

**Determination of the activity level of artificial isotope  
 $^{137}\text{Cs}$  and natural  $^{40}\text{K}$  and the selected heavy metals  
in the Tatra Mountains ecosystem**

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This paper presents the results of determination of gamma emitting radionuclides – artificial  $^{137}\text{Cs}$  and natural  $^{40}\text{K}$  and same heavy metals in soil samples from Tatra Mts. Results show some differences in the vertical distribution of examined radionuclides and metals. It was found that the change of activity of  $^{137}\text{Cs}$  in the soil samples depends mostly on the soil volume density and on the concentration of organic material. The state of "zero"  $^{137}\text{Cs}$  activity was developed in the form of maps.

*For my Friend Stanisław*

## 1. INTRODUCTION

Radioactive substances are considered as one of the numerous types of pollution of the natural environment. However, various radionuclides are abundant in the environment from the Earth formation. The average content of radioactive isotopes in the Earth's crust is approx. 0.1% of which the most important are natural uranium and thorium. These elements are widespread in rocks, soil, and seas, lakes and rivers [1–5].

Among the radionuclides of natural origin, those that have a long half-life time can be distinguished, and their age is close to the age of the

Earth. They were created during the formation of the solar system. An example is the potassium  $^{40}\text{K}$  isotope, the abundance of the natural potassium is equal to 0.0117%, and the half-life  $T_{1/2} = 1.28 \cdot 10^9$  years. The  $^{40}\text{K}$  decays by two ways: 89.3% by beta emission into a stable  $^{40}\text{Ca}$ , and 10.7% by electron capture into the excited state of stable  $^{40}\text{Ar}$ , which emits the 1.46MeV photons of gamma radiation [6].

In contrast, the origin of artificial radioactive elements are a major concern in respect to the natural environment with special emphasis put on the protected natural areas. As the main source of their presence are: nuclear weapon tests conducted in the atmosphere, catastrophes of nuclear reactors (including the largest disaster in Europe – Chernobyl), re-processing of nuclear fuel plants [1–3,7].

The contamination of large areas of Europe after the accident of the Chernobyl nuclear reactor in 1986 has become a challenge for many research centers. Especially important artificial radionuclide is  $^{137}\text{Cs}$  for the reason of its rather long half-life (30 years) and large dispersion in the environment.

Between the years 2000–2015 there were made extensive studies of anthropogenic  $^{137}\text{Cs}$  and natural  $^{40}\text{K}$  activity levels and concentrations of selected heavy metals in soil [8–18]. These studies were carried out in several southern Polish mountain ecosystems. This paper presents the research concerned the area of the Tatra Mountains. It was observed a large variation in the spatial distribution of  $^{137}\text{Cs}$  in the soil depending on the soil density, type and mineralogical composition. These variations were related to the height and geomorphological configuration of the sample collected area, and the amount of precipitation during the radioactive cloud passing through that area.

Mountain ecosystems, due to their enormous sensitivity to disruption of homeostasis, there are ideal places to observe contamination, both chemical and radiochemical. In the present study the Central Carpathians and therefore the highest alpine mountain range in the region – Tatry, were of concern. Moreover, special attention was attracted to the areas under legal protection or National Parks.

## 2. MATERIALS AND METHODS

The research material was collected in the period from June till October of the years 2000–2013. Soil samples were obtained from the top layer using a cylindrical probe having diameter and height of 10 cm. The

exact location (latitude and longitude coordinates and altitude) of the sampling points was determined using a satellite navigation system (GPS) and Garmin 76CS maps.

The collected soil core was divided into three equal parts namely: a, b and c. The part "a" corresponds to the top layer of the soil, and "c" was the deepest layer. The soil samples delivered to the laboratory were dried at  $105^{\circ}\text{C}$  for 72 hours. The samples were weighted (total mass) deprived of stones and large fragments of plants, and then grounded and sieved through the mechanical sieves (mesh diameter of 2 mm). After screening, the samples were placed into test vessels, weighed, and their bulk density was determined. All the activity measurements were given using the specific activity [ $\text{Bq/kg}$ ] and [ $\text{Bq/m}^2$ ].

