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Applied Radiation and Isotopes 53 (2000) 251–257

Applied Radiation and Isotopes

www.elsevier.com/locate/apradiso

Plutonium and other alpha-emitters in bones of wild, herbivorous animals from north-eastern Poland

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Received 22 October 1999; accepted 31 December 1999

Abstract

The results of the investigation of $^{239+240}$Pu, ^{241}Am and thorium isotope activity concentrations in bones of wild herbivorous animals (deer, roe-deer, boars, elks) from north-eastern Poland are presented. The area on which the animals were living had relatively high Chernobyl plutonium fallout. Possible traces of plutonium were seen only in four samples, but only for one it was it 3σ above background, at 6.2 ± 2.4 mBq/kg (ash). The ^{241}Am activity concentration was below the detection limits in all samples. The maximum ^{228}Th concentration in the samples was 7.81 ± 0.44 Bq/kg (ash), calculated under the assumption of 100% thorium recovery. This isotope seems to originate in bones not from direct incorporation but from the decay of ^{228}Ra. Large variations in activity concentration wose observed, as well as some differences between boars and the chewing animals.

Keywords: Environmental radioactivity; Animal bones; Actinides; Chernobyl fallout

1. Introduction

The isotopic composition (but not the activities) of Chernobyl fallout which occurred in north-eastern Poland was similar to that from locations closer to Chernobyl. Generally low radiocesium activity (below 5 kBq/m^2) was accompanied by relatively high deposition of non-volatile isotopes. For example, Chernobyl-origin plutonium alpha emitters were present at the levels up to 30 Bq/m^2 (Mietelski and Wąs, 1995) and ^{241}Pu up to 1 kBq/m^2 (Mietelski et al., 1999). We found Chernobyl plutonium also in samples of the lichen *Pseudevernia furfuracea* (which grows on the trees) collected in this area in 1995 (Mietelski and Kozik, 1996). The activity concentration of $^{239+240}$Pu in the dry mass of lichens varies from 1.02 ± 0.07 Bq/kg to 1.55 ± 0.09 Bq/kg, about 70% of it can be attributed to Chernobyl fallout.

It is most likely, that the quasi-continuous fallout of the number of small 'hot particles' occurred there from a high altitude radioactive cloud, which moved toward Scandinavia on the 26th April 1986. An Interesting question is if those radionuclides are now bio-available? If yes, they should be accumulated (at least partially) in bones of wild herbivores, since most of those radionuclides (plutonium, strontium, americium) are known as 'bone seekers'.

2. Material and method

The investigations on the accumulation of radio-

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0969-8043/00/$ - see front matter
PII: S0969-8043(00)00140-8

nuclides in bones of wild herbivors started in our laboratory in 1998. Thirty-nine samples of bone from the front leg of deer (*Cervus elaphus*), *roe-deer* (*Capreolus capreolus*), boars (*Sus scrofa*) and elks (*Alces alces*) were obtained (see Table 1) from hunts organised in north-eastern Poland (no animal was killed purposely for our project). The sampling locations were situated in about a 100 km diameter circle defined by the towns: Bialystok, Augustów, and Łomża (about 23° E, 54° N, see Fig. 1).

Samples were dried, homogenised and then analysed on an HPGe low background gamma spectrometer for the presence of any gamma emitters. The results of the gamma ray measurements will be published separately. The samples were then ashed at 600°C for two days and analysed for the presence of plutonium, americium, curium, rare earth radionuclides and, for comparison with natural levels, for thorium. Samples were spiked with tracers: ^{236}Pu ($T_{1/2} = 2.851a$; 11.6 mBq per sample at 1 March 1999) and ^{148}Gd ($T_{1/2} = 90a$; 32 mBq per sample). Four blank samples were analysed also. The blanks were made of 30, 50, 80 and 100 g of $Ca(H_2PO_4)_2{\cdot}H_2O$. The sample masses varied from 30 to 100 g of bone ash.

