectable continuously down to the depth dated AD 1967. These findings are in agreement with the observed mobility of Cs in the peat environments.[24–26]

The average ^{137}Cs activity within the same interval of layers (21–41 cm depth) considered for ^{241}Am, was ~16 mBq g^{-1}, reflecting the global fallout.

Considering the above mentioned ^{241}Am and ^{137}Cs average activities, our estimates of $^{240+239}$Pu activity from eqn (1)–(4) are in the range of 0.7–4 mBq g^{-1}. These values are consistent with the measurements of $^{240+239}$Pu activities ranging between 0.25 and 9.4 mBq g^{-1} in moss samples from a bog in the Eastern Italian Alps,[23] with the levels found in Austrian soil profiles,[27] with the river sediment in Southern Italy[28] and with peat profiles from southwest Spitsbergen.[29]

The estimated activities translate into a ^{239}Pu concentration within the range of ~10^8 to 10^9 atoms per gram or ~100 to 1000 fg g^{-1} and a corresponding ^{240}Pu concentration of ~10 to 100 fg g^{-1}.

AMS measurements of ^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu isotopic ratios

The ^{240}Pu/^{239}Pu isotopic ratios and the ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu isotopic ratios in the peat layers, from a depth of 6 cm down to 47 cm, are presented in Fig. 2 and 3, respectively.

As highlighted in Fig. 2, the ^{240}Pu/^{239}Pu isotopic ratios are constant along the core with a mean value of 0.191 ± 0.018 ($N = 32$). This result is consistent with the acknowledged average ^{240}Pu/^{239}Pu isotopic ratio from the global fallout in the Northern Hemisphere of 0.180 ± 0.014,[2] which is represented with the blue line in Fig. 2. Comparing the mean value of the ^{240}Pu/^{239}Pu isotopic ratio measured along the investigated peat core by a 2 tailed *t*-test with the value of ^{240}Pu/^{239}Pu $= 0.180$,[2] $t = 3.42$ is obtained, showing agreement on a statistical significance level of 99.8%.

Similarly, ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu isotopic ratios show no trend as a function of depth of the peat core (Fig. 3), but rather reveal the same isotopic distribution in all peat layers. The average ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu isotopic ratios along the investigated peat profile are 0.0012 ± 0.0005 and 0.004 ± 0.001, respectively. Taken together, the Pu isotopic ratios displayed in Fig. 2 and 3 clearly indicate that the global fallout is the predominant source of Pu in this peat core. In Fig. 4 the average ^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu isotopic ratios considering all peat layers are highlighted; the circles represent the Pu ratios as measured in June 2012, while the square represents the ^{241}Pu/^{239}Pu isotopic ratio decay-corrected to the year AD 1960 ($t = 0$); negligible decay of ^{239}Pu, ^{240}Pu and ^{242}Pu is assumed, since their half-lives are significantly higher than the time span considered. The decay corrected ^{241}Pu/^{239}Pu isotopic ratio is 0.021 ± 0.007 and fits the exponential mass trend of

