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Original Research

Concentrations of ^{137}Cs, ^{40}K Radionuclides and Some Heavy Metals in Soil Samples of Chochołowska Valley from Tatra National Park

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Abstract

This paper presents the results of determination of artificial ^{137}Cs and natural ^{40}K activity concentrations and some heavy metals in soil samples from the region of one of the main valleys of Tatra National Park (Chochołowska). Our investigation concentrated on ^{137}Cs and heavy metal levels in mountain soil taken from Chochołowska Valley, which revealed great variability in their concentration. The results show considerably small amounts of radionuclides ^{137}Cs and ^{40}K in the soils. Larger amounts of those elements can be found in the organic surface horizons of the soils. The evaluation of the content of those elements must be based on the bulk density analysis of the soil.

Keywords: caesium, heavy metals, Tatra National Park, soil profiles

Introduction

The whole area of the Tatra Mountains (both Polish and Slovak) is under protection in the form of national parks: Tatra National Park (TPN, Poland) and Tatra National Park (TANAP – Slovakia).

The Tatra Mountains belong to the International Biosphere Reserve and they remain a good place to run research aimed at evaluating artificial pollution levels introduced to this particular region. Radioactive elements are obviously a kind of chemical contamination. Following the Chernobyl accident and nuclear tests conducted in the middle of the 20th century, this region of Europe has been radioactively contaminated with, for instance, the gamma-emitting radionuclide ^{137}Cs ($T_{1/2}$ = 30.7 year) [1, 2].

The main purpose of this work is to show the transect survey of artificial ^{137}Cs in comparison to the level of natural ^{40}K and to some heavy metal concentrations (Zn, Cr and Pb) determinated in selected soil samples taken from the region of one of the main Tatra Valleys (Chochołowska) [3, 4]. Regarding similar physical and chemical properties of caesium and potassium, it seems that they are competitive in the natural environment. This scrutiny is the continuation of analysis concentrated on the level of contaminants in Tatra National Park [5-8].

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Experimental Methods

Surface soil samples were collected from Chochołowska Valley during the summers of 2001-05 at least four times in order to have reliable knowledge of average radinuclide concentration levels [9, 10]. The precise localization (geographical coordinates) and altitude of certain sampling places were determined using a GPS system [GPSmap 76S]. Soil profiles were collected with 10 cm diameter plastic cylinders. Sampling depth was 10 cm. Monolith cores were taken out and preserved in the cylinders. The cores were sliced into 3-3.5 cm thick slices. The soil slices (levels) corresponded with the concentrations of analyzed elements found at different depths (level *a*- from 0 to 3 cm, *b* 3-6 cm and *c* 6-10 cm) in the soil profile. The samples were taken from different genetic soil levels. The profile of investigated soils had a Podzols characteristic coloured sequence of the genetic horizons: Ofh (raw humus) – E (albic) – Bhfe (spodic) – C (parent material). It is essential to note that both the depth of the soil profile and the depth of the horizons were almost equal in all investigated soils (Table 1). The collected samples were subjected to standard pedological analysis (among others: texture, pH,% of the organic matter, C/N). The mineral composition of the bulk soils material (<1mm) as well as the clay fractions using the X-ray diffraction technique were analyzed [11]. The clay fractions were separated by centrifugation proceeded to chemical treatment including organic matter removal, disposal of free Fe^{3+} oxides, according to Mehra and Jackson method and sodium saturation followed by dialysis. After treatment, separated clay fractions were weighed.

Before the gamma-measurements, the organic particles were removed and the soil material was dried at 105°C and sieved using a vibrating screen (diameter of circular –hole screen was about 2 mm). The radionuclide content of the samples was measured by gamma-spectroscopy with a HPGe detector of 10% efficiency for 72 hours (for each sample). The gamma spectrometer was calibrated by standards IAEA-154, Soil-6, IAEA-375 from International Atomic Energy Agency (IAEA) of Vienna, according to the method previously described [12]. The soil samples were collected during the period of 2001-05 but the data of the gamma-measurements were calculated and normalized for 01.09.2000.