### *2.1. Measurements of $^{137}\text{Cs}$ and $^{40}\text{K}$ activity by gamma-ray spectrometry*

Measurements of activity of  $^{137}\text{Cs}$  and  $^{40}\text{K}$  were performed using semiconductor gamma-ray spectrometers equipped with coaxial, high purity germanium (HPGe) detectors, characterized by 15% relative efficiency. To perform efficiency calibration the Reference Materials obtained from the International Atomic Energy Agency in Vienna were used: IAEA-154 of certified activity of  $^{137}\text{Cs}$  – 3749 Bq/kg, and  $^{40}\text{K}$  – 1575 Bq/kg, and IAEA-375, the certified activities were:  $^{137}\text{Cs}$  – 5280 Bq/kg, and  $^{40}\text{K}$  – 424 Bq/kg. In order to maintain similar properties of the samples and the reference materials (such as matrix, density, sample collection height) further correction factors were included in the efficiency calibration. The most important correction factor was related to self-absorption. This phenomenon is correlated with the sample density, and refers to partial absorption of emitted gamma rays by the sample itself [17–20]. All samples were measured for 72 hours (259 200 seconds) in life time, that is the actual measurement time– including dead time of the detector.

Studies in the Tatra Mountains were performed during 15 years [8–18, 20–23]. In order to keep results comparable, the measured activities of  $^{137}\text{Cs}$  ( $T_{1/2} = 30,05$  years) are recalculated to the date of 1st September 2000.

### *2.2. Measurements of heavy metals concentration using atomic absorption spectrometry and fluorescence analysis PIXE*

Quantitative determination of Pb, Zn, Cd and Cr were carried out by means of atomic absorption spectrometry (AAS) [24, 25]. For these measurements the dry and homogenized soil samples (from soil layers

a, b and c) were used. The samples (approx. 0.5 g of soil) were digested in the mineraliser (UniClever manual Plazmatronika) under high pressure of 45 atm and at temperature up to 320°C in the mixture of concentrated HNO<sub>3</sub> and HCl in ratio of 4:1 (about 5 cm<sup>3</sup>). In the case of soils with high content of minerals the mixture of HNO<sub>3</sub> and HF in the ratio of 4:1 was used.

For comparative purposes in several soil samples a wide range of elements was determined using fluorescence analysis: PIXE (Proton Induced X-ray Emission). It consisted of recording the characteristic X-ray spectra emitted from the excited atoms of the sample exposed to a beam of protons with an energy of 2.5 MeV coming from the van de Graaff accelerator. Registration of a characteristic X-ray spectra was carried out using a Si(Li) detector (Canberra detector of FWHM energy resolution 160 V at 5.9 keV). This method belongs to the non-destructive ones, therefore samples digestion was not necessary.

### 2.3. Tatra Mountains

Tatra Mountains lie in the southern Poland, in the border zone between Poland and Slovakia. Despite the fact that they are the highest mountains in the Carpathian Mountains, their surface area is relatively small. Approximately their size corresponds to the average size of a single Alpine valley [26–29].

It is assumed that the area of the Tatra Mountains is equal to 78.5 thousand km<sup>2</sup>, of which only 25% is on the Polish side of the border (175 km<sup>2</sup>), and 75% is on the Slovakia side (610 km<sup>2</sup>). The entire Tatras area is legally protected through the establishment of national parks. The Polish part is included in Tatra National Park (TNP), founded in 1954, while the Slovak Tatra Narodny Park (TANAP) exists since 1st January 1949. Due to its unique landscape and nature, the best preserved forest fragments of the Lower and Upper montains, UNESCO acknowledged the Tatras as a World Biosphere Reserve.

The object of this study was to determine the spatial distribution of gamma radionuclides: artificial <sup>137</sup>Cs and for comparison natural <sup>40</sup>K, and some heavy metals (Zn, Cr, Cd and Pb) in the soil samples taken from the whole region of the Tatras.

