Concentrations of 137 Cs and 40 K radionuclides and some heavy metals in soil samples from the eastern part of the Main Ridge of the Flysch Carpathians

Barbara Kubica · Katarzyna Szarlowicz · Marcin Stobinski · Stefan Skiba · Witold Reczynski · Janusz Gołas

Received: 19 July 2013/Published online: 7 January 2014 © The Author(s) 2014. This article is published with open access at Springerlink.com

Abstract The aim of the study is to present the results of determination of radioactivity of artificial ¹³⁷Cs and natural ⁴⁰K and certain heavy metals in soil samples collected from the eastern part of the Main Ridge of Carpathians, including the Beskid Niski Mts and the Bieszczady Mts. The evaluation of level of radionuclides was based on the bulk density analysis of the soil. A valuable finding of the study was a good linear correlation between the level of ¹³⁷Cs concentration and bulk density of the soil as well as an inverse correlation between radioactivity of natural ⁴⁰K and tested soil density. This might indicate though a high competitiveness of these elements between each other. Moreover, a good correlation between the concentrations of artificial element ¹³⁷Cs and Pb has been also observed in soil samples collected from the Beskid Niski Mts. In most cases, the level of artificial ¹³⁷Cs was lower comparing to an average ¹³⁷Cs concentration established for soils in Poland.

Paper presented during the 6th All Polish Conference on Radiochemistry and Nuclear Chemistry, Krakow (Poland), 21–24.04.2013.

B. Kubica (☒) · K. Szarlowicz · M. Stobinski · J. Gołas Faculty of Energy and Fuels, AGH University of Science and Technology, al. A. Mickiewicza 30, 30-059 Kraków, Poland e-mail: bkubica@agh.edu.pl

S. Skiba

Faculty of Biology and Earth Sciences, Jagiellonian University, ul. Gronostajowa 7, 30-387 Kraków, Poland

W. Reczynski

Faculty of Materials Science and Ceramics, AGH University of Science and Technology, al. A. Mickiewicza 30, 30-059 Kraków, Poland

Keywords $^{137}\text{Cs} \cdot ^{40}\text{K} \cdot \text{Soil} \cdot \text{Heavy metals} \cdot \text{Gamma}$ spectrometry

Introduction

The natural environment is exposed to various chemical contaminants, including the radioactive elements. Some of these radioactive elements are long-lived naturally occurring radionuclides. These radionuclides have always been present in the Earth's crust and atmosphere. There are approximately 60 natural radionuclides and one of the most abundant elements in the Earth's crust is ⁴⁰K that remains to this point in time. Another source of radioactivity has a cosmogenic origin and it is the result of interaction between certain gases in the Earth's atmosphere and cosmic rays [1]. Besides such sources of naturally occurring radiation exposure, the natural environment may be subjected to radioactive contamination caused by human activity. The main sources of anthropogenic radioactive material were (and still are) nuclear weapons tests conducted in the atmosphere, the accidents of nuclear power plants, and either the processing or storage of nuclear fuel and large amounts of nuclear waste [2-4]. An example of the world's worst civilian nuclear disaster was spreading into the atmosphere of Central and Eastern Europe a massive amount of radiocaeasium due to the explosion and fire at the Chernobyl power plant in April 1986.

The current state of knowledge concerning radioactivity on the whole area of Polish mountain's soils is still not comprehensive. Though, to address this knowledge gap, a radioactivity study was carried out from 2011 to 2012 by the Department of Coal Chemistry and Environmental Sciences. The experimental area covered the eastern regions of the Main Ridge of the Flysch Carpathians Belt



(the areas including the Beskid Niski Mts and the Połoniny part of the so-called Tarnica Mt in the Bieszczady Mts). The survey was conducted with the sampling and analysis of 27 soil samples in terms of spatial distribution of ¹³⁷Cs and natural ⁴⁰K and certain heavy metals including Cu, Zn, Cd and Pb. Data presented herein provide an update of a national evaluation regarding radioactivity in soils in the southern part of Poland since 2000, which included monitoring carried out in the Central Carpathians (the Tatra Mts) [5–8] and part of the East Carpathians area (the Chornohora Mts) [9].