Additionally, determination of elemental concentration of Fe was made by means of the UV-VIS Spectrometry method (Spectrometr Helios alfa – Spectronic Unicam). Samples were wet digested with the use of microwave system (Plazmatronica, Poland). Each determination was performed three times.

The PIXE technique also has been applied in this study. 2.4 MeV proton beam at the Institute of Nuclear Physics, Polish Academy of Sciences in Kraków has been collimated down to 1 mm^2 on the sample.

The experimental set-up for the PIXE experiments allows collecting two independent spectra at the same time. The PIXE spectrum was detected by a Si(Li) detector with an energy resolution of 180 eV for Mn-K_α line. The spectrum of back-scattered protons used for normalization of all registered PIXE spectra are provided by the surface-barrier detector with an energy resolution of 18 keV for an Am^{241} source. The surface-barrier detector detects particles back-scattered from a thin aluminum foil. The foil separates the high vacuum volume of the target chamber from the low vacuum region where the investigated sample is placed. This arrangement, known as an external beam technique, avoids target charging effects. Such normalization also provides independence on target types and directly proportional to the number of incident particles. The two input data acquisition system built around the ORTEC 919 Multichannel Buffer and controlled by a PC computer was used for x-ray spectra detection.

Results and Discussion

The concentration level of ^{137}Cs and ^{40}K measured in soil samples was collected from the Chocholowska Valley region. The values (Table 2) were expressed either in Bq/kg dry mass or in Bq measured in the area unit (m^2). Minimum detectable activity (MDA) accordingly to definition by Curie [13] were about 10 Bq/kg and 100 Bq/kg for ^{137}Cs and ^{40}K, respectively.

Our data revealed the significant variability in radiocaesium level distribution in the soil samples taken from the Chochołowska Valley area. As shown in Figs. 1a and 1b, respectively, the ^{137} Cs concentration measured in the area unit [Bq/m^2] corresponded with the values of radiocaesium concentration determined per mass unit [Bq/kg].

Table 1. Specific properties given for investigated soil profiles.

Depth	Horizon	Colour	%Skeleton > 2 mm	Texture	pH	% Org.matter
0-5	Ofh	10YR 2/2	20	Raw humus	4.0	37.8
5-10	E	10YR 6/4	30	LS	4.0	Trace
10-30	Bhfe	5YR 3/2	35	LS	4.6	9.2
30-70	Bs/C	10YR 6/5	40	LS	5.1	Trace
70-90	C1		95	bedrock		

Table 2. Activity of radiocaesium and potassium in soils taken from Chocholowska Valley.

Sampling places	a.s.l. [m]	% organic matter	D [g/cm^3]	activity ^{137}Cs[Bq/kg]/ activity ^{40}K [Bq/kg]			activity ^{137}Cs[Bq/m^2]/ activity ^{40}K [Bq/m^2]
			a	a	*b*	c	
Near pathway to Iwaniacka Pass	1061	23.44	0.708	308.9±6.78	109.92±1.48	33.88±1.21	7062.7
				388.17±5.55	457.35±5.45	461.66±5.16	27302.25
Chochołowska Valley near shelter-home near pathway to Wołowiec Mt	1180	44.26	0.27	873.6±71.4	348.8±3	48.10±1.7	5491.966
				296.9±4.7	483 ±6.1	524.4±6.25	8508.726
Bobrowiecka Pass	1355	71.52	0.17	1782.23±13.39	1926.51± 9.18	247.22± 2.05	13095.82
				2.67±0.04	133.8±1.91	464.76±5.68	5390.198
Grześ Mt	1653	46.78	0.38	1584±6.91	682.58±4.56	brak	11152.83
				346.91±5.53	278.90±3.78		3202.359
Wyżnia Chochołowska Glade	1720	52.42	0.16	301.7±4	570±4.3	197.6±2.4	5849.089
				1.23	636±27	814±34	12901.68
Pathway to Grześ Mt	1150		0.33	680.9±3	194.2±1.14	27.4±1.4	9736.666
				177.3±6	470±20	474.2±20	19677.3
Rakoń Mt	1879		0.17	1562.3±8	493.5±3.4	36.7±1.4	7511.852
				51	385.5±16	498.4±21	10582.13
Upłaz Mt	1794		0.58	265.98± 2.6	41.5±1.1	10.74±14	2506.195
				265.98±2.6	41.5±1.1	10.74±14	26962.22
Starorobociańska Valley	1434	49.46	0.46	385.05±4.3	272.2±2	brak	4255.6
				230.07±10	506.4±21	brak	9389.92
Chochołowska Valley near Lejowa Valley	1224		0.62	148.68±1.74	141.14±1.96	42.86±1.12	7423.00
				760.61±8.32	939.4±10.39	815.66±8.6	64754.23