The procedure for plutonium determination involves mineralisation in concentrated nitric acid, subsequent double co-precipitation of radionuclides with calcium oxalate at pH = 2.5, a plutonium oxidation step adjustment (La Rosa et al., 1992), plutonium and thorium separation on anion exchange column DOWEX 1 × 8 200–400 mesh (nitrate form, Fluka). Thorium was eluted using 50 ml of 10 M HCl and plutonium was eluted using 25 ml of a mixture of 0.1 M HCl + 0.1 M HF. The effluent from column was evaporated, diluted to about 1 M HNO_3, converted (using NH_3) to a basic solution to perform co-precipitation of americium, curium and rare earth elements with iron hydroxide at pH = 9. The precipitate was centrifuged and then dissolved in 50 ml of 8 M HNO_3. This solution was put on a new column of DOWEX 1 × 8 with the aim of an additional separation from thorium which might have passed the first column and ingrown from ^{228}Ra present in a sample.

For half of the samples an anion exchange procedure on DOWEX 1 × 8 in methanol (CH_3OH)-acids solutions (Holm and Ballestra, 1989) was done to separate any traces of americium and curium from rare earth elements. Accordingly, the americium and rare earths fraction of the samples were dissolved in 1 M HNO_3 solution in 93% methanol. This solution was passed through the anion exchange column filled with DOWEX 1 × 8. Americium and rare earths remained on the column. Rare earths were eluted with 0.1 M HCl −0.5 M ammonium thiocyanate (NH_4SCN), 80% methanol solution. Then americium was eluted using 1.5 M HCl, 86% methanol solution.

For the other half of the samples we changed the procedure. Samples were passed through columns according to the procedure described above, and then americium together with rare earths were eluted in 1.5 M HCl-86% methanol solution. So for the second half of the samples this step of the procedure was only an

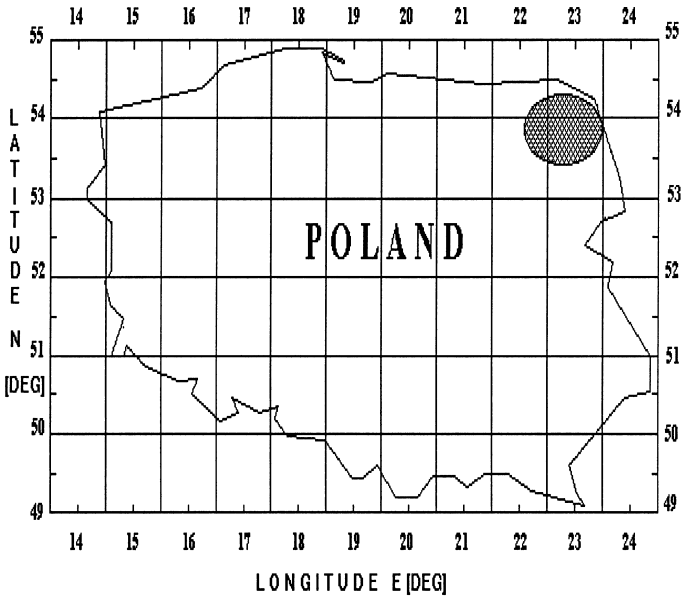

Fig. 1. Localisation of the sampling area (a dark ellipse) on the map of Poland.

additional purification from calcium and other bivalent elements, and not a rare earths and americium separation.

From each fraction a thin, alpha-spectrometric source was prepared using NdF_3 co-precipitation method (Sill, 1987).

All measurements were performed on a Silena AlphaQuattro spectrometer. For plutonium and americium measurements we used a Canberra PIPS detector (450 mm^2 area, nominal FWHM = 20 keV), for thorium measurements we used SBSi detector (manufactured in our Institute, 300 mm^2 area, nominal FWHM = 50 keV). The counting time was 7 days for plutonium or americium and 2–3 days for thorium analyses. Alpha spectra were analysed with ALF software (Mietelski and Wąs, 1995). For thorium spectra peaks were fitted, the integral scorrected for blanks and the count rates and activities calculated.