Experimental

Sampling and methods

To collect the soil samples, 27 sampling locations were selected. Sampling was started in June 2011. The measurements of the gamma emitting radionuclide activity as well as the concentrations of certain heavy metals were performed on soil samples collected from the surface horizons of soil above 500 m ASL. The experimental area includes the Połoniny Caryńska and Wetlińska Mts, "Gniazdo Tarnicy" (Rozsypaniec, Halicz, Krzemień, Tarnica, Tarniczka Mt) in the Bieszczady Mts and the Beskid Niski Mts (specifically, Jaworzyna Krynicka, Spalone and Wołowiec close to Zawoja stream). Detailed positional data of the selected sampling points were established by a Garmin GPS Map 76CS satellite navigation system.

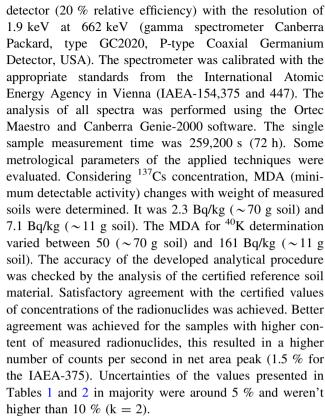
Sampling method and preparation of the samples

Soil samples were collected by the use of a cylidrical sampler that provides "soil cores" (10 cm height, 10 cm diameter). Those cores were cut into three segments that represented different soil layers starting from the soil surface: 0–3, 4–6, 7–10 cm (samples: a, b and c, respectively). That procedure allowed collection of 3 samples from each sampling point. The samples were dried at $105\,^{\circ}\text{C}$ to constant weight (for about 3 days), then the bulk density was determined and the samples were sieved (mesh diameter = 2 mm). The samples were prepared and stored prior to measurements in polyethylene containers.

Analytical procedure

Gamma spectrometric analysis

Measurements of individual gamma radionuclides performed using a gamma spectrometer equipped with HPGe



The radioactivity level of artificial ¹³⁷Cs and natural ⁴⁰K was shown in two modes:

- 1. the radioactivity of ¹³⁷Cs in the upper core part (up to 10 cm) [Bq/m²];
- 2. the concentration of ¹³⁷Cs per mass unit [Bq/kg] in each of tested soil layers (samples a, b, c).

Atomic absorption spectrometry (AAS) analysis

Sieved and homogenized soil samples were wet digested in the microwave system (Anton Paar Multiwave 3000, Switzerland) with concentrated HNO₃ and HClO₄ (Merck, Germany). After digestion, the samples were transferred into quartz crucibles and the excess of reagents was evaporated on a hot plate and the residue was transferred quantitatively to volumetric flasks. Quadruple distilled water was used for glassware preparation and sample dilution. Quantitative determination of Zn and Cu was performed using flame technique at standard conditions (AAS spectrometer Perkin Elmer, Model 3110, USA) and concentrations of Cd and Pb were determined using electrothermal technique (AAS spectrometer with Zeeman background correction, Perkin Elmer 4100 ZL, Germany). Graphite furnace parameters were optimized using the Method development program to obtain high sensitivity and precision of measurements for each of the elements



Table 1 Detailed location of the sampling points given for the Beskid Niski Mts and activities of ¹³⁷Cs and ⁴⁰K presented in Bq per mass units or per surface units together with soil samples bulk density