Also, one can observe the tendency proportional relation between ^{137}Cs activity and sampling point altitude. This correlation was observed before and showed in recent papers concentrated on Tatra's radioisotope contamination [9, 14, 15]. Furthermore, for natural ^{40}K isotope, the changes in its activity measured in given samples in respect to the altitude [asl.] were not noticed. Demonstrated increase in ^{137}Cs activity in correlation to altitude might be elucidated due to the humic development level; in other words, to the number of organic matter present in mountain region soil samples. [16-19]. Specific properties of all mountain region soils including the soil-covered Tatra Mts., is the delay in organic matter decomposition process in relation to the altitude and forming of ectohumic levels [20-22].

The ^{137}Cs concentration, measured in investigated soils, showed an increasing tendency with height [asl.] and soil surface carving and soil volume density [5.14]. Obtained data showing the changes in ^{137}Cs and ^{40}K activity found in ectohumic soil levels are presented in Figs. 2a, 2b and 2c.

Apparently, in all investigated samples radiocaesium concentration declined with the increase of soil volumic density. This means that the artificial ^{137}Cs radioisotope is strongly bound by organic substance forming the soil accumulation levels. Increasing of soil density, which suggests a decrease of organic matter content, reduces caesium concentration (Figs. 2a and 2d). Determined activity of natural ^{40}K are inversely proportional to activity of artificial ^{137}Cs (Fig. 2c). This fact might indicate that K cations are competitive to Cs ions. In opposite to radiocaesium, natural ^{40}K concentration remains the proportional level tendency. With increasing soil density, potassium activity also increases. This phenomenon could be explained by the presence of huge amounts of potassium as a natural component in mineral soils. Apparently, potassium is one of the main elements that form K-feldspars, mica and illic minerals. Measured activity of natural ^{40}K was directly proportional to the total activity of potassium in soil (1 g of potassium contains always 31.7 Bqkg^{-1} of ^{40}K). The highest potassium activity was

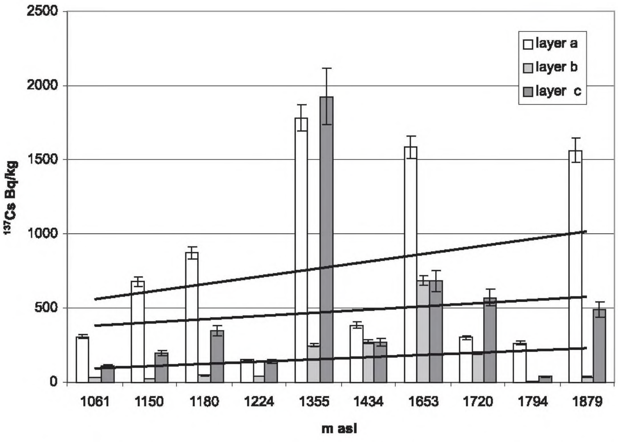


Fig.1a. Altitude-dependent ^{137}Cs activity (Bq/kg) measured in layers (a,b and c) in soil samples from Chochołowska Valley in function of sampling point altitude.

