

^{90}Sr , ^{137}Cs , AND Pu ISOTOPES IN MOSS AND BILBERRY LEAVES FROM THE TATRA MOUNTAINS

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ABSTRACT. This paper presents the results of concentration determination of radioactive pollutants in samples of mosses and bilberry leaves collected in the Tatra Mountains, the Alpine-type mountains located in Central Europe. The nuclides of interest were ^{90}Sr , ^{137}Cs , and $^{238,239+240}\text{Pu}$ isotopes. The main source of strontium and plutonium contamination seems to be the global radioactive fallout; however, some influence of the Chernobyl fallout cannot be excluded. The ^{137}Cs is presumed to come mainly from the Chernobyl fallout. A weak correlation can be observed for both ^{90}Sr and ^{137}Cs activity concentration and the altitude above sea level.

INTRODUCTION

The Tatra Mountains, located on the border between Poland and the Slovak Republic, are the only Alpine-type mountains in Poland and a unique geological structure in Central Europe. The highest peak, Gerlach, in the Slovak Republic, reaches 2655 m asl (the highest peak in Poland is Rysy, at 2499 m asl). National parks have been established on both sides of the border in order to protect the unique environment of the mountains. Such conditions and the relatively clean environment make the Tatra Mountains an ideal place to study the behavior of manmade pollutants, including radioactive pollutants. For some years, we have been conducting research in the area of the Tatra Mountains (Kubica et al. 2002, 2004, 2005).

MATERIALS AND METHODS

Samples of moss (*Polytrichum commune*) and bilberry leaves (*Vaccinium myrtillus*) were collected in spring, summer, and fall from 2001 to 2004 from several locations in the Tatra National Park (Table 1). Moss and bilberries are very common in the whole area of the Tatra Mountains and are well-known for their abilities to accumulate manmade pollutants (Mellin et al. 1994; Mietelski and Jasińska 1996; Mietelski and Vajda 1997), including radioactive ones. Such features make them ideal materials to study the concentrations and behavior of artificial radioactive isotopes such as ^{137}Cs , $^{238,239+240}\text{Pu}$, and ^{90}Sr .

The samples of moss and bilberry leaves were dried at 105 °C for 1 d to determine the dry mass and were then homogenized by grinding. Next, samples were sieved on a vibrating screen (2-mm-diameter pores) and measured for the presence of gamma emitters (mainly ^{137}Cs and ^{40}K) via low-background gamma spectrometry using an HPGe detector. Results of those measurements have been partially published elsewhere (Kubica et al. 2002). In the present study, we compare the previous results for ^{137}Cs (Kubica et al. 2004) with current, unpublished results for ^{90}Sr and plutonium isotopes.

Following the gamma-spectrometric measurements, samples were incinerated at 600 °C in a muffle oven. Next, the ashed residues were treated in a pressurized microwave digestion system with a mixture of concentrated HF, HNO₃, and HCl. After total dissolution of the sample material, the chemical recovery tracers (^{85}Sr and ^{242}Pu) were added. The samples were evaporated to dryness, then redis-

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Table 1 Sample descriptions and sampling sites.

Nr	Sample	Sampling site	Altitude (m asl)
1	Moss	Lejowa Valley	968
2	Moss	Za Mnichem Valley	1900
3	Moss	Palenica Białczańska	980
4	Moss	Czarny Staw near Mt. Rysy	1580
5	Moss	Roztoka Valley	1031
6	Moss	Morskie Oko	1393
7	Moss	Kościeliska Valley	970
8	Moss	Smreczyński Staw	1226
9	Moss	Gąsienicowa Glade	1500
10	Moss	Skupniów Upłaz	1334
11	Moss	Czarny Staw Gąsienicowy	1623
12	Moss	Mt. Kasprowy Wierch	1986
13	Moss	Kuźnice	1200
14	Moss	Kuźnice	1250
15	Moss	Bobrowiecka Pass	1355
16	Bilberry leaf	Lejowa Valley	968
17	Bilberry leaf	Za Mnichem Valley	1900
18	Bilberry leaf	Palenica Białczańska	980
19	Bilberry leaf	Czarny Staw near Mt. Rysy	1580
20	Bilberry leaf	Roztoka Valley	1031
21	Bilberry leaf	Morskie Oko	1393
22	Bilberry leaf	Dolina Kościeliska	970
23	Bilberry leaf	Smreczyński Staw	1226
24	Bilberry leaf	Chuda Pass	1850
25	Bilberry leaf	Skupniów Upaz	1334
26	Bilberry leaf	Czarny Staw Gąsienicowy	1623
27	Bilberry leaf	Mt. Kasprowy Wierch	1986
28	Bilberry leaf	Mt. Myślenickie Turnie	1360
29	Bilberry leaf	Mt. Rakoń	1879