As a result of nuclear weapons tests which took place in the sixties of the XX<sup>th</sup> century, as well as the nuclear reactor fire in the Chernobyl nuclear power plant, vast areas of Europe (especially eastern and central) have been heavily contaminated with, among the others, <sup>137</sup>Cs gamma



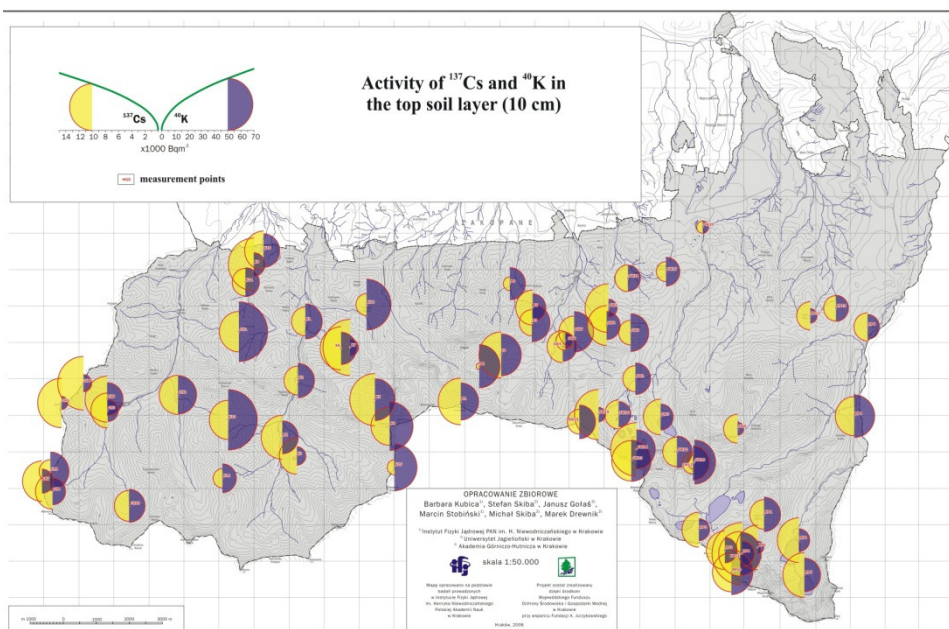


Fig. 2. The concentration of gamma radionuclides: artificial  $^{137}\text{Cs}$  and natural  $^{40}\text{K}$  expressed in  $\text{Bq}/\text{m}^2$  in soil samples.

Figures 1 and 2 show  $^{137}\text{Cs}$  specific activity in  $\text{Bq}/\text{kg}$  for a given layer. As it is seen, the cesium activity concentrations vary substantially, the highest content of this radionuclide was observed in the TPN in the High Tatras and on the ridge connecting Grześ Mt and Wołowiec Mt in the Western Tatras. There is also a trend indicating the competitiveness of potassium and cesium sorption in soil. In places where the soil was depleted in potassium the activity of cesium was higher.

Analyses of  $^{137}\text{Cs}$  activity concentration in the Tatra soils show a great diversity of this radionuclide which ranged from  $55.8 \text{ Bq}/\text{kg}$  ( $417.8 \text{ Bq}/\text{m}^2$ ) for Tomanowa Pass (1685 m a.s.l.) to  $5111 \text{ Bq}/\text{kg}$  ( $8,400 \text{ Bq}/\text{m}^2$ ) for Pass Krzyżne (2112 m a.s.l.). After falling down cesium is readily bound by organic matter in the soil. Soil composition and properties in the Tatra Mts, as in other mountainous systems, are closely related to climate, construction of multi-storey vegetation etc. With increasing height the thickness of humus level increases (a phenomenon typical of subalpine floors) which is characterized by a high sorption and ion exchange capacity. With the increasing soil density which, in turn, is concomitant with decrease of organic matter content in soil (what corresponds with decreased sampling point height m a.s.l.) the cesium content is markedly decreased. Potassium follows the

invers proportional tendency: with increasing density of the soil, natural potassium content also increases, because the mineral components of the soil, for example potassium feldspar, mica, clay minerals, either contain or adsorb it.

Fig. 3 shows changes in the activity concentration of cesium in  $\text{Bq/m}^2$  in the Tatra mountains.

