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Activity ratios of thorium isotopes in living species compared with other environmental samples

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Abstract. The paper presents the results of alpha spectrometric measurements of $^{228}Th/^{232}Th$ and $^{230}Th/^{232}Th$ activity ratios for many samples of some living species analyzed within last years in our laboratory within different projects. The results were compared with typical values for soil or other non-biological samples. All results were obtained by means of alpha spectrometry.

Key words: activity ratio $^{228}Th/^{232}Th$ • activity ratio $^{230}Th/^{232}Th$

Introduction

Since about ten years our laboratory is conducting studies on the determination of Pu in many environmental samples, among them also the biological ones. Plutonium results were already discussed elsewhere [1, 4, 5, 8–21, 27]. In the course of radiochemical procedure for plutonium separation a thorium fraction was separated for each sample. Since we had not used any thorium tracer in the past, thorium activities were not determined. However, always alpha sources were prepared and then measured. This produced a relatively large archive of thorium alpha spectra from which one can study activity ratios of thorium isotopes. Two ratios seems to be interesting. The first is the ^{228}Th to ^{232}Th activity ratio. Both these isotopes are the Th-series members and, therefore, one might expect equilibrium. Usually this is not the case.

Another subject is the activity ratio between ^{230}Th and ^{232}Th. One can tell that there is no relation between these two isotopes and, therefore, this ratio should not bring any information. The first isotope belongs to the U series, it is a decay product of ^{234}U. The second one is just a primordial parent of the Th series. So, one can expect, that this ratio will generally reflect the activity ratio between the U and Th series for a given environment. However, this ratio might be modified by weak effects and this possibility should be taken into consideration.

Material and method

Biological samples were originating from many different organisms (mammals and birds, invertebrates, plant and mushrooms) as well as from geological samples (air particles, soil, sediments) collected in Poland, Antarctic and Belarus. In case of vertebrates the analyzed material

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were bones. For plants, twigs and leaf/needles were the main kind of sample. In case of mushroom they were fruiting bodies. The whole bodies were taken in case of invertebrates.

All samples were ashed at 600°C in a muffle oven, then were wet-mineralized in different chemical procedures, depending on the kind of matrix [1, 4, 5, 8–21, 27]. Dissolved samples in 8 M HNO_3 were loaded on an anion exchange column filled with Dowex-1 resin. Thorium was then eluted from the column using concentrated HCl. It was evaporated to dryness, dissolved in 2.5 ml of concentrated HCl, diluted with de-ionized water to 10 ml, transferred to a plastic vessel and washed to obtain finally about 20 ml of approximately 1 M HCl solution. Then, a thin alpha spectrometric source was produced using the NdF_3 co-precipitation method [24]. Sources were measured using alpha spectrometers Silena AlphaQuattro or Ortec 576A, both equipped with silica implanted or surface barrier detectors.

Results and discussion

The main statistical parameters for the results of alpha spectrometric measurements of $^{228}Th/^{232}Th$ and $^{230}Th/^{232}Th$ activity ratios for many samples of living species and geological samples analyzed within last years (2001–2006) in our laboratory, within different projects [1, 4, 5, 8, 10–21, 27], are presented in Table 1.

In our past piloting studies [9] for the thorium isotopic ratio $^{228}Th/^{232}Th$ within the Th series, a strong disequilibrium was observed in not numerous cases of plant and animal samples, whereas such disequilibrium was not found in mushroom samples. This feature can be understood if one would notice that there is ^{228}Ra (and ^{228}Ac) between those Th isotopes within the Th series ($^{232}Th \rightarrow {}^{228}Ra \rightarrow {}^{228}Ac \rightarrow {}^{228}Th \rightarrow \ldots \rightarrow {}^{208}Pb$). Since Ra is much more mobile in the environment than Th the transfer factors of radium for both plants and animals are higher than the transfer factor of Th. Therefore, it is radium, which is uptaken by plants or by animals, not Th. Then, ^{228}Ra decays to ^{228}Th by two subsequent beta decays and we see ^{228}Th in the sample. Mushrooms apparently do not incorporate Ra, and, therefore, elevated levels of ^{228}Th are not observed. Such a mechanism was proposed for interpretation, and a current study was undertaken to gather more data on this topic.

For analyzed air filters or samples of atmospheric precipitation, one can notice a tendency to equilibrium within the thorium series, between ^{232}Th and its grand-granddaughter, ^{228}Th. The activity of thorium isotope from the Th series (^{232}Th and ^{228}Th) is lower than the thorium from the uranium series (^{230}Th). This suggests a higher activity of U series than the thorium series in arable soils, whose aeolian erosion is expected to be the main source of those radionuclides in atmosphere. The results are typical only of our local geological conditions. In other regions of the earth the activity ratios $^{228}Th/^{232}Th$ and $^{230}Th/^{232}Th$ may be different [6].