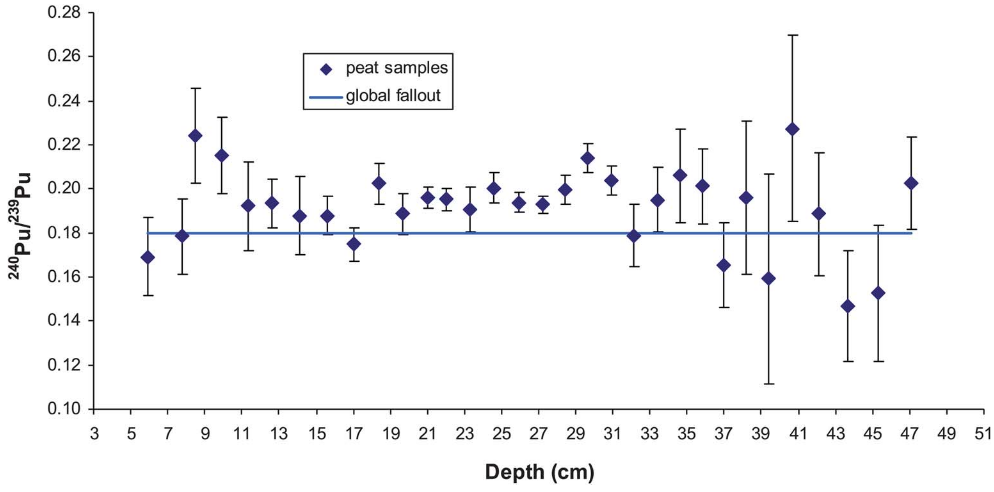

Fig. 2 ^{240}Pu/^{239}Pu isotopic ratios along the peat core as a function of depth; the blue line represents the global fallout ^{240}Pu/^{239}Pu ratio in the Northern Hemisphere. Depths refer to the lower boundaries of the peat layers.

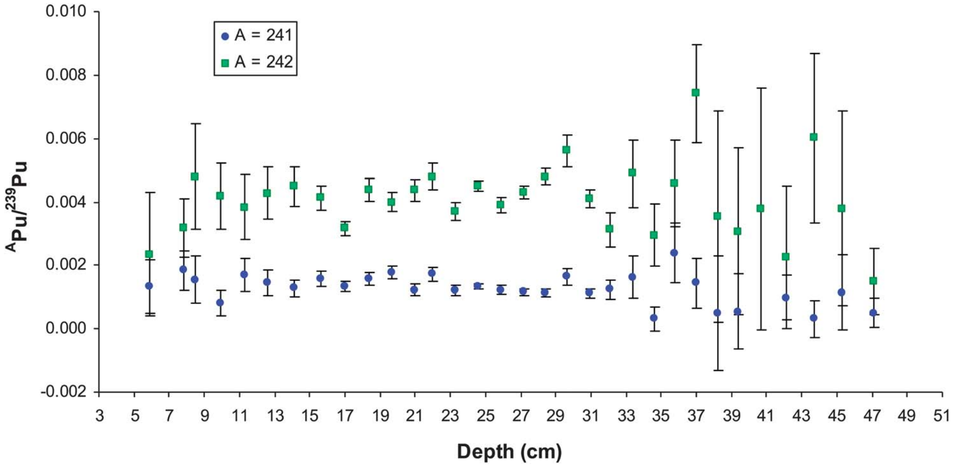

Fig. 3 Patterns of ^{242}Pu/^{239}Pu and ^{241}Pu/^{239}Pu isotopic ratios as measured in June 2012 along the peat core using accelerator mass spectrometry. Depths refer to the lower boundaries of the peat layers.

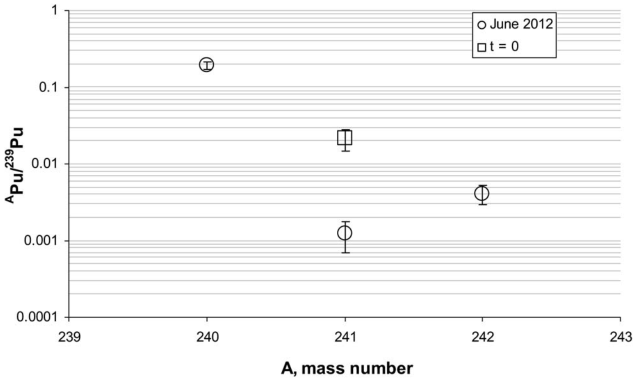

Fig. 4 Average ^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu and ^{242}Pu/^{239}Pu isotopic ratios in the peat core; the square represents the estimated ^{241}Pu/^{239}Pu ratio at the time of irradiation.

^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu and ^{244}Pu expected from the global fallout origin.[6] This finding underpins the hypothesis that all Pu in the peat core originates from the global fallout.