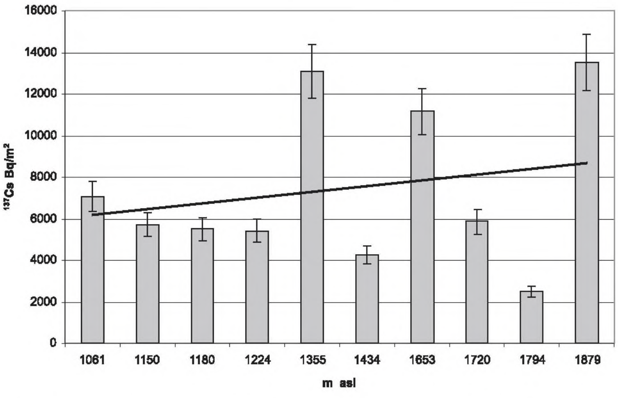


Fig.1b. The change in ^{137}Cs concentration (Bq/m^2) showed as an area unit in relation to altitude of sampling.

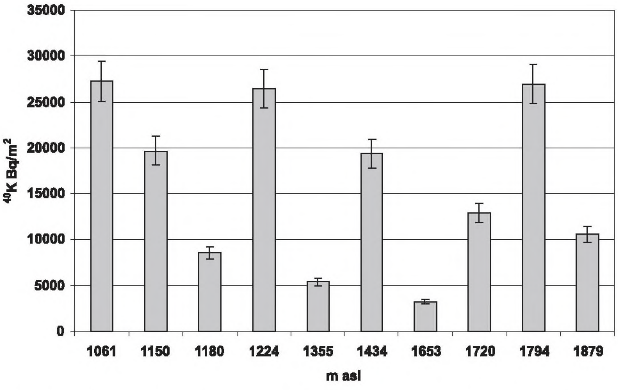


Fig.1c. Altitude dependence of ^{40}K activity (Bq/m^2) in samples taken from mountain region soils.

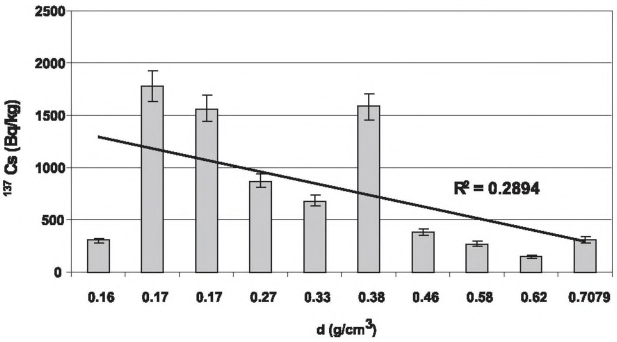


Fig. 2a. Content of ^{137}Cs and volumic density in all investigated soil samples (Chochołowska Valley).

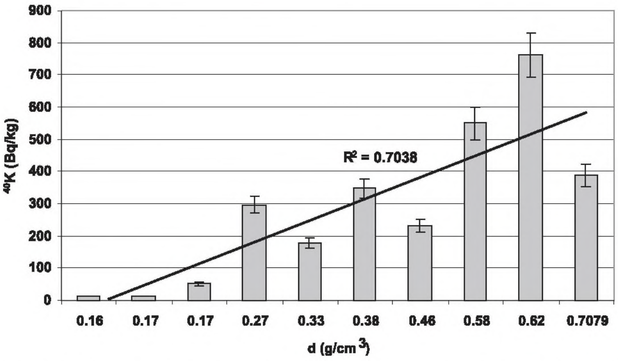


Fig. 2b. Content of ^{40}K and volumic density in all investigated soil samples (Chochołowska Valley).