Results on $^{228}Th/^{232}Th$ activity ratio for the examined forest soil, litter or peat show values close to 1. This means that the secular equilibrium conditions were there almost fulfilled. However, all plant samples, like bilberry (*Vaccinium myrtillus*), swamp sawgrass (*Cladium mariscus*) [7], twigs and needles of Norwegian spruce (*Picea excelsa*) or pine (*Pinus sylvestris*) confirm the observed previously strong disequilibrium. These samples represent quite different plants. For all of them, the activity ratio $^{228}Th/^{232}Th$ is much greather than 1. This is opposite of moss and lichen and this suggests that moss similarly to lichens takes the analyzed radionuclides directly from atmospheric deposition, not from the soil. The analyzed moss and lichens originated predominantly from the Antarctic environment, but the mosses from the Tatra Mountains show similar properties.

Another biological samples analyzed in our laboratory were invertebrates, and within this set the majority were dung beetles (*Anaplotrupes stercorosus*). In this

Table 1. Statistical parameters of activity ratios $^{228}Th/^{232}Th$ and $^{230}Th/^{232}Th$ in analyzed samples

No.	Kind of sample	Number of analyzed samples	Activity ratio $^{228}Th/^{232}Th$			Activity ratio $^{230}Th/^{232}Th$		
			Mean value	±SD	Median	Mean value	±SD	Median
1	Air filters (Poland)	27	0.99	0.10	1.01	1.43	0.11	1.41
2	Rainwater (Poland)	4	0.85	0.23	0.84	1.30	0.27	1.33
3	Fe/Mn deep ocean clusters	8	0.98	0.11	0.93	3.60	1.65	4.03
4	Sediments from bottom of lakes (Poland)	22	0.92	0.28	0.99	1.01	0.18	0.98
5	Soil – Tatra Mountains	31	1.00	0.46	0.92	1.43	1.37	0.88
6	Soil – Gorce Mountains	33	0.90	0.20	0.97	0.83	0.18	0.77
7	Peat – Tatra Mountains	8	1.05	0.11	1.02	1.28	0.20	1.25
8	Forest litter (Poland)	12	0.97	0.13	0.93	1.04	0.20	1.05
9	Bilberry leaf (Poland)	5	11.50	6.80	10.40	1.24	0.39	1.08
10	Swamp sawgrass (Poland)	3	5.60	0.47	5.74	1.01	0.10	1.03
11	Bark (spruce or pine)	5	1.83	1.01	1.70	1.47	1.01	0.99
12	Needle of spruce – Tatra Mountains	28	3.90	2.43	3.26	1.08	0.56	1.16
13	Moss (Antarctic)	4	1.11	0.27	0.99	1.03	0.15	1.00
14	Lichen (Antarctic)	3	0.95	0.56	1.10	0.85	0.05	0.83
15	Invertebrates (mostly beetles)	17	0.67	0.45	0.53	1.01	0.34	0.94
16	Bones of foxes	15	44.90	70.90	16.70	2.84	4.59	1.28
17	Bones of birds	7	2.77	3.06	1.57	0.87	0.35	0.86

case the $^{228}Th/^{232}Th$ ratio was typically below 1, which might suggest that radium is rather not accumulated but thorium is accumulated. This was also confirmed by the presence of ^{230}Th from the U series. However, one of the important differences between beetles and other analyzed animals is the much shorter lifespan of invertebrates, which makes the ingrown of ^{228}Th from ^{228}Ra decay less important.

Among the analyzed samples of animal bones, two groups of animals are distinguishable. They concerned different birds of prey and carnivorous mammals (foxes). In both cases the activity ratio of $^{228}Th/^{232}Th$ is much higher than 1, which can be explained by accumulation of ^{228}Ra in bones. Moreover, the bones of a fox have this ratio significantly higher than that of birds of prey. The activity ratio of $^{230}Th/^{232}Th$ is different for those groups. For birds, the ratio is close to 1, whereas for foxes is not. We have not any good explanation for this observation yet. The main pathway of incorporation of radionuclides are inhalation and ingestion. Since both birds of prey and foxes are carnivorous, the difference is likely resulting from the different inhalation exposure. It can be also affected by the age of animals and the differences in metabolism.