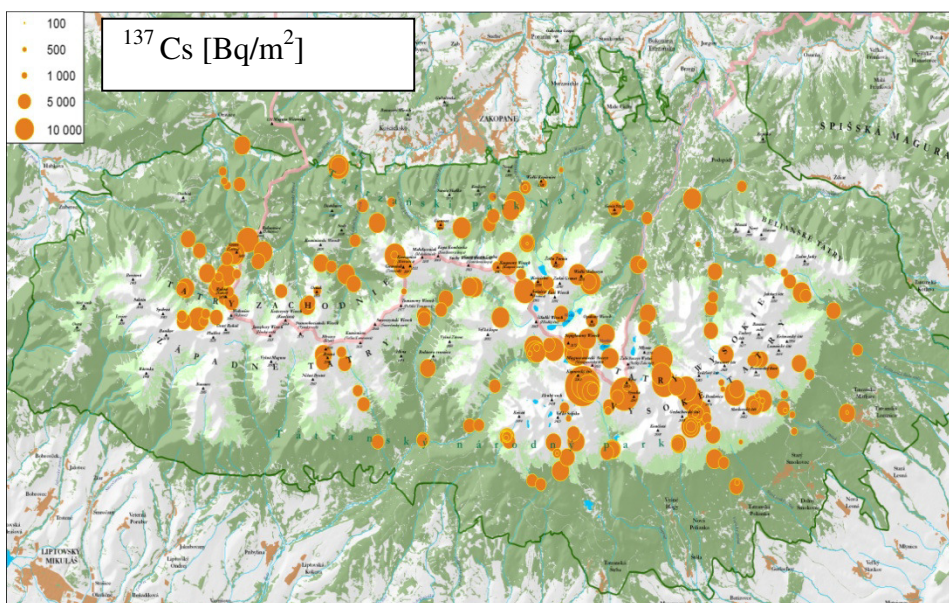


Fig. 3. Changes of the activity of  $^{137}\text{Cs}$  [ $\text{Bq/m}^2$ ] in the surface layer of soil in the Tatra mountains.

It can be seen from Fig. 3 that there is also a very large diversity of the  $^{137}\text{Cs}$  in the considered region. The highest  $^{137}\text{Cs}$  activity was observed in the area of the High Tatras on both side of the Polish and Slovakia border.

In order to assess the change in the activity of cesium and delivery mechanism of this gamma radionuclide in the Tatras since 2007, twelve points were selected (basing on the above presented maps – Figs. 1, 2) for annual monitoring. The measuring points were positioned in at least two places in five main valleys in the Polish part of the Tatras. In the same measurement points activity of natural isotope  $^{40}\text{K}$  was determined. The results are presented in the form of graphs (Figs. 4 and 5). On these graphs changes in the  $^{137}\text{Cs}$  activity since the year 2000 till 2012 are

presented. In some locations the activity levels exceeds several times the average values reported for Poland. The average value of  $^{137}\text{Cs}$  activity for the soil in Poland determined on the basis of 254 measurement points is  $2.41 \text{ kBq/m}^2$  [41].

#### West Tatra Mts -monitoring in the years 2000-2012

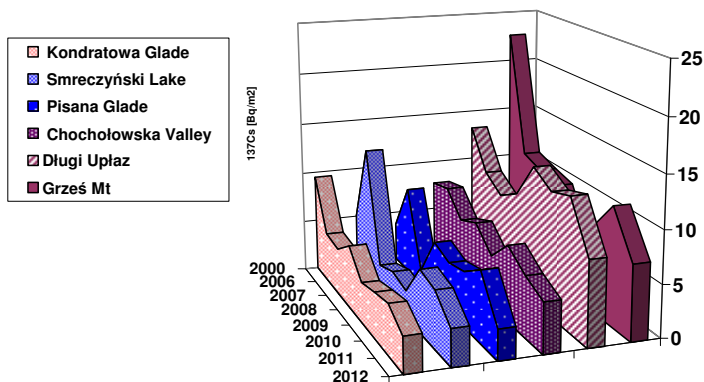


Fig. 4. Changes in the activity of  $^{137}\text{Cs}$  in the soil samples collected in the Western Tatras – monitoring in years 2006-2012.