Generally, plutonium or americium spectra did not differ too much from the blank sample spectra. For them only the summing of counts in defined region of interest (ROI) was performed and the obtained values were corrected for average background. In one plutonium spectrum the fit was possible. Therefore, to attempt quantitative analyses of the spectra the most important were questions: 'what we considered a background?' and 'how we defined the minimum detectable activity?'. We decided to use the alpha spectra of

Table 1
Data on animal bone samples taken for alpha-spectrometric measurements

Sample code	Species	Location (closer village/town)	Ashed sample mass (g)	Ash to dry mass ratio
2	Deer, male	Gródek	100	0.62
16	Deer, male	Wasilków	100	0.63
17	Deer, female	Supraśl	40	0.62
18	Deer	Supraśl	80	0.59
19	Deer, young	Supraśl	100	0.61
20	Deer, female	Supraśl	100	0.62
21	Deer	Knyszyn	100	0.63
22	Deer	Czarna Białostocka	30	0.45
23	Deer	Supraśl	30	0.53
24	Deer, male	Czarna Białostocka	30	0.54
25	Deer	Supraśl	30	0.54
26	Deer	Płaska	100	0.54
27	Deer	Czarna Białostocka	30	0.56
37	Deer	Płaska	30	0.58
29	Boar	Płaska	80	0.42
30	Boar	Tykocin	30	0.50
33	Boar	Płaska	30	0.46
34	Boar	Płaska	30	0.58
35	Boar	Mielnik	35	0.59
38	Boar	Płaska	30	0.47
1	Elk, young	Gródek	35	0.56
28	Elk, young	Trzcianne	80	0.54
32	Elk, young	Gródek	40	0.62
3	Roe-deer	Tykocin	70	0.55
4	Roe-deer	Radziłów	30	0.55
5	Roe-deer	DąbrowaDąbrowa Białostocka	30	0.58
6	Roe-deer	Grabowo Guty	33	0.59
7	Roe-deer	Choroszcz	25	0.58
8	Roe-deer	Piątnica	30	0.60
9	Roe-deer	Gródek	30	0.58
10	Roe-deer	Rutki	30	0.54
11	Roe-deer	Gródek	35	0.56
12	Roe-deer	Zabłudów	35	0.58
13	Roe-deer	Mały Płock	35	0.58
14	Roe-deer	Łapy	30	0.56
15	Roe-deer	Kolno	34	0.61
31	Roe-deer	Wąsocz	33	0.69
39	roe-deer	Ciemianka	40	0.74

blank samples as a true background. For the samples and the blanks the same region of interest (ROI) from 5.00 to 5.20 MeV was used for plutonium spectra, for americium the ROI was from 5.30 to 5.50 MeV. For plutonium blanks the mean ROI count rate was 2.3×10^{-5} counts/s with a standard deviation σ of 0.8×10^{-5} count/s. For americium blanks the mean was 2.5×10^{-5} counts/s and $\sigma = 0.5 \times 10^{-5}$ counts/s. The mean values were used as the background count rates. The lower limit of detection was defined as the count rate equal to $k\sigma$ above the background count ratio, where $k = 2$ or 3. Thus, the minimum detectable activity (MDA, in Bq/kg) after subtracting the background, was defined as

$$\mathrm{MDA} = \frac{k\sigma}{EYm} \quad (1)$$

where E is the detector efficiency (0.40), Y, the chemical yield (recovery of the tracer), m, the mass of sample, and $k = 2$ or 3.

3. Results and discussion

3.1. Thorium

The results of the thorium measurements are presented in columns two, three and four of Table 2 These results are calculated under the assumption that

Table 2
Results for the activity concentrations of thorium, plutonium and americium isotopes in animal bone ash[a]