The ratio of thorium from the U and Th series, and the activity ratio ($^{230}Th/^{232}Th$) for organisms seems to be usually higher than that of the non-living surrounding. Perhaps the mechanism is similar to such that makes the activity ratio of $^{234}U/^{238}U$ in water higher than 1 [22, 25, 26]. The ^{234}U is more soluble than ^{238}U due to the alpha particle decay preceding its formation. The ^{232}Th in minerals is mainly encapsulated into grains, therefore it is not bio-available, whereas ^{230}Th comes from both: encapsulated in minerals or more leachable one, coming from the decay of that additional ^{234}U present in the water in soil.

One of the more exotic group of samples analyzed in our laboratory were Fe-Mn deep ocean clusters (known also as Fe-Mn nodules). They originated from the depth of about 4 km in the Pacific Ocean, 400 km apart from Fiji island. The examined clusters showed equilibrium conditions within Th series and an three-four fold excess of ^{230}Th activity compared with that of ^{232}Th. This suggests that heavy radionuclides (Th, U) are incorporated from seawater, where the uranium activity is much higher than that of thorium [2, 3, 23, 28]. Then, uranium decays to thorium which results in the ratio $^{230}Th/^{232}Th$ much higher than 1.

Conclusions

A strong thorium isotope disequilibrium within the Th series ($^{228}Th/^{232}Th$ ratio) was confirmed for all the examined samples of different parts of higher plants and animal bones, whereas such disequilibrium was not found for lichen and moss. In the past, the disequilibrium was also not observed for mushroom samples. All this confirms that ^{228}Th observed in the majority of biological samples is incorporated as ^{228}Ra and, since Ra is much more mobile than Th in the environment, the transfer factors for radium for both high plants and animals are much higher than the transfer factor for Th. Therefore, it is radium which is uptaken by plant or animal, not Th. Subsequently, ^{228}Ra decays to ^{228}Th and the latter is observed in the examined samples.

In case of moss or lichen not favourable intake of Ra exist, suggesting a passive accumulation of those radionuclides from atmosphere.

The much higher activity of ^{230}Th than thorium form the Th series was observed in deep ocean clusters which resulted from the incorporation of radionuclides from seawater, where the excess of uranium over thorium is obvious.

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References

1. Boroń K, Mietelski JW, Lipka K, Gaca P, Jasińska M (2001) Radionuclides in raised bogs on example of "Bór za Lasem" in Orawsko-Nowotarska Valley in Tatra Mountains Foothill, Poland. J Environ Monit 3;3:324–329
2. Chen J, Yao Y (1995) Geochemistry of manganese nodules from offshore areas of Mariana Island and Johnston Island. J Southeast Asian Earth Sci 11:61–70
3. Dubinin AV, Uspenskaya TYu (2006) Geochemistry and specific features of manganese ore formation in sediments of oceanic bioproductive zones. Lithol Miner Resour 41:1–14
4. Gaca P, Mietelski JW, Kitowski I, Grabowska S, Tomankiewicz E (2005) ^{40}K, ^{137}Cs, ^{90}Sr, $^{238,239+240}Pu$ and ^{241}Am in skulls of small mammals eaten by owls and in some skeletons of owls from Poland. J Environ Radioact 78;1:93–103
5. Gaca P, Tomankiewicz E, Mietelski JW, Grabowska S, Kubica B (2006) Radionuclides in two rised-peat profiles collected from Kościeliska Valley in Tatra Mountains. J Radioanal Nucl Chem 267:443–448
6. Golchert N, Kolzow R (1998) Site environmental report for calendar year 1998. Argonne National Laboratory – East is operated by the University of Chicago for the US Department of Energy 4:4–20
7. Komosa A, Chibowski S, Kitowski I, Krawczyk R, Orzeł J, Reszka M (2006) Transfer of selected heavy metals and radionuclides from calcareous peat to saw sedge (*Cladium mariscus*) in eastern Poland. J Radioanal Nucl Chem 269:195–201
8. Kubica B, Mietelski JW, Gołaś J *et al.* (2002) Concentration of ^{137}Cs, ^{40}K, ^{238}Pu, $^{239+240}Pu$ radionuclides and some heavy metals in soil samples from two main valleys from Tatra National Park. Polish J Environ Studies 11;5:537–545
9. Mietelski JW, Baeza AS, Guillen J *et al.* (2002) Plutonium and other alpha emitters in mushrooms from Poland, Spain and Ukraine. Appl Radiat Isot 56;5:717–729
10. Mietelski JW, Gaca P, Grabowska S (2004) Study of radionuclides content at ca. 11 km altitude by use of cabin filters from airliners. In: Int Conf on Isotopes in Environmental Studies – Aquatic Forum 2004, 25–29 October 2004, Monaco. Book of extended synopsis. IAEA, Vienna. IAEA-CN-118, pp 411–412