solved in 10M HCl with 2 g of H₃BO₃, heated, evaporated, and converted to 1M HNO₃ solution. Pu oxidation state adjustment was performed by subsequently adding hydrazine, HNO₃, and NaNO₂ (LaRosa et al. 1992). Pu was separated from 8M HNO₃ via a Dowex-1 anion exchange resin (Sr not retained), and Sr was subsequently separated from the same solution using Sr-selective resin by extraction chromatography. Pu was eluted from the anion exchange resin with 0.1M HF-0.1M HCl, and Sr was eluted from the extraction chromatography resin with 0.01M HNO₃ (Horwitz et al. 1991, 1992; Vajda et al. 1992). The eluted Sr fraction was additionally purified from traces of ²¹⁰Pb by PbI₂ precipitation, and the liquid fraction was evaporated with the addition of concentrated HNO₃. Alpha-spectrometric sources for Pu were made by NdF₃ coprecipitation (Sill 1987). Strontium chemical recovery was determined by gamma-ray measurement of ⁸⁵Sr, followed by liquid scintillation (LS) spectrometry for ⁹⁰Sr and its daughter ⁹⁰Y (Vajda et al. 1992).

RESULTS AND DISCUSSION

The results of measurements are presented in Table 2. The mean activity concentrations of ⁹⁰Sr, ¹³⁷Cs, ²³⁸Pu, and ^{239,240}Pu for moss and bilberry leaf samples are presented in Table 3. The mean

chemical recovery for Pu was $72 \pm 25\%$ (1σ) and $78 \pm 14\%$ (1σ) for Sr. A representative LS spectrum of ⁹⁰Sr-⁹⁰Y and ⁸⁵Sr is presented in Figure 1.

Table 2 Results of ⁹⁰Sr, ¹³⁷Cs (Kubica et al. 2002), ²³⁸Pu, and ^{239,240}Pu measurements (dry weight) in moss and bilberry leaf samples.^a

Nr.	⁹⁰ Sr (Bq/kg)	¹³⁷ Cs (Bq/kg)	²³⁸ Pu (mBq/kg)	^{239,240} Pu (mBq/kg)
1	12.2 ± 1.1	612 ± 41	27 ± 6	644 ± 52
2	—	230 ± 11	5 ± 2	32 ± 5
3	9.8 ± 0.8	201 ± 11	6 ± 5	230 ± 25
4	5.9 ± 0.5	729 ± 14	<2	215 ± 22
5	9.7 ± 0.8	173 ± 12	4 ± 2	21 ± 3
6	8.8 ± 0.8	208 ± 10	37 ± 6	149 ± 17
7	15.3 ± 1.0	382 ± 14	—	—
8	15.1 ± 1.2	279 ± 10	18 ± 4	43 ± 8
9	9.6 ± 0.6	12 ± 2	<2	6 ± 2
10	8.2 ± 0.8	221 ± 10	<2	<2
11	6.0 ± 0.5	129 ± 6	93 ± 31	3178 ± 286
12	5.9 ± 0.4	23 ± 3	5 ± 3	48 ± 7
13	10.1 ± 0.8	475 ± 7	—	—
14	11.1 ± 0.9	211 ± 4	4 ± 1	43 ± 7
15	29.3 ± 1.3	68 ± 3	<2	5 ± 2
16	27.3 ± 2.0	122 ± 14	<2	72 ± 13
17	67.2 ± 4.2	94 ± 7	4 ± 2	36 ± 9
18	32.1 ± 2.9	137 ± 59	<2	65 ± 12
19	13.0 ± 1.1	99 ± 13	<2	2 ± 1
20	13.1 ± 1.0	365 ± 31	<2	16 ± 3
21	20.0 ± 1.5	397 ± 21	<2	12 ± 2
22	14.9 ± 1.3	481 ± 33	—	—
23	16.1 ± 1.2	509 ± 21	<2	10 ± 2
24	—	32 ± 4	<2	16 ± 4
25	11.3 ± 0.8	129 ± 5	6 ± 2	237 ± 20
26	30.6 ± 2.4	159 ± 5	<2	<2
27	11.8 ± 0.9	72 ± 6	2 ± 1	51 ± 12
28	79.8 ± 6.1	100 ± 4	5 ± 3	92 ± 21
29	39.6 ± 1.9	135 ± 4	<2	5 ± 2

^a— means analyses not successful.

Table 3 Mean activity concentrations of ¹³⁷Cs, ⁹⁰Sr, ²³⁸Pu, ^{239,240}Pu obtained for moss and bilberry leaf samples.