Dating of plutonium irradiation

The dating of the irradiation time of Pu, estimated according to eqn (5) and (6) (ref. 4) is presented as a function of the radiometric age date of the peat layer with the ^{210}Pb method[11] in Fig. 5 and Table 1. The AMS count rates of Pu isotopes in deeper layers (from 38 cm down to 47 cm depth) were much lower than in the middle of the core and were, therefore, affected by correspondingly higher uncertainties which propagate into the estimation of the related date of Pu irradiation. Nevertheless, the obtained Pu irradiation dates are consistent along the core with a global fallout (AD 1956–AD 1980) origin of Pu (blue lines in Fig. 5). As shown in Fig. 5, there is no

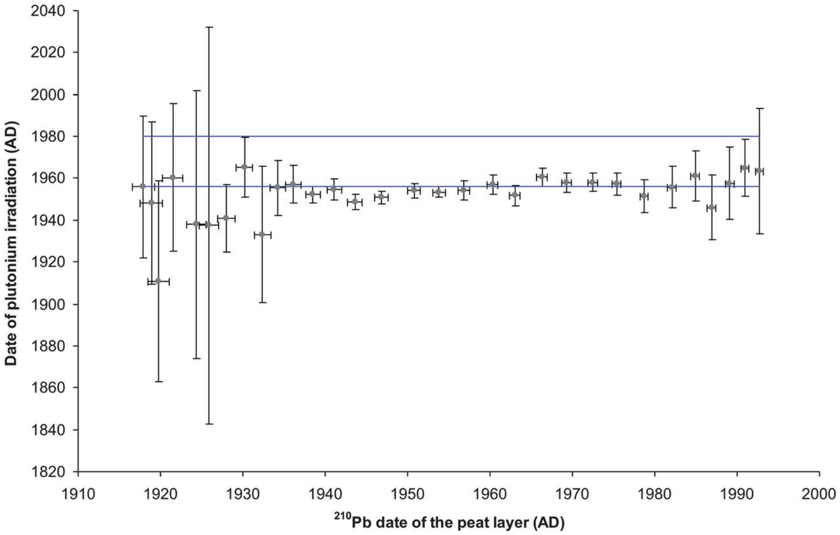

Fig. 5 Date of irradiation of Pu estimated with the assumption: ^{242}Pu/^{240}Pu = ^{241}Pu/^{239}Pu at the time of irradiation of Pu *versus* ^{210}Pb date of the layers along the peat core; the blue lines indicate the period when the global fallout occurred, *i.e.* AD 1956–AD 1980.

Table 1 Age of the peat layers as determined with the ^{210}Pb method, date of irradiation of plutonium estimated with the assumption: ^{242}Pu/^{240}Pu = ^{241}Pu/^{239}Pu at the time of irradiation, and the concentration of ^{239}Pu in each layer. Depths refer to the lower boundaries of the peat layers[a]

Depth (cm)	Age of the peat layer (AD)	Date of irradiation (AD)	^{239}Pu (10^7 atoms per gram)
6	1992.0 ± 0.5	1963 ± 30	7 ± 4
8	1989.6 ± 0.5	1965 ± 13	7 ± 3
9	1988.4 ± 0.5	1958 ± 17	5 ± 2
10	1985.9 ± 0.5	1946 ± 16	8 ± 4
11	1983.4 ± 0.5	1961 ± 12	10 ± 5
13	1980.5 ± 0.5	1956 ± 10	16 ± 8
14	1977.1 ± 0.5	1951 ± 8	28 ± 14
16	1973.9 ± 0.5	1957 ± 5	38 ± 19
17	1970.9 ± 0.6	1958 ± 4	62 ± 31
18	1967.7 ± 0.6	1958 ± 5	61 ± 30
20	1964.7 ± 0.6	1961 ± 4	75 ± 38
21	1961.5 ± 0.6	1952 ± 5	110 ± 55
22	1958.8 ± 0.7	1957 ± 5	89 ± 45
23	1955.3 ± 0.7	1954 ± 5	158 ± 79
25	1952.3 ± 0.7	1953 ± 3	193 ± 96
26	1948.8 ± 0.8	1954 ± 3	180 ± 90
27	1945.1 ± 0.8	1951 ± 3	222 ± 111
28	1942.4 ± 0.8	1949 ± 4	265 ± 133
30	1939.9 ± 0.9	1955 ± 5	111 ± 56
31	1937.3 ± 0.9	1952 ± 4	301 ± 150
32	1935.2 ± 0.9	1957 ± 9	47 ± 23
33	1933.3 ± 0.9	1955 ± 13	15 ± 8
35	1931.3 ± 1.0	1933 ± 33	12 ± 6
36	1929.1 ± 1.0	1965 ± 14	11 ± 6
37	1927.0 ± 1.1	1941 ± 16	8 ± 4
38	1925.1 ± 1.1	1937 ± 95	25 ± 12
39	1923.5 ± 1.2	1938 ± 64	23 ± 11
41	1922.1 ± 1.2	n.d.	22 ± 11
42	1920.7 ± 1.2	1960 ± 35	38 ± 19
44	1919.4 ± 1.3	1911 ± 48	38 ± 19
45	1918.4 ± 1.3	1948 ± 39	44 ± 22
47	1917.3 ± 1.3	1956 ± 34	45 ± 23