11. Mietelski JW, Gaca P, Jasińska M (2000) Plutonium and other alpha-emitters in bones of wild, herbivorous animals from north-eastern Poland. Appl Radiat Isot 53;1/2:251–257
12. Mietelski JW, Gaca P, Olech MA (2000) Radioactive contamination of lichens and mosses collected in South Shetlands and Antarctic Peninsula. J Radioanal Nucl Chem 245;3:527–535
13. Mietelski JW, Kitowski I, Gaca P, Grabowska S, Tomankiewicz E, Szwałko P (2006) Gamma emitters, ^{90}Sr, $^{238,239+240}$Pu and ^{241}Am in bones and liver of eagles from Poland. J Radioanal Nucl Chem 270;1:131–135
14. Mietelski JW, Kitowski I, Gaca P, Tomankiewicz E (2003) Elevated plutonium and americium content in skulls of small mammals. J Radioanal Nucl Chem 256;3:593–594
15. Mietelski JW, Kitowski I, Tomankiewicz E, Gaca P, Błażej S (2008) Plutonium, americium, ^{90}Sr and ^{137}Cs in bones of fox (*Vulpes vulpes*) from Eastern Poland. J Radioanal Nucl Chem 280 (in print)
16. Mietelski JW, Kozak K, Wąs B, Jasińska M, Krupa JO (1999) Plutonium isotopes concentration in the ground level air and rain samples from Kraków. Czech J Phys 49;1:115–117
17. Mietelski JW, Kozik R (1996) Plutonium and other radionuclides in some lichens samples from Poland. J Radioecology 4;2:7–17
18. Mietelski JW, Kubica B, Gaca P *et al*. (2008) ^{238}Pu, $^{239+240}$Pu, ^{241}Am, ^{90}Sr and ^{137}Cs in mountain soil samples from the Tatra National Park (Poland). J Radioanal Nucl Chem 280 (in print)
19. Mietelski JW, Olech MA, Gaca P *et al*. (2005) ^{137}Cs, ^{238}Pu, $^{239+240}$Pu and ^{90}Sr in various kind of samples from the King George Island (Southern Shetlands), Antarctic environment. In: Strand P, Borretzen P, Jolle T (eds) Proc from the 6th Int Conf on Environmental Radioactivity in the Arctic and Antarctic, 2–6 October 2005, Nice, France. NRPA, Oesteras, pp 130–133
20. Mietelski JW, Szwałko P, Tomankiewicz E *et al*. (2004) ^{137}Cs, ^{40}K, ^{90}Sr, $^{238,239+240}$Pu, ^{241}Am and $^{243+244}$Cm in forest litter and their transfer to some species of insects and plants in boreal forests: three cases study. J Radioanal Nucl Chem 262;3:645–660
21. Mietelski JW, Szwałko P, Tomankiewicz E, Gaca P, Grabowska S (2003) Geotrupine beetles (*Coleoptera*: *Scarabaeoidea*) as bio-monitors of man-made radioactivity. J Environ Monit 5;2:296–301
22. Miyake Y, Saruhashi K, Sagimura (1973) The isotopic ratio ^{234}U/^{238}U in sea water and its bearings on the isotopic ratio in the river waters. Rec Oceanogr Works Japan 12(I):23
23. Palumbo B, Bellanca A, Neri R, Roe MJ (2001) Trace metal partitioning in Fe-Mn nodules from Sicilian soils, Italy. Chem Geol 173:257–269
24. Sill CW (1987) Precipitation of actinides as fluorides or hydroxides for high resolution alpha spectrometry. Nucl Chem Waste Management 7:201
25. Skwarzec B, Boryło A, Strumińska I (2002) ^{234}U and ^{238}U isotopes in water and sediments of the southern Baltic. J Environ Radioact 61;3:345–363
26. Skwarzec B, Boryło A, Strumińska I (2004) Activity disquilibrium between ^{234}U and ^{238}U isotopes in southern Baltic. Water, Air, Soil Pollut 159;1:165–173
27. Tomankiewicz E, Mietelski JW, Gaca P, Grabowska S (2006) Difference between radionuclides behavior in needles of Norway spruce (*Picea abies*) tree. Nukleonika 51;2:59–68
28. Verlaan PA, Cronan DS, Morgan CL (2004) A comparative analysis of compositional variations in and between marine ferromanganese nodules and crust in the South Pacific and their environmental controls. Prog Oceanography 63:125–158