Sample	Mean activity concentration ± standard deviation			
	⁹⁰ Sr (Bq/kg)	¹³⁷ Cs (Bq/kg)	²³⁸ Pu (mBq/kg)	^{239,240} Pu (mBq/kg)
Moss	11 ± 6	264 ± 206	22 ± 29	385 ± 898
Bilberry leaf	29 ± 22	202 ± 161	4 ± 2	51 ± 66

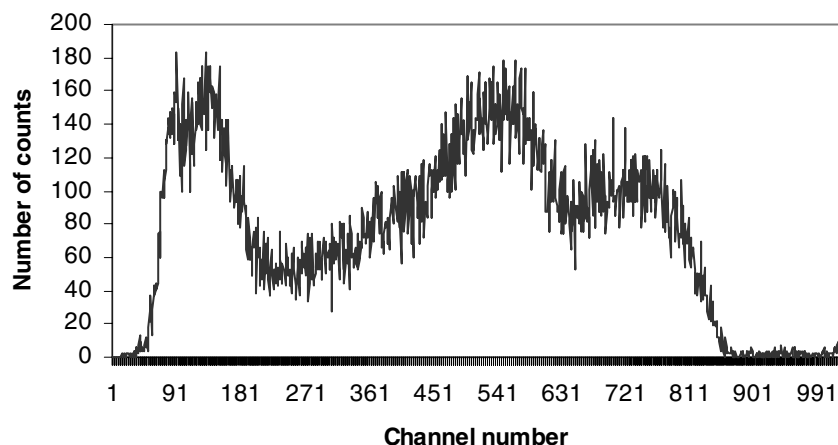


Figure 1 Sample of bilberry leaf (sample #17). Spectrum of beta radiation $^{85,90}\text{Sr}$ - ^{90}Y obtained with a 1414-003 Wallac Guardian LS counter. The measurement time is 45,000 s.

The mean values of $^{239,240}\text{Pu}$ activity concentration for moss and bilberry leaf samples are not significantly different in terms of a Mann-Whitney non-parametric statistical test (perhaps due to the small number of samples). The same is true for ^{137}Cs , whereas the result of this test for the mean ^{90}Sr activity concentrations is very significant, with a p value of 0.009.

In general, higher concentrations of Pu isotopes and lower content of ^{90}Sr can be observed in moss. ^{137}Cs activity remains similar in both groups of samples. There is also lack of correlation among analyzed isotopes. A strong correlation between ^{238}Pu and $^{239,240}\text{Pu}$ activity concentration can be seen only in moss samples. The slope of the correlation line, which can be interpreted as a mean value of the activity ratio between those isotopes, is equal to 0.026; this points to global fallout as the source of Pu. Because of the low number of results obtained for Pu, and especially because of the large uncertainties of ^{238}Pu results, such correlation for bilberry leaf samples is clearly visible. A correlation can be seen between activity concentration and the altitude above sea level (asl) for both ^{137}Cs and ^{90}Sr . In the case of ^{137}Cs , using data taken for all samples, the activity concentration slightly decreases for both moss and bilberry leaf samples regardless of soil type. ^{90}Sr seems to behave in a different way. For moss samples, the activity concentration of this nuclide decreases with the altitude, whereas for the bilberry leaf samples the activity concentration increases. The data on correlation among different nuclides, together with the data on the correlation between the altitude above sea level and the activity concentrations of ^{137}Cs and ^{90}Sr , are presented in Table 4.

Table 4 Slope values and R^2 correlation factors found for different isotopes in samples of mosses and bilberry leaves, as well as for ^{137}Cs , ^{90}Sr activity concentrations (Bq/kg dry weight), and the altitude (m asl).

	Mosses		Bilberry leaves	
	slope	R^2	slope	R^2
^{90}Sr - ^{137}Cs	-0.0042 ± 0.080	0.022	-0.056 ± 0.038	0.169
^{137}Cs - $^{239,240}\text{Pu}$	$-6 \times 10^{-5} \pm 0.0013$	0.00024	-645 ± 703	0.08
^{90}Sr - $^{239,240}\text{Pu}$	-2.04 ± 2.27	0.083	-1.8 ± 116	2.7×10^{-5}
^{238}Pu - $^{239,240}\text{Pu}$	0.026 ± 0.0038	0.870	0.014 ± 0.085	0.589
^{137}Cs -altitude	-0.21 ± 0.17	0.103	-0.238 ± 0.104	0.304
^{90}Sr -altitude	-0.007 ± 0.006	0.107	0.015 ± 0.017	0.064