[a] n.d. = not determined.

correlation between the estimated irradiation date and the ^{210}Pb dating of the corresponding peat layer (AD 1918–AD 1999). This implies that the global fallout-derived Pu is found also in the peat layers preceding the era of atmospheric nuclear testing.

The weighted mean (weighted by $1/\sigma^2$) considering all the peat layers gives an age of Pu irradiation equal to AD 1956 ± 0.6.

The samples were measured less than 30 days after the separation of Pu, this implies that at most 0.4% of ^{241}Pu had decayed to ^{241}Am in the meantime; if for Am a two-fold higher ionization yield compared to Pu (ref. 4) is assumed, this would increase the count rate of mass 241 by 0.4%, translating into an apparently younger age of Pu of around 1 month, which is a negligible contribution to the overall uncertainty (Table 1).

In a previous study,[4] it has been observed that the applied dating method (eqn (5) and (6)) results in a younger age (*ca.* 8 years) in the case of material produced in nuclear explosions; if this shift holds also for the results of the investigated peat samples, then the corrected average age of Pu would be AD 1964, a date very close to the maximum of the global fallout.

Measurement of plutonium levels using AMS and comparison with the estimated values

Without the use of a Pu tracer, no accurate information on the chemical yield of the Pu separation and on the overall efficiency of the analysis is available. Nevertheless, even in the absence of a tracer, an estimation of the Pu concentration in the sputtering cathodes of AMS is possible, as the detector count rate is proportional to this concentration. The proportional constant depends on the source conditions, the sample matrix and the investigated element. The use of an external Pu standard allows the determination of the proportionality between count rates and concentrations. In this experiment an in-house reference material with a known Pu concentration was used as an external Pu standard. Three sputtering cathodes of this reference material were prepared in the same way as the peat samples in order to obtain a similar matrix to Pu embedded in iron oxide. Such sputtering cathodes containing the reference material were always included in each measurement run of the peat samples for normalization. According to the performances of the ion source, this proportional constant was equal to $\sim 2 \times 10^8$ (atoms per milligram) (counts per second)$^{-1}$ and to $\sim 3 \times 10^7$ (atoms per milligram) (counts per second)$^{-1}$ in two different measurement runs. This estimation of the Pu content in the sputtering cathodes of the peat samples using the normalization to the external reference material can be considered accurate within a factor of two.

Before preparing the actual peat samples, the chemical separation procedure was tested with a similar peat material, but spiked with ^{242}Pu; the chemical yield amounted to ~98%. Assuming such a chemical yield for the Pu separation from the investigated peat samples, Fig. 6 represents the minimum Pu concentration in each peat layer as a function of depth. These values, with their large uncertainty (a conservative accuracy of 50%), may not reflect accurately the Pu content of the samples, but constitute an indication of the order of magnitude. Even when taking into account this uncertainty, a clear trend of the Pu concentration along the peat core is observed.