No	Location	Activity, dry mass				Altitude m	Bulk density
			137Cs Bq/m ²	⁴⁰ K Bq/kg	⁴⁰ K Bq/m ²	ASL	g/cm
0	Jaworzyna Krynicka 49°25′15″ N 20°53′12″E	52	440	242	2,069	1,049	0.49
1	Near Waholowski Wierch 49°24′38" N 22°02′30"E	25	364	537	9,160	605	0.97
2	On the way to Tokarnia 49°25′41″ N 22°02′29″E	63	843	702	10,035	762	0.82
3	Near Tokarnia 49°25′16″ N 22°03′13″E	16	202	672	8,944	518	0.76
4	On the way to Wilcze Budy 1 49°26′30″N 22°00′37″E	111	1,375	623	7,727	723	0.73
5	On the way to Wilcze Budy 2 49°26′53″N 21°59′43″E	40	709	612	6,534	719	0.72
6	On the way to Puławy Górne 49°28′45″N 21°56′25″E	48	303	646	11,336	720	1.0
7	Before intersection the trail Red and green on the way to Skibice $49^{\circ}28'32''N\ 21^{\circ}56'21''E$	227	2,972	517	3,252	743	0.63
8	On the way to Skibice and the Kozie Żebro Mt (about 45 min.) 49°28′27″N 21°56′36″E	1,127	8,463	253	1,901	758	0.43
9	The entrance to Kozie Żebro 49°27′52″N 21°12′40″E	322	4,364	78	1,030	637	0.76
10	On the way to Rotunda from Regietów 49°28′16″N 21°13′36″E	514	7,647	114	1,548	684	0.38
11	On the way to PopoweWierchy 49°30′12″N 21°15′51″E	165	1,378	316	4,707	554	0.48
12	On the way to Wołowiec near the stream Zawoja 49°30′23″N 21°19′11″E	245	2,039	618	2,275	558	0.48

Table 2 Detailed location of sampling points given for the Bieszczady Mts and activities of ¹³⁷Cs and ⁴⁰K presented in Bq per mass units or per surface units together with soil samples bulk density

No	Location	¹³⁷ Cs Bq/kg	¹³⁷ Cs Bq/m ²	⁴⁰ K Bq/kg	⁴⁰ K Bq/m ²	Altitude m ASL	Bulk density g/cm ³
13	Smerek Mt 49°11′07″N 22°28′45″E	250	2,312	499	4,605	1,189	0.61
14	Połonina Wetlińska 3 49°09′26″N 22°33′05″E	201	1,674	317	2,633	1,218	0.49
15	Połonina Wetlińska 2 49°09′58″N 22°31′41″E	143	1,385	507	4,902	1,206	0.67
16	Połonina Wetlińska 1 49°10′06″N 22°31′06″E	218	873	585	2,348	1,182	0.48
17	Połonina Caryńska 2 49°08′18″N 22°36′09″E	171	1,216	389	277	1,294	0.52
18	Połonina Caryńska 1 49°08′07″N 22°36′26″E	230	1,338	441	2,557	1,247	0.41
19	TarnicaMt 49°04′37″N 22°43′30″E	163	1,432	50	5,522	1,324	0.65
20	Tarniczka Mt 49°04′46″N 22°43′24″E	180	1,885	844	9,085	1,293	0.63
21	Krzemień Mt 49°05′07"N 22°44′22"E	500	1,865	220	844	1,314	0.23
22	Krzemień Mt 49°04′52″N 22°44′51″E	374	1,107	266	825	1,251	0.24
23	Halicz Mt 49°04′43″N 22°45′59″E	609	3,505	293	1,685	1,250	0.41
24	Halicz Mt 49°04′21″N 22°46′08″E	198	2,095	916	9,685	1,323	0.65
25	Rozsypaniec Mt. 49°03′45″N 22°46′12″E	356	1,594	196	8,989	1,261	0.34
26	Rozsypaniec Mt 49°03′22″N 22°46′06″E	236	1,596	221	1,496	1,204	0.52

determined by means of ET AAS technique. Uncertainties of the elements quantitative determinations (RSD data presented in Table 2) were not higher than Cu 5.4 %, Zn 2.6 %, Cd 5.6 %, Pb 4.7 %. The accuracy of the analytical procedure was estimated by the use of the certified reference material (IRMM BCR-280, Lake Sediment). Satisfactory accuracy and precision was achieved.