Activity concentration Sample code	^{232}Th[Bq/kg ash]	^{230}Th[Bq/kg ash]	^{228}Th[Bq/kg ash]	$^{239+240}$Pu[mBq/kg ash]	^{241}Am [mBq/kg ash]
2	< 0.004	< 0.007	0.12 ± 0.01	1.4 ± 0.6(1.3)	< 1
16	< 0.005	< 0.007	1.40 ± 0.08	< 1	< 1
17	< 0.006	< 0.017	0.72 ± 0.06	< 2	< 2.5 [b]
18	< 0.033	< 0.069	7.81 ± 0.44	< 2	< 1.2
19	< 0.010	< 0.016	7.16 ± 0.38	< 0.8	< 1.0
20	< 0.009	< 0.015	6.66 ± 0.35	< 1	[c]
21	< 0.012	< 0.015	4.08 ± 0.22	< 1.3	[c]
22	[d]	[d]	[d]	< 4	[c]
24	< 0.012	< 0.015	5.66 ± 0.29	< 3	[c]
23 + 25 + 27	< 0.017	< 0.028	4.66 ± 0.28	1.2 ± 0.4(0.7)	[c]
26	< 0.017	< 0.022	5.39 ± 0.29	6.2 ± 2.4(1.5)	< 1
37	< 0.046	< 0.084	5.42 ± 0.36	< 3	< 3[b]
29	< 0.002	< 0.003	< 0.01	< 2	< 1.3[b]
30	< 0.011	< 0.019	0.31 ± 0.02	< 2	< 3
33	0.03 ± 0.01	0.08 ± 0.02	0.37 ± 0.02	< 2	< 3
34	< 0.006	< 0.008	< 0.03	< 3	< 3
35	< 0.008	< 0.012	0.06 ± 0.01	< 2	< 3
38	0.010 ± 0.004	0.04 ± 0.01	0.33 ± 0.02	< 4	< 3
1	< 0.023	< 0.042	3.51 ± 0.23	< 3	[c]
28	< 0.024	< 0.041	7.16 ± 0.40	< 1	[c]
32	< 0.026	< 0.034	0.31 ± 0.03	< 2	< 2.5[b]
3 + 14	< 0.023	< 0.035	4.30 ± 0.24	< 0.7	< 1[b]
4	< 0.023	< 0.044	1.78 ± 0.10	< 4	< 3[b]
5	< 0.023	< 0.036	1.32 ± 0.10	< 3	< 3
7	< 0.020	< 0.036	4.28 ± 0.24	< 3	< 4
8	< 0.009	< 0.016	0.72 ± 0.04	< 4	< 3[b]
9	< 0.040	< 0.068	6.45 ± 0.52	< 3	< 3
10	< 0.016	< 0.027	1.71 ± 0.10	< 3	< 3
11	< 0.013	< 0.020	0.70 ± 0.05	< 2	[c]
12	< 0.006	< 0.008	< 0.01	< 4	[c]
13	< 0.008	< 0.012	< 0.01	< 3	< 2.7[b]
15 + 6 + 31	< 0.009	< 0.012	0.94 ± 0.05	0.6 ± 0.2(0.6)	[c]
39	< 0.010	< 0.016	0.54 ± 0.03	< 2	< 2.5[b]

[a] Then brackets (or after symbol <) present the 2σMDA (see Eq. (1)).
[b] Am fraction not separated from rare earths' fraction.
[c] Problem with purification from thorium.
[d] Thorium fraction of sample lost during analyses.

the chemical yield for thorium was 100%. Therefore the true values are at least (i.e., 'greater or equal to') those given in Table 2. The results for ^{228}Th are corrected for the very low amount of ^{228}Th, which was added as the decay product, together with ^{236}Pu tracer. In Fig. 2 a typical spectrum of thorium fraction is shown. Only ^{228}Th and its daughters (^{224}Ra, ^{220}Rn, ^{216}Po, ^{212}Bi, ^{212}Po) are seen.

The most interesting feature of thorium analyses was, on the one hand, almost complete lack of ^{230}Th and the ^{232}Th isotopes, and on the other hand, easily measurable amounts of ^{228}Th. For all except two boar samples the concentrations of ^{230}Th and ^{232}Th were below the detection limits. The ^{228}Th activity concentrations shows large variations. The maximum activity concentration of ^{228}Th was 7.81 ± 0.44 Bq/kg (ash), and was found in bone of a deer shot near the small town of Suprasśl. The highest ^{228}Th activity concentrations were observed for deer (mean value $\langle A \rangle = 4.46$ Bq/kg, standard deviation $\sigma = 2.50$ Bq/kg, $n = 11$) then elks ($\langle A \rangle = 3.66$ Bq/kg, $\sigma = 2.79$ Bq/kg, $n = 3$), roe-deer ($\langle A \rangle = 2.27$ Bq/kg, $\sigma = 1.92$ Bq/kg, $n = 10$) and significantly lower values were observed for boars ($\langle A \rangle = 0.267$ Bq/kg, $\sigma = 0.122$ Bq/kg, $n = 4$). For those statistical calculations two samples of boars and two samples of roe-deer were excluded, since the activity concentration were below the detection limit.

The lack of ^{230}Th and ^{232}Th isotopes suggests, that thorium appears in bones predominantly as a product of ^{228}Ra decay. However, it is hard to say, whether the thorium was already discriminated before incorporation to leaves (or generally - to other animal fodder), or the discrimination appears in the intestine of the animal. Or both those occur. The presence of traces of ^{232}Th and ^{230}Th in bones of boar is most likely a result of boars eating of the soil together with bulbs or roots.