The ^{239}Pu concentration varies along the peat profile over two orders of magnitude within the range of 1–100 fg g^{-1}. In terms of the number of ^{239}Pu atoms per dry mass of peat, the ^{239}Pu concentration increases from values of $\sim 10^7$ atoms per gram in the upper layers gradually up to a value of $\sim 10^9$ atoms per gram at 21 cm depth (AD 1961); it reaches a maximum at 31 cm depth (AD 1939) and then decreases abruptly down to $\sim 10^8$ atoms per gram at 32 cm depth, remaining essentially constant at the same low level in the deepest layers (Fig. 6 and Table 1).

In this context it is important to note that the four chemistry blanks revealed a ^{239}Pu concentration $< 2 \times 10^5$ atoms per gram; this value is two orders of magnitude lower than the lowest ^{239}Pu concentration of $\sim 10^7$ atoms per gram, which was measured in the upper peat layers. Therefore, the Pu concentrations measured in each layer of the peat core are well above the background of the procedural blank, underpinning the reliability of our Pu concentration estimates. No counts of ^{240}Pu, ^{241}Pu and ^{242}Pu were detected in the chemistry blanks.

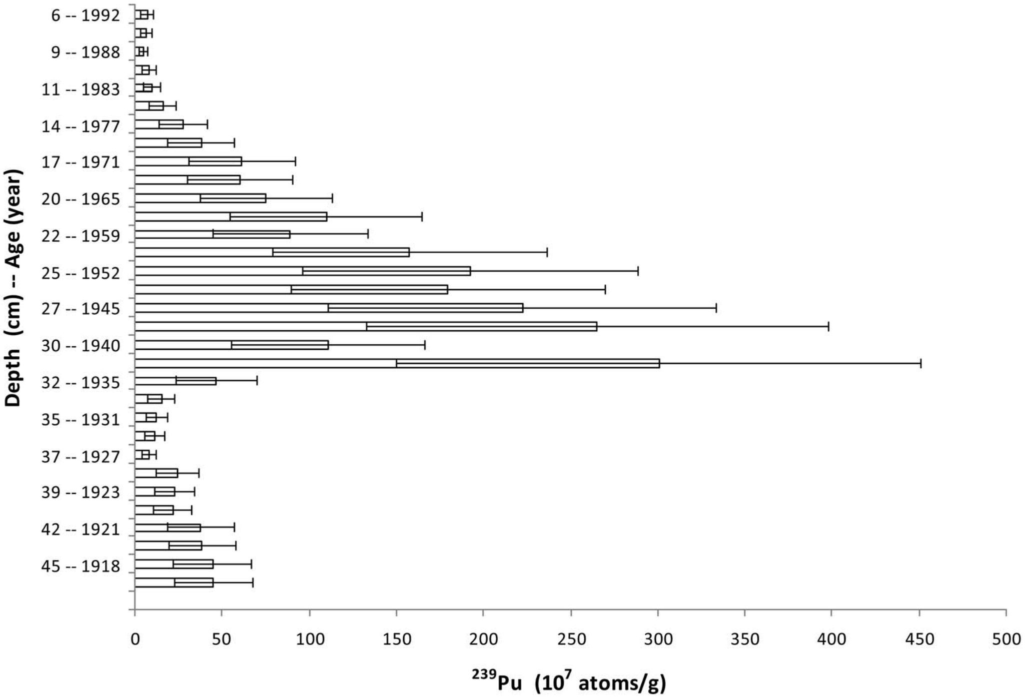

Fig. 6 Minimum ^{239}Pu concentrations along the investigated peat core as a function of depth-age of the layers (see text and Table 1 for details). Depths refer to the lower boundaries of the peat layers.

The concentration of the heavier and less abundant Pu isotopes, ^{241}Pu and ^{242}Pu in the peat samples, is within the range of 1–100 ag g^{-1}, since their abundances are three orders of magnitude lower than those of ^{239}Pu, as can be seen from Fig. 3 and 6.