Results and discussion

The surface horizons of soil consist of organic matter in various stages of humification, lying directly on the weathered rocks flysch substrate initial soils -Lithic Leptosols or as the level of accumulation in Rankers –Umbric Leptosols, Cambic Leptosols (Skeletic) and Dystric



Cambisols [10]. In this survey, the material belonging to initial and poorly formed types of soil was analyzed. It forms the specific structure of the soil cover occurring above the 500 m ASL. The soils are rocky outcrops of initial soils-Lithic Leptosols and Rankers Cambic Leptosols. On the Pleistocene regolith—initial soils were formed Hyperskeletic Regosols. Characteristic properties of all mountain soils including the soils of three searched areas of the Carpathians (Tatra Mts and Charnohora Mts) are as follows: decreasing pace of organic matter decomposition linked to the increase of altitude above the sea level and the presence of ectohumus horizons in the depths. The organic matter of those horizons shows similar chemical properties regardless the parent rock. Thus, there are similar forms of ectohumus both in the initial soils (Lithic Leptosols), rankers (Umbric Leptosols), rendzinas (Rendzic Leptosols)and in Podzols [11]. Below this level, there is little stale bedrock (typically sandstones) or weathering hyperskeletic regolith of flysch rocks.

The radioactivity of artificial ¹³⁷Cs and natural ⁴⁰K in the soils collected from the Main Ridge of the Flysch Carpathians, specifically from region of the Beskid Niski Mts and from the region of the Bieszczady Mts is given in Tables 1 and 2, respectively. The data obtained from selected soil covers (the Beskid Niski Mts and the Bieszczady Mts area) showed high variation. The ¹³⁷Cs concentration in the Beskid Niski Mts area ranged between 16 and 1,137 Bq/kg in the first layer (a-layer) of soil cores and from 843 to 8,463 Bg/m² for the entire 10 cm depth soil core (Tab 1). The concentration of ¹³⁷Cs in the Bieszczady Mts varied from 143 to 609 Bq/kg (for the layer "a") and from 1,385 to 3,505 Bg/m² for the sum of the layers a, b and c (Table 1). It is noticeable, that the ¹³⁷Cs radioactivity level was relatively low (about 107 Bg/kg) in the Beskid Niski Mts with exception of three sampling points located near Kozie Żebro Mt (points 8-10) (Table 1; Fig. 1). Fluctuations of the radionuclides concentration in the soils could strongly depend on the meteorological conditions. Thus, the elevated activity of ¹³⁷Cs around Kozie Żebro Mt might have contributions from increased precipitation that occurred in May and June 1986 year (approximately 119–167 dm³/m²). In April that year, the rainfalls observed in the Beskid Niski Mts as well as in the Bieszczady Mts (apart from a few of small regions-Kozie Żebro) were rather small (24 dm³/m²) [12]. As mentioned above, the concentration of ¹³⁷Cs in the western part of the Beskid Niski was low, however, the radioactivity rapidly increased close to Skibice 1,127 Bq/kg, (8,463 Bq/m², sampling point no 8) and again was slightly reduced to approximately 165 Bq/kg (1,378 Bq/m², sampling point no 11). This trend is also observed in the Bieszczady Mts, both on Połonina Wetlińska and Caryńskie (sampling points 14–18) with noticeable elevation of ¹³⁷Cs occurred in the so-called "Socket Tarnica" (sampling point 19). All sampling sites with high level of ⁴⁰K showed low concentration of ¹³⁷Cs (Figs. 1, 2). These two isotopes belong to the same group of alkali metals, have similar chemical properties and are strong reducing agents. That is an explanation for competitive-sorption behavior of these two elements in the soil. The competitiveness between 40K and 137Cs in mountain soils has been already demonstrated in the previous studies [8–11, 13]. Also, for all sampling sites, the correlations between the ¹³⁷Cs level, altitude and soil bulk density were found. It is well documented, that mountain soil properties are altered with the altitude, particularly the features of upper soil layers (O horizon, first 10 cm). In the surface soil layers, the level of organic material increases with the altitude (included the subalpine zone). It is noticeable, that not only the quantity of organic mass changes but also its decomposition stages and the content of humic and fulvic acids (the ratio of humic acids in humus organic matter) [14]. The humus modification implies the perturbations on soil bulk density, contributes to the small immobilization of radiocaesium in organic part of soils and hence to its higher availability to plants [15]. In this context, the relation between soil bulk density and ¹³⁷Cs concentration might reflect the interdependence between the altitude and ¹³⁷Cs concentration. The radioactivity obtained for both gamma emitters was also presented in relation to the volume density of the soils (Figs. 3, 4). The concentration of ¹³⁷Cs underwent massive fluctuations in sampled soils however, we found a good linear correlation between ¹³⁷Cs radioactivity expressed in mass units in the first layer (a) of soil core, and the soil density (Fig. 4). This correlation was less clear when comparing the radioactivity of this radionuclide expressed in units of surface (Fig. 3) and calculated for the entire 10 cm layer of soil a, b and c. There was significantly better correlation between the activity of ⁴⁰K and the soil density observed in the Beskid Niski Mts and the Bieszczady Mts area. It is also noticeable, that the radioactivity of 137Cs and 40K per area unit corresponded well to the concentrations of these radionuclides expressed per mass units. Obtained results are in line with the data from similar studies carried out on the other mountain areas (the Tatra Mts and the Charnohora Mts). Our findings also confirmed the hypothesis of the radioactive caesium sorption in the organic soil layers. With increase of the soil density, the concentration of 137Cs decreased and in the same time, the amount of natural 40K increased what was shown in Figs. 1 and 2. For all sampling points, the ratio of ¹³⁷Cs activity to the potassium (both for the first layer "a" and for the whole profile) presented as the function of the soil density was calculated (Fig. 5). Given results might