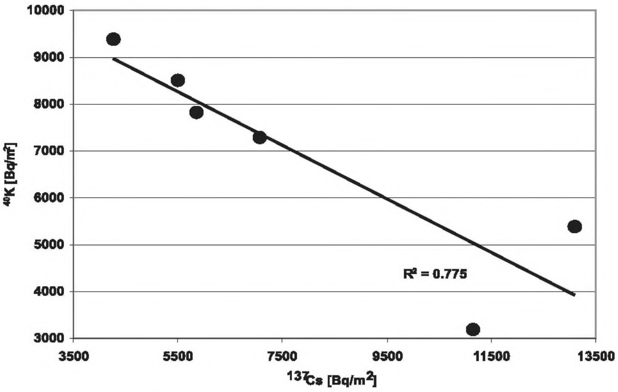


Fig. 2c. The correlation between activity of artificial ^{137}Cs and natural ^{40}K in all investigated soil samples (Chochołowska Valley).

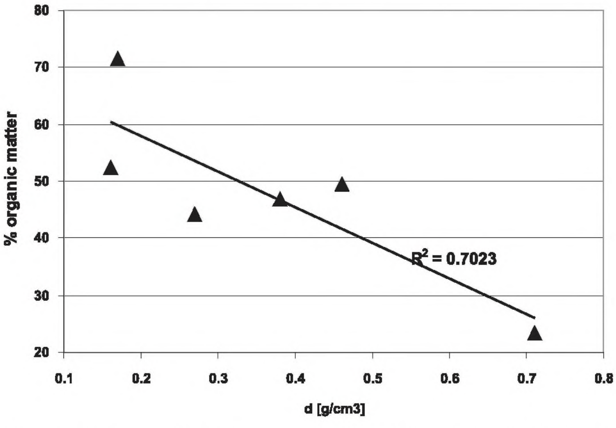


Fig. 2d. The correlation between volumic density and % organic matter in investigated soil samples (Chochołowska Valley).

found in layer "c" (depth of 7-10cm). Furthermore, the difference in the potassium concentration is not related to altitude and ^{40}K activity was comparable with the value of potassium concentration determined for the Carpathian Foothills [23].

Also, the aim of presented survey was to present data showing heavy metals contamination in the Tatras. In analyzed samples the concentration of Zn, Pb and Cr

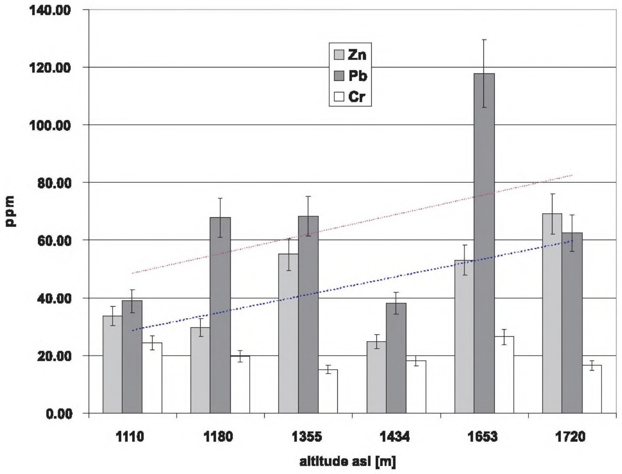


Fig. 3a. Altitude dependence of of heavy metals (ppm) concentration in samples taken from mountain region soils.

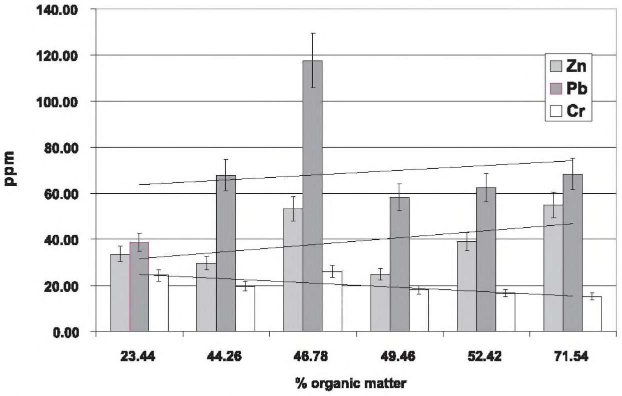


Fig 3b. Content of organic matter dependence of heavy metals (ppm) in samples taken from mountain region soils.

were measured. Data obtained from the investigation are shown in Figs. 3a and b.