Considering the measured global fallout ratio of ^{240}Pu/^{239}Pu $\sim$ 0.19 (Fig. 2), the $^{240+239}$Pu activity corresponding to the described range of ^{239}Pu concentration, ranges from $\sim$0.07 mBq g^{-1} to $\sim$5 mBq g^{-1}. These activities are in good agreement with literature data[23,27–29] on the global fallout levels of Pu in the Northern Hemisphere and with our estimates from the existing data on ^{241}Am and ^{137}Cs,[11] (Fig. 1) using eqn (1)–(4).

Comparison of the plutonium profile with those of caesium and americium

The investigated peat core presents the ^{137}Cs profile (Fig. 1) typical of an ombrotrophic peat,[16,25,26] where the maximum of the ^{137}Cs activity observed in correspondence of the top layer is ascribed to the active uptake of living plants, and where the temporal fallout pattern is poorly retained. In fact, in the analysed peat core, the Chernobyl peak (AD 1986) of ^{137}Cs is recorded at depths corresponding to AD 1982–1975, while the global fallout peak (AD 1963) is not visible, but ^{137}Cs is detectable continuously down to the depth dated AD 1967. The trend of ^{137}Cs activity does not resemble the profile of ^{239}Pu concentration along the peat core (Fig. 1, 6 and Table 1). The mobility of ^{137}Cs in ombrotrophic peat bogs[16,24–26,30,31] is due to the lack of suitable mineral particles for adsorption of alkali metal cations like Cs. A rain-fed bog peat typically contains no more than 1 or 2% of mineral matter, on the other side, peats containing relatively elevated concentrations of mineral matter (*e.g.* with a LOI significantly lower than 98%) are capable of a higher degree of ^{137}Cs fixation.[29,30]

In the actual peat core, ^{241}Am is detectable only in the layers from 21 cm depth (AD 1961) down to 41 cm depth (AD 1922) (Fig. 1). This interval of depths partially superimposes on the peak of ^{239}Pu concentration, which, as presented in Fig. 6 and Table 1, increases from the upper layers gradually up to the level of $\sim$10^9 atoms per gram at 21 cm depth (AD 1961), reaches the maximum at 31 cm depth (AD 1939), and decreases then abruptly at 32 cm depth. This observation is partially in agreement with documented correspondences between the peaks of ^{241}Am and Pu.[25,29] As discussed previously for Pu, Am is as well found in the peat layers preceding the era of atmospheric nuclear testing, suggesting in this way its migration downward the peat profile.

Conclusions

The analysis of the isotopic distribution of plutonium (^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu) at fg to ag levels with AMS has allowed the identification of the source of Pu contamination. Our measured Pu concentrations established with AMS are in good agreement with literature[23,27–29] data and with our *a priori* estimates based on eqn (1)–(4) from the existing data on ^{241}Am and ^{137}Cs (ref. 11) (Fig. 1). Plutonium, whose date of production, estimated by eqn (5) and (6),[4] is consistent with atmospheric nuclear weapon tests (AD 1956 until AD 1980), is found along the investigated peat core at depths dated AD 1917 to AD 1992 using the ^{210}Pb method. The presence of the global fallout derived Pu at depth-ages preceding AD 1956 is evidence of the post-depositional migration of Pu vertically downwards into the peat bog.

The profile of Pu concentration along the investigated peat core is characterized by two main features:

(1) The position of the Pu maximum concentration (~10^9 ^{239}Pu atoms per gram) appears to be translated by ~10 cm vertically downwards the peat profile, from 21 cm depth equivalent to the ^{210}Pb age of AD 1961 to 31 cm depth (AD 1939).

(2) From the depth of 32 cm downwards, the Pu concentration decreases abruptly to ~10^8 ^{239}Pu atoms per gram and remains essentially constant at the same low level up to the deepest analysed layer at 47 cm depth.