Fig. 1 Spatial distribution of radioactivity [Bq/kg] of gamma radionuclides (¹³⁷Cs and ⁴⁰K) in the 27 samples of mountain soil collected from the Beskid Niski Mts and the Bieszczady Mts

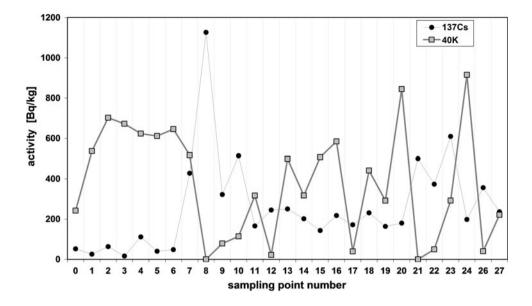


Fig. 2 Spatial distribution of radioactivity presented in Bq per surface [m²] of gamma radionuclides (¹³⁷Cs and ⁴⁰K) in the 27 samples of mountain soil collected from the Beskid Niski Mts and the Bieszczady Mts

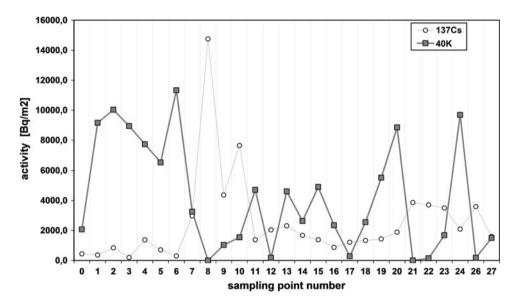


Fig. 3 Correlation between the gamma radionuclides activity (137 Cs and 40 K) and the density of the tested soil samples

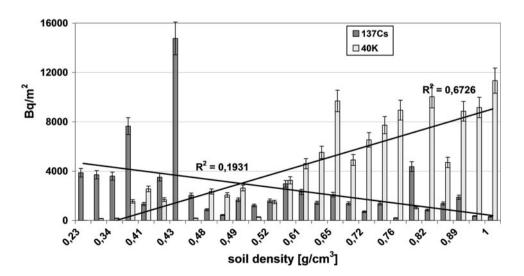




Fig. 4 Correlation between the gamma radionuclides activity (¹³⁷Cs and ⁴⁰K) measured in the surface layer "a" (0–3 cm) of the collected soil cores and the density of the tested soils