The presence of the natural long-lived gamma emitters are due to the connected mineral bedrock.

Presented values of heavy metal concentrations in investigated soil samples, in the majority were in the range of values given for Polish soils or in some cases were slightly higher regarding these data [24, 25]. Furthermore, obtained results were comparable to those described for other mountain regions, for instance Karkonosze or the Bieszczady Mts. [26-28].

The lead concentration in samples collected from Chochołowska Valley is 38.8–117.7 mg/kg (see Figs. 3a and 3b, respectively). The level of Pb contamination changes from 26 to 471 mg/kg on the TPN area but the most frequently observed is in the range between 50 mg/kg to 125 mg/kg. The increase of measurable Pb concentration with increase of the altitude might be explained by the quantity of organic matter found in samples in dependence of sampling altitude.

The Zn concentration in samples taken from Chochołowska Valley from selected points (m asl) varies from 34.3 to 55.0 mg/kg and to some extent the values grow directly proportional with either altitude or content of organic matter. For soils covered the whole area of TPN, the scale of changeableness of Zn concentration level is from 11 mg/kg to 664 mg/kg (wet mass). The most often measured values are 27-75 mg/kg [29].

Also, Cr concentrations were determinated in soil samples. It occurred that the amount of this heavy metal is between 15.1 mg/kg to 24.4 mg/kg. The concentration of Cr exhibits no correlation with the altitude and the number of organic matter.

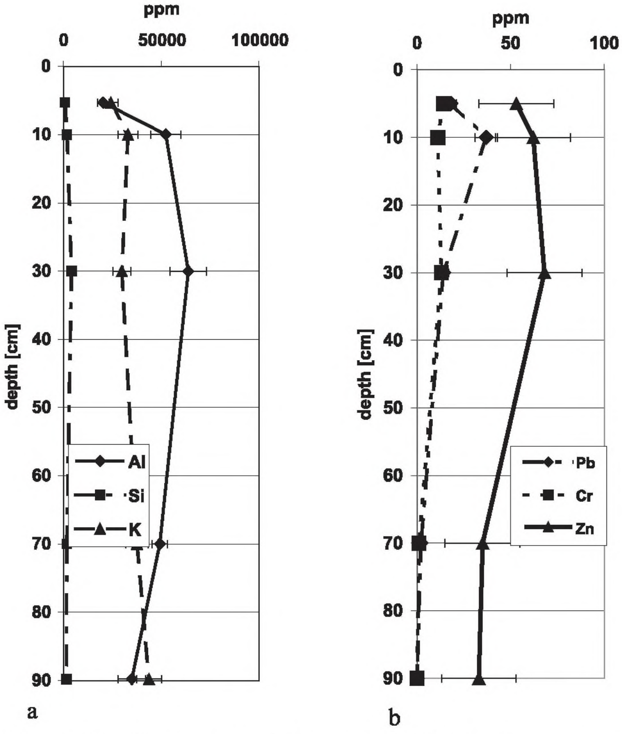
We conducted some standard measurements to determine the radioisotopes ^{137}Cs and ^{40}K and other elements (Al, Si, K, Cr, Zn, Pb) in soil profiles collected from Trzydniowiański Mt.(1750 m asl).

This mountain is situated in the eastern part of Chochołowska Valley. The results of the investigation are given in Figs. 4a and b, respectively [7].