#### High tatra Mts, monitoring in the years 2000-2012

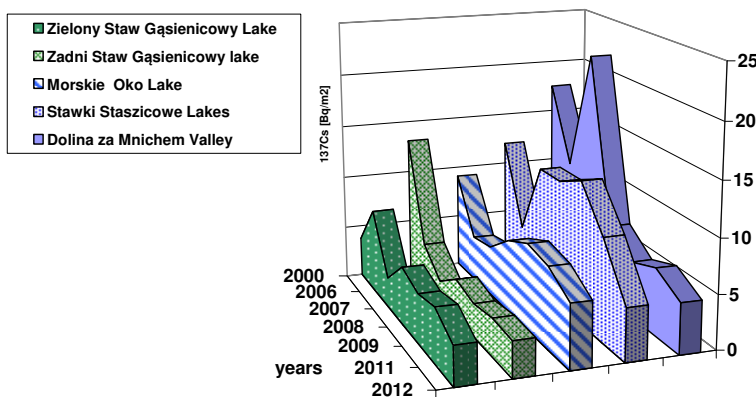


Fig. 5. Changes in the  $^{137}\text{Cs}$  activity in the soil samples collected in the High Tatras – monitoring in years 2006-2012.

The activity concentrations of  $^{137}\text{Cs}$  in many places of the Tatra Mts showed decreasing tendency which may be explained both by radioactive decay and by migration processes occurring in the environment. Especially, the process of cesium penetration into deeper soil layers with



the organic forms and its sorption on aluminosilicates should be taken into consideration.

In the region of the Polish Tatras, activity of  $^{137}\text{Cs}$  in the year 2012 changed from 10.04 kBq/m<sup>2</sup> for soil samples collected at the region of Staszicowe Lakes to 8.07 kBq/m<sup>2</sup> for the samples located in the vicinity of Morskie Oko lake, which is almost 4 times higher comparing to the national average.

In most cases, for the years 2000–2012 it was observed the decreasing tendency of cesium content in the surface layer of the soil. This is obviously a result of  $^{137}\text{Cs}$  movement downwards in the soil profile. Figures 4 and 5 present changes in the  $^{137}\text{Cs}$  activity in soil covering the monitoring framework in years 2000–2012. Very interesting phenomenon was observed in two totally different locations i.e. TNP – in Eastern Tatras in Staszicowe Lakes (Rybi Potok Valley) and in Długi Uplaz (Western Tatras - Chochołowska Valley).

In the Figure 6 changes of the  $^{137}\text{Cs}$  content in the soil samples taken from the Tatras over thirteen years of monitoring expressed in percent units, is presented. Percentage distribution was calculated in relation to the average of  $^{137}\text{Cs}$  activity values measured within 13 years.

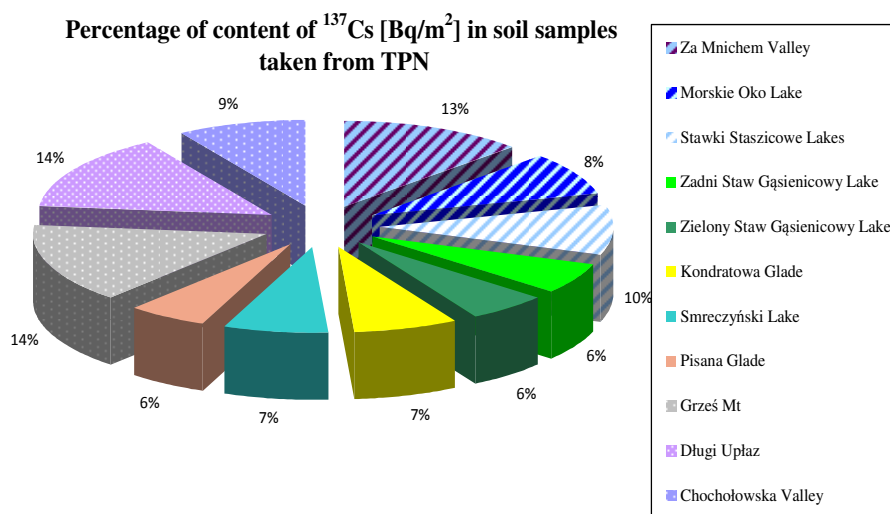


Fig. 6. Percentage of content of  $^{137}\text{Cs}$  in the soil samples taken from the Tatras over thirteen years of monitoring.