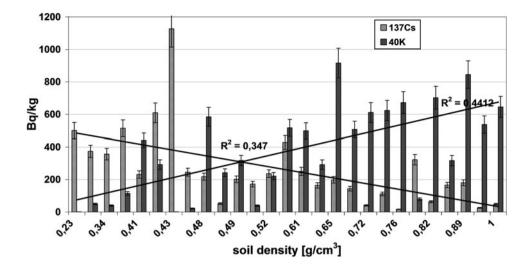
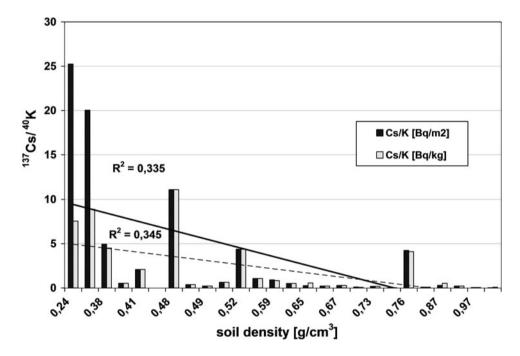


Fig. 5 Radioceasium-137/ potassium-40 activity ratio presented as a function of the density of tested soil samples



also indicate that in some cases ⁴⁰K was present not only in the mineral, but also in organic layer of the tested soils.

Heavy metals level in soils of the Beskid Niski Mts area

The results of quantitative analysis of the selected metals (Cu, Zn, Cd and Pb) is presented in Table 2; Fig. 6a, b. The given values are the mean of 4 repetitions of the element concentration measurements. Copper concentrations were in the range from 3.77 to 14.31 [μ g/g], zinc in the range 17.50 to 41.63 [μ g/g]. The level of elements considered as toxic—Cd and Pb were in the ranges 0.18–1.10 [μ g/g] and 27.27–216.10 [μ g/g], respectively. Pb concentration in the soils collected from three locations (sampling point no 4,8

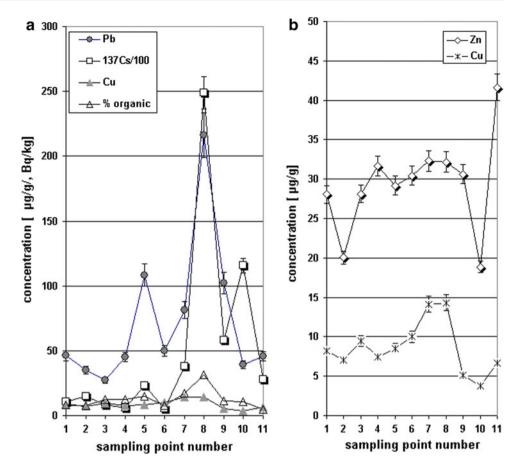
and 9) was substantially higher comparing to all others (see Table 2; Fig. 6a), probably due to higher amount of precipitation observed in these sampling areas.

In Fig. 6a changes of the elements (being the constituents of inorganic material) concentrations in relation to the soil sampling point number are presented. The sampling point elevation ASL of the sampling points differed only a little in the considered geographical region (see Tab. 1).

The concentration fluctuations observed for Zn and Cu in tested soil samples were similar for both elements (Table 2; Fig. 6b). It indicates that these elements predominantly originate from natural sources (mother rock erosion) and that mineral composition of Flysch Carpathian Belt in sampling area is more or less homogenous. The



Fig. 6 Spatial distribution of the level of anthropogenic (a) and natural (b) elements in the soils samples collected from 11 different localizations in the Beskid Niski Mts



changes of the anthropogenic origin elements i.e. Pb and ^{137}Cs (presented in µg/g for Pb and activity Bq/kg units for ^{137}Cs) with percentage of organic matter in tested soils were showed in Fig. 6a. The fluctuations in the concentration of Pb and ^{137}Cs were related to the organic matter content and can indicate Pb and Cs immobilization in organic matter. The findings were clearly visible in the sampling points no 7,8 and 9—the level of elements increased with the amount of organic matter (Table 2; Fig. 6a).

Conclusions

1. The content of ¹³⁷Cs, ⁴⁰K and certain heavy metals in soils collected from the eastern Carpathians areas was found to be greatly variable: The Beskid Niski Mts area—from 25 Bq/kg (364 Bq/m²) for the Waholowski Peak (605 m,sampling point 1) to 1,127 Bq/kg (8,463 Bq/m²) for the Kozie Żebro Mts (758 m, sampling point 8); The Bieszczady Mts area—from 143 Bq/kg (1,385 Bq/m²) for the Połonina Wetlińska 2 (1,206 m ASL, sampling point 15) to 609 Bq/kg (3,505 Bq/m²) for the Halicz Mt (1,250 m ASL, sampling point 23).