Figs. 4a and 4b show the activity of ^{137}Cs and ^{40}K in mass unit for the samples taken from the genetic levels of analyzed soil samples [Ofh-E-Bhf-C] were prepared.

The maximum of ^{137}Cs concentration was measured in Ofh levels (raw humus), formed in the process of delayed humification of organic matter [5, 16, 30].

The content of radioceasium concentration of ^{40}K exhibits a growing tendency in depth of soil profile, which is strongly related to an increase of mineral matter concentration. The increase of mineral mass quantity is confirmed also by growing concentration of Al, K, Si and Fe concentration in particular in the case of transition from Ofh layer to C level (Fig. 4a).



Figs. 4. The changes in natural (a) and artificial (b) element concentrations in soil depth profile measured in samples collected from Trzydniowiański Wierch.

For elements, in particular, with artificial origin (Pb, Cr and partly Zn) declining trend in concentration regarding the depth of soil profile was observed. The presence of such elements below 30 cm (soil cores) suggests that there are the components of parent rock or these certain elements associated with organic matter were conveyed along the soil profile. Higher values of Pb concentration measured in organic levels might indicate direct deposition of this element from atmosphere on the accumulation layers. Similarly to ^{137}Cs, anthropogenic-originated lead is strongly bound by organic soil components. The ratio Pb/Al shows the excess of Pb, which was released from air and accumulated in soil [31, 32].

Given results revealed great variability in distribution of either radionuclides or heavy metals observed in investigated samples from Chochołowska Valley area. It is probably caused by different sorts of physico-chemical soil properties which are the result of geological background, various surface area carving and unequal intensity of pollutant fall.

- ^{137}Cs levels in mountain soil taken from the Tatra region revealed great variability in concentration. The values were changing from 148.69 Bq/kg (3761, 44 Bq/m^2) in selected samples from Chochołowska Valley, in samples taken from an area situated between Chochołowska and Lejowa Valley (1224 m a.s.l) to 1782, 2 Bq/kg (13095 Bq/m^2) for Bobrowiecka Pass (1335 m a.sl).
- The changeableness of radiocaesium concentration depends strongly on organic matter content in surface horizon levels of investigated soils.
- Potassium ions play an essential role in ceasium bioaccumulation in soils. Potassium as the element which belongs to the same group of Table of Elements as caesium, has similar physical and chemical properties and that is the reason why K might be very competitive in the ability of releasing heavier and larger Cs ion.