The post-depositional migration of Pu must reflect the physicochemical state of both the element and its environment at the time of deposition and afterwards. Ombrotrophic peat bogs are waterlogged milieus where fossil organic material accumulates as peat, and whose pore waters are acidic, rich in dissolved organic acids, and predominately anoxic.[32] While the waters are always acidic and rich in dissolved organic acids, they alternate in redox state from oxic to anoxic conditions, depending on seasonal variations in the depth of the water table. There are a number of physical, chemical and perhaps even biological processes which might have contributed to the post-depositional migration of Pu in the peat core. In particular, the observed mobility of Pu, as well as that of Am, might be explained with the complexing of the trivalent species of the two actinides[33,34] and the tetravalent Pu (ref. 35) by humic and fulvic acids and their transport as colloids. However, an unambiguous interpretation of the migration of these actinides might be possible solely with the assessment of their partitioning among the physicochemical phases of the peat. The findings of this study pave the way for future experiments on *in situ* speciation of Pu, as well as Am, in acidic and organic rich environments.

More important at this time is to emphasize that the peat core reveals a translocation of the global fallout Pu peak by ~10 cm downwards, yielding a relatively high (~10^8 ^{239}Pu atoms per gram) and constant concentration of Pu at depth-ages preceding AD 1956.

If there is post-depositional migration of Pu in peat bogs, it can reasonably be expected to be mobile in other organic-rich, acidic environments such as other wetland types (fens, marshes, and swamps), as well as forested soil environments characterized by acidic pH. The broader significance of the Pu mobilization documented here should be duly considered.

The Pu detected at levels of ~10^7 ^{239}Pu atoms per gram in the upper layers, which are younger than AD 1980, is unlikely to have been caused by an upward migration of Pu (because the dominant direction of water movement is vertically downward), but might reflect the re-mobilization of the global fallout Pu which previously had been deposited elsewhere.

Analysing the occurring Pu contamination along the peat profile and identifying the contamination source, we could observe the migration patterns of this radionuclide directly *in situ*, on an environmental scale experiment. These results reveal the mobility of Pu in this peat bog and constitute the first direct observation of the behaviour of Pu at fg to ag levels in the environment.

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References

1 W. Shotyk, M. E. Goodsite, F. Roos-Barraclough, R. Frei, J. Heinemeier, G. Asmund, C. Lohse and T. S. Hansen, *Geochim. Cosmochim. Acta*, 2003, **67**, 3991–4011.

2 J. M. Kelley, L. A. Bond and T. M. Beasley, *Sci. Total Environ.*, 1999, **237/238**, 483–500.

3 M. E. Ketterer, K. M. Hafer and J. W. Mietelski, *J. Environ. Radioact.*, 2004, **73**, 183–201.

4 P. Steier, E. Hrnecek, A. Priller, F. Quinto, M. Srncik, A. Wallner, G. Wallner and S. Winkler, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 2013, **294**, 160–164.

5 M. E. Ketterer and S. C. Szechenyi, *Spectrochim. Acta, Part B*, 2008, **63**, 719–737.

6 P. Steier, F. Dellinger, O. Forstner, R. Golser, K. Knie, W. Kutschera, A. Priller, F. Quinto, M. Srncik, F. Terrasi, C. Vockenhuber, A. Wallner, G. Wallner and E. M. Wild, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 2010, **268**, 1045–1049.

7 X. Dai, M. Christl, S. Kramer-Tremblay and H. A. Synal, *J. Anal. At. Spectrom.*, 2012, **27**, 126–130.

8 UNSCEAR, *Sources and effects of ionizing radiation*, United Nations Publications, New York, 2000, vol. II, annex j.

9 P. Lindahl, P. Roos, M. Eriksson and E. Holm, *J. Environ. Radioact.*, 2004, **73**, 73–85.

10 J. W. Mietelski, *Radioact. Environ.*, 2001, **1**, 401–412.

11 M. Lindemann, Diplomarbeit, *Ruprecht-Karls-Universität Heidelberg*, Institut für Geowissenschaften, Heidelberg, Germany, 2010.