The increase of  $^{137}\text{Cs}$  content in the region of Morskie Oko lake in the High Tatras (Fig. 5) and on the ridge connecting Grzes Mt in the Western Tatras (Fig. 4) can be explained by the higher rainfall rate and

which caused introduction of radiocesium into the environment from the upper parts of the atmosphere. It is supposed that in the higher parts of atmosphere cesium coming from the Chernobyl accident was present for much longer time. In order to prove this thesis, in two locations mentioned above special devices (probes) containing a cesium selective composite sorbent with magnetic elements were installed (hereinafter referred to as NiNCF) [42–43].

Assuming that the average rainfall in these regions is amounted approximately 1700 mm per year, the calculated activity of cesium should be in the range from 5.61 mBq to 37.4 mBq. The results (Table 1) indicate higher activity of  $^{137}\text{Cs}$  (from 33.3 mBq to 98.4 mBq). This fact can confirm the supposition that between 2007–2012 cesium was introduced to the Tatras area along with atmospheric precipitation.

Table 1. The values of  $^{137}\text{Cs}$  activity concentration collected on composite magnetic sorbent (NiNCF) in different places in the TNP.

Sampling points	2008 $^{137}\text{Cs}$ [mBq/kg]	2009 $^{137}\text{Cs}$ [mBq/kg]	2010 $^{137}\text{Cs}$ [mBq/kg]	2011 $^{137}\text{Cs}$ [mBq/kg]	2012 $^{137}\text{Cs}$ [mBq/kg]	2013 $^{137}\text{Cs}$ [mBq/kg]
Długi						
Upłaz Mt (1603 m asl)	65.0±31.1	82.8±16.1	45.5±26.6	98.4±42.7	77.9±49.2	88.6±37.5
Grześ Mt (1639 m asl)	52.9±15	61.5±15.0	67.2±35	56.2±31	54.0±30.5	58.0±34.1
Staszicowe						
Lakes (1893 m asl)	65.3±14.5	84.8±19.3	61.2±22.1	85.7±37.2	65.1±22.4	76.4±32.6

In the collected soil samples from the Tatra Mts, besides gamma spectrometry, heavy metal concentrations (Zn, Cd, Pb and Cr) were determined as well. The results of analyses for the TNP are summarized in Table 2 and for TANAP in Table 3.

As one can see, the accumulation of chromium in the soil samples taken from the Main Valleys located in the Tatra National Park are in the ranges recommended for the mountainous regions [18,44]. The high concentration of lead and cadmium in the soils collected from the region of Sucha Woda Valley is likely associated with anthropogenic activity, mainly mining and ore processing plant established in Kuźnice in the nineteenth century. Furthermore, the measuring points situated in the

Skupniów Uplaz are close to the Balzer road - an important communication route with very heavy traffic.

Table 2. Range of concentrations of heavy metals (Zn, Cd, Pb and Cr) in the soil samples taken from the Tatra Mts (TNP).

Valley	Zn [mg/kg]	Cd [mg/kg]	Pb [mg/kg]	Cr [mg/kg]
Chochołowska	55–12	lack	68–38	24–15
Kościeliska	260–52	trace amounts	113–24	52–9
Sucha Woda	160–23	2.8–0.3	174–15	20–4.5
Rybi Potok	50–25	1–0.25	118–23	26–1.5
Range of concentration of mountain soils [44]	125–30	1–0.5	100–30	24–7

Table 3. Range of concentrations of heavy metals (Zn, Cd, Pb and Cr) in the soil samples taken from the High Tatra Mts (TANAP) [18].