Such features are likely to be related to a fundamental difference between these 2 plants. Moss grows for many years, whereas bilberry forms new leaves every year. For moss, the main source of contamination is the cumulative deposition of the fallout from the atmosphere, including resuspension (or accumulation) from the surrounding soil. Since mosses grow for many years, the deposition can be partially washed out as well. The washout should be proportional to the amount of water that soaks the plant. The higher one goes in the mountains, the more atmospheric precipitation is expected; therefore, the ⁹⁰Sr concentration can be lower there. Bilberries take nutrients, and also radioactive contaminants, mainly by the root uptake, and each year they accumulate radiostrontium in newly grown leaves, likely reflecting the soil content. Direct deposition plays a much smaller role. The decrease in ¹³⁷Cs activity concentration with increased altitude for both groups of samples seems to be caused by the different chemical properties of Cs and Sr. Cs can be removed from the bio-available pool of nutrients relatively easier than Sr. Cs can also be more strongly accumulated in soil by clay particles. Strontium, which is less absorbed by soil particles, can be washed down the soil profile more easily; however, because of the same reason, it is also more available for root uptake. Therefore, for a more passive bio-accumulator such as moss, the Sr activity concentration behavior resembles Cs. Usually, the higher the altitude, the more difficult the living conditions become. Under such arduous conditions, Sr can become a valuable nutrient, and is strongly absorbed by bilberries.

Results for Pu isotopes are very scattered, showing no correlation with altitude or with other nuclides. For the moss, it can be interpreted in 2 ways: 1) as result of different local rates of washing out Pu that has been deposited many years ago; or 2) as the differences in local growth rate of moss that occurred after deposition of contaminants.

CONCLUSIONS

The environment of the Tatra Mountains is contaminated with Pu and ⁹⁰Sr of mainly global fallout origin (Kubica 2004). The influence of Chernobyl fallout cannot be excluded, but it seems to be very weak. The majority of ¹³⁷Cs, however, does come from the Chernobyl fallout. The correlations among the isotopes analyzed are not significant. Some correlation can be observed separately for ¹³⁷Cs or ⁹⁰Sr activity concentration and the altitude of the sampling sites, but for bilberries they have different signs. This is probably caused by the different chemical properties of Cs and Sr and by the different ways that mosses and bilberries take in nutrients.

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REFERENCES

- Horwitz EP, Dietz ML, Fischer DE. 1991. Separation and preconcentration of strontium from biological, environmental and waste samples by extraction chromatography using a crown ether. *Analytical Chemistry* 63(5):522–5.
- Horwitz EP, Chiarizia R, Dietz ML. 1992. A novel strontium-selective extraction chromatographic resin. *Solvent Extraction and Ion Exchange* 10(2):313–36.
- Kubica B, Mietelski JW, Gołaś J, Skiba S, Tomankiewicz E, Gaca P, Jasińska M, Tuteja-Krysa M. 2002. Concentration of ¹³⁷Cs, ⁴⁰K, ²³⁸Pu, ²³⁹⁺²⁴⁰Pu radionuclides and some heavy metals in soil samples from two main valleys from Tatra National Park. *Polish Journal of Environmental Studies* 11(5):537–45.
- Kubica B, Skiba S, Mietelski JW, Gołaś J, Kubica M, Stobiński M, Tuteja-Krysa M, Tomankiewicz E, Gaca P, Krzan Z. 2004. Transect survey of artificial ¹³⁷Cs and natural ⁴⁰K in moss and bilberry leaf samples from two main valleys from Tatra National Park. *Polish Journal of Environmental Studies* 13(2):153–9.
- Kubica B, Skiba M, Skiba S, Gołaś J, Kubica M, Stobiński M, Tuteja-Krysa M. 2005. Dislocation of the

- ^{137}Cs and ^{40}K radionuclides in the podsol profiles of the Tatra Mountain soils (south Poland). *Journal of Radioanalytical and Nuclear Chemistry* 266(1):3–9.
- LaRosa JJ, Cooper E, Ghods EA, Jansta V, Makarewicz M, Shawky S, Vajda N. 1992. Radiochemical methods used by the IAEA's laboratories at Seibersdorf for determination of ^{90}Sr , ^{144}Ce and Pu radionuclides in the environment samples collected for the International Chernobyl project. *Journal of Environmental Radioactivity* 17(2–3):183–209.
- Mellin J, Wallberg L, Suomela J. 1994. Distribution and retention of cesium and strontium in Swedish boreal forest ecosystems. *Science of the Total Environment* 157:93–105.
- Mietelski JW, Jasińska M. 1996. Radiocesium in bilberries from Poland: comparison with data for mushroom samples. *Journal of Radioecology* 4:15–25.
- Mietelski JW, Vajda N. 1997. Chernobyl ^{90}Sr in bilberries from Poland. *Journal of Radioanalytical and Nuclear Chemistry* 222(1–2):183–7.
- Sill CW. 1987. Precipitation of actinides as fluorides or hydroxides for high resolution alpha spectrometry. *Nuclear Chemical Waste Management* 7:201–15.
- Vajda N, Ghods-Esphahani A, Cooper E, Danesi PR. 1992. Determination of radiostrontium in soil samples using a crown ether. *Journal of Radioanalytical and Nuclear Chemistry* 162(2):307–23.