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References

1. LILJNZIN J.O., SKALBERG M., PERSSON G., INGEMANSSON T.,.ARONSSONP.O; Radiochimica Acta; **43**, 1, **1988**.
2. PIEŃKOWSKI L., JASTRZĘBSKI J., TYS J., BATSCH T., JARACZ P., KURCEWICZ W., MIROWSKI S., SZEFLIŃSKA G., SZEFLIŃSKI Z., SZWERYN B., WILHELMI Z., JÓZEFOWICZ E.T; Journal of Radioanalytical and Nuclear Chemistry, Letters; **6**, 379, **1987**.
3. J. NYKA, Tatra Mts- Guide, SiT,Warszawa **1972**.
4. Z. MIREK, Nature of the Tatra National Park, TPN, Kraków-Zakopane **1996**.
5. B. KUBICA, J. W.MIETELSKI, J. GOŁAŚ, S. SKIBA, E. TOMANKIEWICZ, P. GACA, M. JASIŃSKA, M. TUTEJA-KRYSA, Polish J. Environ. Stud., **11**, 537, **2002**.
6. B. KUBICA, S. SKIBA, J.W. MIETELSKI, J. GOŁAŚ, M. KUBICA, M. STOBIŃSKI, M. TUTEJA-KRYSA, E. TOMANKIEWICZ, P. GACA, Z. KRZAN, Polish J. Environ. Stud., **13**,153, **2004**.
7. B. KUBICA, M. SKIBA, S. SKIBA, J. GOŁAŚ, M. KUBICA, M. STOBIŃSKI, M. TUTEJA- KRYSA, J.Radioanal. Nucl.Chem **266**, (1), 3, **2005**.
8. GÓRSKI M., UZIAK S; Annales UMCSSect.C; **46**, 1, **1991**.
9. STREBL F., RINGER W., GERZABEK M.H.; Journal of Environmental Radioactivity **58**, 143, **2002**.
10. DUBOIS G.,BOSSEW P. Journal of Environmental Radioactivity **65**, 29, **2003**.
11. MYSTKOWSKI K., Conference of European Clay Groups Association, EUROCLAY. September 5-9, Krakow, Poland. Book of abstracts, 114, **1999**
12. MIETELSKI.J.W., JASIŃSKA M., Applied Radiation and Isotopes. **47**,(9/10), 1089, **1996**.
13. CURRIE L., Anal. Chem. **40**, 585, **1968**.
14. SKIBA S., KUBICA B., SKIBA M., Bieszczady Mts Ann. **13**, 325, **2005**.
15. SKIBA S., KUBICA B., SKIBA M., STOBIŃSKI M., Polish Journal of Soil Sciences, **38**,(2), 119, **2005**.
16. SKIBA S., DREWNIK M., DROZD J.; IHHS, 497, **1997**.
17. ABSALOM J.P., YOUNG S.D., CROUT N.M.J., CROUT N.M., SANCHEZ A., WRIGHT S.M., SMOLDERS E., SMOLDERS A., NISBET A.F., GILLETT A.G.; Journal of Environmental Radioactivity **52**, 31, **2001**.
18. REZZOUNG S., MICHEL H., FERNEX F., BARCI-FUNEL G., BARCI V. ; Environmental Radioactivity **85**, 369, **2006**.
19. SKIBA M., Geologica Carpathica, **53**, (**2002**)special issue (edition on CD as analogue version).
20. ATUN G., KILISLIOGLU A., J.Radioanal.Nucl.Chem. **258**, 605, **2003**.
21. LETTNER H., GIESEBNER A., PEER T., HUBNER A.K., PINTARIC M.; Environmental Radioactivity **86**, 12, **2006**.
22. SAWHNEY L., Clays and clay Minerale, **20,** 93, **1971**.
23. CHEŁMICKI W., KLIMEK M., KRZEMIEŃ K., JASIŃSKA M., KOZAK K., MIETELSKI J.W., Folia Geographica, Ser. Geogr. Phys., **XXVIII**, 35, **1996-1997**.
24. KABATA-PENDIAS A., PENDIAS H., Biogeochemistry of trace elements, PWN, Warszawa **1999**.

25. J. NIEMYSKA-ŁUKASZUK, A. MIECHÓWKA, Changes of the Nature Environment of the Tatra Mts. Institute of Botany Polish Academy of Sciences, Kraków **2002**.
26. SKIBA S., DREWNIK M., SZMUC R., Bieszczady Mts Ann., **4**, 111, **1995**.
27. SKIBA S., DREWNIK M., SZMUC R., Phytopathologia Polonica, pp. 418, **1995**.
28. SKIBA S., DREWNIK M., SZMUC R., Abstracts of II National Conference "Ecological Research of Karkonosze Mts", Dziekanów Leśny, 17 – 19 January, **1994**.
29. OLEKSYNOWA K., BARSZCZ E., Changes of the Nature Environment of the Tatra Mts., Institute of Botany Polish Academy of Sciences, Kraków **2002**.
30. SKIBA M., Minerals Soc. of. Poland. Special Papers. **17**, 240, **2000**.
31. BRULAND K.W., BETRINE K., KOIDE M., GOLDERG E.D., Environ.Sci. Technol., **8**, 520, **1974**.
32. HYUN-JU CHA, MUN-JA KANG, GEUN HO CHUNG, GEUN SIK CHOI, CHANG WOO LEE, J.Radioanal. Nucl. Chem., **267** (2), 349, **2006**.