12 K. Irlweck and E. Hrnecek, *J. Radioanal. Nucl. Chem.*, 1999, **242**(3), 595–599.

13 J. Lachner, M. Christl, T. Bisinger, R. Michel and H. A. Synal, *Appl. Radiat. Isot.*, 2010, **68**, 979–983.

14 K. Bunzl and W. Kracke, *J. Environ. Radioact.*, 1988, **8**, 1–14.

15 N. Givelet, G. Le Roux, A. K. Cheburkin, J. Frank, M. E. Goodsite, H. Kempter, M. Krachler, T. Nørnberg, N. Rausch, S. Rheinberger, F. Roos-Barraclough, A. Sapkota, C. Scholz and W. Shotyk, *J. Environ. Monit.*, 2004, **6**, 481–492.

16 C. Olid, J. Garcia-Orellana, A. Martínez-Cortizas, P. Masqué, E. Peiteado and J. A. Sanchez-Cabeza, *Environ. Sci. Technol.*, 2008, **42**, 8858–8864.

17 G. Le Roux and W. A. Marshall, *Mires and Peat*, 2010/11, **7**, 1–14.

18 C. Olid, J. Garcia-Orellana, P. Masqué, A. Martínez-Cortizas, J. A. Sanchez-Cabeza and R. Bindler, *Sci. Total Environ.*, 2013, **443**, 597–607.

19 P. G. Appleby, P. J. Nolan, D. W. Gifford, M. J. Godfrey, F. Oldfield, N. J. Anderson and R. W. Battarbee, *Hydrobiologia*, 1986, **143**, 21–27.

20 M. Krachler, J. Zheng, D. Fisher and W. Shotyk, *Anal. Chim. Acta*, 2005, **530**, 291–298.

21 M. Krachler, C. Mohl, H. Emons and W. Shotyk, *Spectrochim. Acta, Part B*, 2002, **57**, 1277–1289.

22 M. Krachler, C. Mohl, H. Emons and W. Shotyk, *J. Anal. At. Spectrom.*, 2002, **17**, 844–851.

23 S. F. Boulyga, D. Desideri, M. A. Meli, C. Testa and J. S. Becker, *Int. J. Mass Spectrom.*, 2003, **226**, 329–339.

24 P. G. Appleby, W. Shotyk and A. Fankhauser, *Water, Air, Soil Pollut.*, 1997, **100**, 223–231.

25 N. Schleich, D. Degering and S. Unterricker, *Radiochim. Acta*, 2000, **88**, 803–808.

26 C. Zaccone, C. Cocozza, A. Cheburkin, W. Shotyk and T. Miano, *Water, Air, Soil Pollut.*, 2007, **186**, 263–271.

27 M. Srncik, E. Hrnecek, P. Steier, A. Wallner, G. Wallner and P. Bossew, *Radiochim. Acta*, 2008, **96**, 733–738.

28 F. Quinto, P. Steier, G. Wallner, A. Wallner, M. Srncik, M. Bichler, W. Kutschera, F. Terrasi, A. Petraglia and C. Sabbarese, *Appl. Radiat. Isot.*, 2009, **67**, 1775–1780.

29 E. Łokas, J. W. Mietelski, M. E. Ketterer, K. Kleszcz, P. Wachniew, S. Michalska and M. Miecznik, *Appl. Geochem.*, 2013, **28**, 100–108.

30 W. R. Schell, M. J. Tobin and C. D. Massey, *Sci. Total Environ.*, 1989, **87/88**, 19–42.

31 A. B. MacKenzie, J. G. Farmer and C. L. Sugden, *Sci. Total Environ.*, 1997, **203**, 115–127.

32 P. Steinmann and W. Shotyk, *Chem. Geol.*, 1997, **138**, 25–53.

33 G. R. Choppin, *Radiochim. Acta*, 1992, **58/59**, 113–120.

34 K. Schmeide, T. Reich, S. Sachs and G. Bernhard, *Inorg. Chim. Acta*, 2006, **359**, 237–242.

35 O. Blinova, A. Novikov, I. Perminova, T. Goryachenkova and R. Haire, *J. Alloys Compd.*, 2007, **444/445**, 486–490.