- Radioactive cesium activity in the mountain soils showed the tendency to decrease with increasing density of the soil due to high amount of the organic matter. The humus, as the main component of the sorption complex, was responsible for the immobilization of ¹³⁷Cs ions.
- 3. Our results confirmed strong competitive-sorption behavior of ¹³⁷Cs and ⁴⁰K in the soil sorption complex.

Acknowledgments The work was supported by the NCN Grant No. N N304 17040 and the AGH University of Science and Technology Grant No. 11.11.210.244.

Open Access This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

References

- Hrynkiewicz A (1993) Doses and biological effects of ionizing radiation. National Atomic EnergyAgency IFJ
- Broda R (1987) Gamma spectroscopy analysis of hot particles from the Chernobyl fallout. Acta Physica Polonica vol B 18(10):935–950
- 3. Broda R, Kubica B, Szeglowski Z, Zuber K (1989) Alpha emitters in chernobyl hot particles. Radiochim Acta 48:89–96



- Krasnov WP (1998) Radioekologia lisiwPolissja Ukrainy, Wyd. Wolyn–Zhytomyr, 112
- 5. Kubica B, Mietelski JW, Golas J, Skiba S, Tomankiewicz E, Gaca P, Jasińska M, Tuteja-Krysa M (2002) Concentration of ¹³⁷Cs, ⁴⁰K, ²³⁸Pu and ²³⁹⁺²⁴⁰Pu radionuclides and some heavy metals in soil samples from two main valleys from the Tatra National Park. Pol J Environ Stud 11:537–545
- 6. Kubica B, Skiba S, Mietelski JW, Golas J, Kubica M, Stobinski M, Tuteja-Krysa M, Tomankiewicz E, Gaca P, Krzan Z (2004) Transect survey artificial ¹³⁷Cs and natural ⁴⁰K in moss and bilberry leaf samples from two main Valleys from Tatra National Park. Pol J Environ Stud 13(2):153–159
- Kubica B, Skiba M, Skiba S, Gołaś J, Kubica M, Stobiński M, Tuteja-Krysa M (2005) Dislocation of the radionuclides ¹³⁷Cs and ⁴⁰ K n in the Podzols Profiles of the Tatra mountain soils (South Poland)J. Radioanal Nucl Chem 266(1):3–9
- Kubica B, Skiba S, Drewnik M, Stobiński M, Kubica M, Gołaś J, Misiak R (2010) The radionuclides (¹³⁷Cs and ⁴⁰K) in soil samples taken from Tatra National Park (TPN, Poland). Nukleonika 55(3):377–387

- Skiba S, Kubica B, Skiba M, Stobiński M (2005) Content of the gamma radionuclides of ¹³⁷Cs and ⁴⁰K in the soils samples of the Tatra Mts (Poland) and Czarnohora Mts (Ukraina). Pol J Soil Sci 38(2):119–126
- Skiba S, Kubica B, Skiba M (2005) The content of gamma radionuclides ¹³⁷Cs and ⁴⁰K in soils northwestern part of Chornohora. Eastern Carpathians, Ukraine
- Skiba S(2002) Changes of the nature environment of the Tatra mountains, 21
- 12. Unpublished of data from the Institute of Meteorology
- 13. Skiba S, Drewnik M, Prędki R, Szmuc R (1998) The soils of the Bieszczady National Park. Monogr Bieszcz 2:88
- Drewnik M (2002) Transformation of the natural environment of the Tatra mountains, TPN-PTPNoZ. Krakow-Zakopane, 101–1064
- Ciuffo LEC, Bellia M, Pasqualea A, Menegonc S, Velascob HR (2002) ¹³⁷Cs and ⁴⁰K soil-to-plant relationship in a seminatural grassland of the Giulia Alps, Italy. Sci Tot Environ 295(2002): 69–80