Valley	Zn [mg/kg]	Cd [mg/kg]	Pb [mg/kg]	Cr [mg/kg]
Mięguszowiecka	365–20	lack	89–34	27–3
Wielicka	60–5	lack	118–23	18–1
Staroleśna	160–10	3.5–0.5	134–72	23–3
[44]	125–30	1–0.5	100–30	24–7

For decades, the gasoline containing organolead compounds (like tetramethyllead TML or tetraethyllead TEL) had been widely utilized in the vehicles in Poland. The breakdown products of TEL and TML combustion were released into the atmosphere as elemental lead or its compounds (e.g. chlorides or bromides). Since 2005, there was no further need to add these substances (fuel technology improvement or application of substitutes for leaded gasoline) which resulted in minor reduction of lead contamination noted in this part of the Tatras.

There are the antimony deposits located in the Dolina za Mnichem Valley (part of the Rybi Potok Valley). The main antimony ore mineral is stibnite ( $\text{Sb}_2\text{S}_3$ ) which forms antimony-quartz veins, often enriched in silver, lead and gold sulphides.

Overestimated accumulation of zinc and lead measured in the Kościeliska Valley is likely associated with relatively high concentration of these metals in the natural occurring minerals (e.g. goethite, limonite and pyrite) found at that area. The pyrite, for instance, being iron sulfide often contains traces of zinc sulfides. Thus, the presence of zinc sulfide in the bedrock might be responsible also for high levels of zinc accumulation in the soil. The soils taken from the Ciemniak Mt are the same kind as those collected from the Hala Piec and belong to the rendzinas – soils types formed on limestone rocks. The soil-related scientific reports performed in the Tatras indicate that the highest zinc deposition was found in the rocks enriched in calcium [17, 45].

Studies of other authors also showed a massive amounts of Zn in superficial soils of the Ciemniak Mt and the Hala Piec [17, 46]. The significant lead concentration in the Smreczyński Pound sample or on the Grześ Mt is linked most likely with natural occurring copper and silver deposits that contained pyrite and tetraedrite often accompanied by galena (PbS).

The accumulation of Zn and Cr measured at the Slovak part of the Tatras, similarly to the TPN area, fluctuates from 15.40 mg/kg (the measuring point at the crossroads on the way to the Popradzki Lake (1496 m a.s.l.) to 35.50 mg/kg (the measuring point located on the road to the Popradzki Lake (1486 m a.s.l.)). The chromium concentrations in the investigated samples ranged from 4.60 mg/kg (for the sample collected at the Hińczowe Lakes (1954 m a.s.l.) to 16.70 mg/kg (at the intersection with the red trail on the way to the Hińczowe Lakes (1678 m a.s.l.)). However, in the vicinity of Chata pod Rysami, value of concentration of zinc it was equal to 365.60 mg/kg, which is ten times higher value than measured at Popradzki Lake (1486 m a.s.l.). The concentration of chromium in three valleys of the High Tatras in the Slovak part falls into the typical concentration range of the mountain soils.

#### 4. CONCLUSIONS

1. The concentration of  $^{137}\text{Cs}$  in Tatras soils varies significantly – from 55.8 Bq/kg (417.8 Bq/m<sup>2</sup>) for Tomanowa Pass (1685 m a.s.l) to

5111 Bq/kg (8400 Bq/m) for Krzyżne Pass (2112 m a.s.l.). In the most cases, the values are not high, moreover, they are lower than the average radiocaesium concentrations established for Poland area.

2. The differences in  $^{137}\text{Cs}$  activity concentration in the soil samples taken from Tatra Mts depend mostly on the soil volume density and on the concentration of organic material that is the main agent of soil sorption complex formation.
3. The  $^{40}\text{K}$  concentration increases with the depth of soil profile whereas the  $^{137}\text{Cs}$  level declines, in the soil surface layer (first 10 cm) because of different origin of these two isotopes.
4. Monitoring of  $^{137}\text{Cs}$  activity concentration in the surface layer of soil had showed in most cases a downward migration trend.
5. Spatial distribution of heavy metals (Pb, Zn, Cd and Cd) was found to be diversified. In several locations across the Tatra Mountains high concentrations of these metals were observed. Determined concentrations highly exceeded the average level found for Polish soils.

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