An order of magnitude lower then for other animals, average ^{228}Th activity concentration and the presence of traces of ^{232}Th and ^{230}Th in boar bones apparently are the result of a different feeding habits between boars and chewing animals.

Similar level of ^{212}Pb, another thorium series member, 3.04 Bq/kg for poultry bones have been reported recently (Chibowski and Gladysz, 1999).

There is no obvious regularity in the observed activity concentration levels within one species. First assumption was that if ^{228}Th originated from ^{228}Ra, and it is accumulated during the life-time the ^{228}Th activity concentration should increase with an age of the animal. This is not that case, since some animals were especially marked as young ones, and despite this high ^{228}Th activity concentration was observed (for example sample '19' — young deer, or '28' and '1' — young elks, but not '32' the another young elk).

3.2. Plutonium

The results for plutonium ($^{239+240}$Pu) are presented in the fifth column of Table 1. Average chemical yield for Pu analyses (^{236}Pu recovery) was 91%. The MDA value for plutonium $^{239+240}$Pu activity concentration for each sample, calculated for $k = 2$, are presented in Table 2 as the upper limit for concentration (i.e., after ' < ' symbol) or in brackets after determined value. It was not less then 0.6 mBq/kg for 100 g sample, and proportionally higher for smaller samples. For four samples the measured $^{239+240}$Pu activity concentration exceeds the 2σ MDA value. Only sample '26', a deer from the forest inspectorate of Płaska, Augustów Primeval Forest, exceeds the 3σ MDA value, with a value of 6.2 ± 2.4 mBq/kg ash (i.e., 3.4 ± 1.4 mBq/kg dry weight, after taking into account the ash to dry mass ratio for this sample presented in Table 1). This result is obtained from the fit to the spectrum displayed on

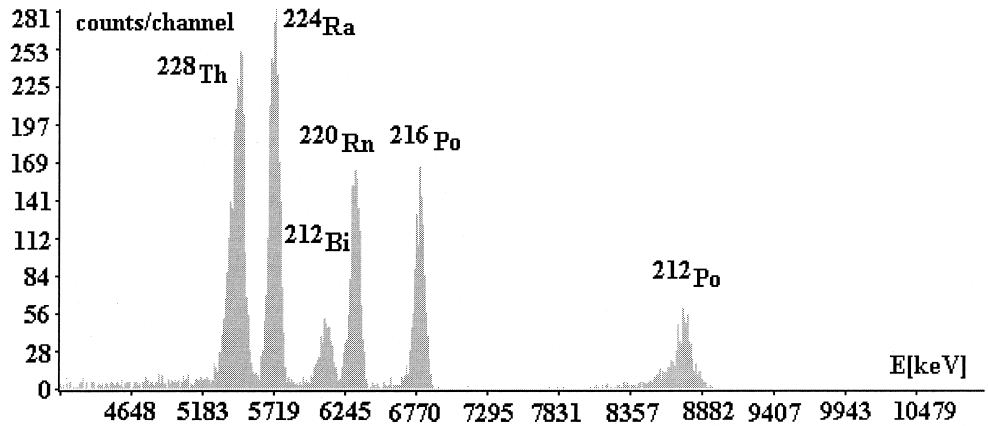

Fig. 2. Example of obtained alpha spectrum of thorium fraction (sample 31 + 15 + 6, det. SBSi 300 mm^2, measurement time 160793 s, 10.72 keV per channel).

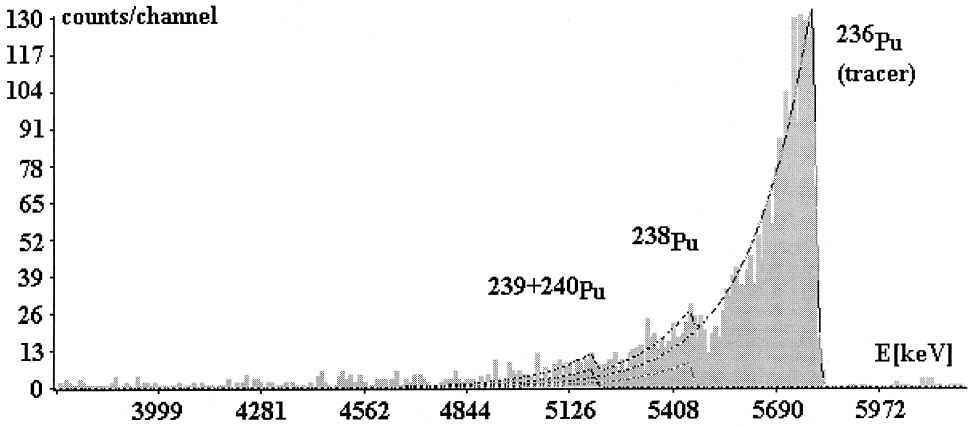

Fig. 3. Example of obtained alpha spectra of plutonium fraction (sample 26, det. Canberra PIPS 450 mm^2, measurement time 602545 s, 9.72 keV per channel).

Fig. 3. On this figure, besides traces of the 5.15 MeV $^{239+240}$Pu peak one can notice even traces of ^{238}Pu peak at 5.5 MeV. However, the count rate of those peaks and even their existence are strongly dependent on the fit quality, since they lie on a relatively large tail of the ^{236}Pu peak. This result is relatively high, between two and three times higher than the $^{239+240}$Pu concentrations reported recently (Paatera and Jaakkola, 1998) for the ribs bones of reindeer collected in 1987 in Finland.

In the area where the deer coded '26' had lived (Płaska Forest Inspectorats) we have collected in 1991 samples of two upper layers of forest litter. Then those samples were analysed for plutonium alpha emitters ^{238}Pu and $^{239+240}$Pu (Mietelski and Wąs, 1995), americium (Mietelski and Wąs, 1997) and for pure beta emitter ^{241}Pu (Mietelski et al., 1999). In these articles the sample from Płaska was coded '120'. Forest litter samples had $^{239+240}$Pu concentrations equal to 3.98 ± 0.33 Bq/kg dry weight in the top layer and 6.88 ± 0.53 Bq/kg dry weight in deeper layers, respectively 82% and 54% of this plutonium was attributed to the Chernobyl fallout. This was recalculated to the deposition of 4.0 ± 0.3 Bq/m^2 and 22.2 ± 1.7 Bq/m^2, respectively in both layers. Therefore the sum of deposition in the two analysed litter layers was 26.2 ± 1.8 Bq/m^2. The $^{239+240}$Pu activity concentration in animal bone divided by the deposition value gives a rough approximation of the aggregation coefficient from forest litter to deer bone, equal to 2.4×10^{-3} (m^2/kg bone ash).

3.3. Americium and rare earths

All americium results are below their 2σ MDA values (see last column of Table 2). For nine of the analysed samples in americium fraction some problem occurred with the second purification from thorium and for them results are not available. The results for rare earths alpha emitters are not promising either. These measurements are not completed yet, but till now we have not observed any interesting feature.

4. Conclusions

Possible traces of plutonium were seen only in four samples, from which only one sample (deer, code '26') was above the 3σ background. The observed activity was still very low, about 6 mBq per 1 kg of ashed bone. Such plutonium concentration in other than reindeer animal bone can be considered enhanced.

Unfortunately, the achieved detection limits were too large for the determination of ^{241}Am activity concentration.

Only ^{228}Th, which originates from the decay of ^{228}Ra, was found to be measurable for all samples. The maximum ^{228}Th concentration in sample was three order of magnitude higher than observed maximum activity concentration of $^{239+240}$Pu. Large variation in thorium activity concentration was observed, as well as two differences between boars and the chewing animals. One was the presence of traces of ^{232}Th and ^{230}Th in two boar bone samples. The other one was an order of magnitude lower average content of ^{228}Th in boar's bones as compared to other animals. Those differences are the results of different feeding habits.

Acknowledgements

The authors wish to thank Dr Jerome J. LaRosa (IAEA Marine Environmental Laboratory, Monaco) and Dr Riitta Pilviö (University of Helsinki and

IRMM, Geel) for remarks suggestions and fruitful e-mail discussion on radiochemical problems that can occur with ashed bone matrix.

The Polish State Committee for Scientific Research (KBN) is warmly acknowledged for support of this project (grant No 6 P04G 09014).

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