Investigation of natural radioisotope activities in forest soil horizons

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Abstract. Activities of radioisotopes were measured in samples of forest soil. The samples were collected in forests situated along the roads from Złoty Stok (Poland) to Hradec Králové (Czech Republic). Each soil profile was separated into individual horizons and subhorizons. Activities of radioisotopes were measured in the sample of each soil horizon. Activities of the following radioisotopes were determined by gamma-ray spectrometry: ^{214}Pb, ^{214}Bi, ^{231}Th, ^{235}U, ^{212}Pb, ^{212}Bi and ^{228}Ac. Distributions of the data concerning radioactivities were positively skewed. The lowest activity was found for ^{235}U (median value was 2.25 Bg/kg) and the highest one for ^{228}Ac (16.26 Bg/kg in median). In organic horizons activities of radionuclides were lower than in organic ones. Interrelation between activities was examined using ordinary and robust regression methods. It was found that activities of the radioisotopes were well correlated.

Key words: natural isotopes • radioactivity • robust regression • forest soils

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Introduction

Recently, the attention paid to artificial radionuclides has been very conspicuous, e.g. [2, 3, 5, 6, 20]. Less attention was devoted to investigations of natural radionuclides, though it is known that the contribution of artificial radionuclides to our environment is much smaller than the natural ones [14].

Natural radioactivity is wide spread in the earth's environment. It exists in soil, plants, water and air, e.g. [8, 11, 13, 19]. Environmental natural gamma radiation is formed from terrestrial and cosmic sources, e.g. [4, 12]. Natural radionuclides in soil generate a significant component of the background radiation exposure of the population [9]. Gamma radiation intensity in a region depends on soil type and geophysical structure of bedrock. The natural radioactivity in soil comes mainly from the ^{238}U, ^{232}Th decay series and natural ^{40}K, respectively [17].

The knowledge of the distribution and of the behavior of the radionuclides in soil, is important in understanding several issues of the natural environment, e.g. the exchange of radionuclides between the soil solid matrix and surface and/or ground waters, the exchange of radionuclides between the upper soil layers and the atmosphere.

The intensity of natural radiation and the resulting exposure depend on the geological and geographical environment, therefore in various regions it is different [17]. The distribution of radionuclides in soil has been very widely explored. But, because of soil complexity, the quantitative evaluation of their activities is frequently ambiguous. The behavior of many radionuclides in soil is caused by the processes of their distribution between two main phases – solid and liquid (leaches of soil). These processes are formed by reversible or irreversible absorption-dissipation, precipitation-dissolution, coagulation-peptide formation phenomenons [14].

The aims of the current researches were to assess the radioisotopic composition in different types of forest soil collected in the region extending from Złoty Stok to Hradec Králové. We have expected that the results of our measurements would be burdened by many uncertainties. Starting from selection of proper sampling location and following samples collection, subsample preparation, and finally measurement procedure – on each of these steps might appear unrecognized and uncontrolled factors strongly affecting the results obtained. To reduce influence of these factors on final conclusions, statistical methods in data processing were used.

Measurement methodology

The distribution of the main uranium and thorium series radionuclides was investigated in forest soil samples. In the samples investigated activities of the following radionuclides were determined: ^{214}Pb, ^{214}Bi, ^{228}Ac, ^{212}Pb, ^{212}Bi, ^{235}U and ^{231}Th. The measurement of activities of the uranium, actinium and thorium series radionuclides in samples of woodland soil were carried out by means of a gamma-spectrometer with a germanium detector (HPGe, Canberra) of high resolution: 1.29 keV (FWHM – full width at half maximum) at 662 and 1.70 keV FWHM at 1332 keV. Relative efficiency: 21.7%.

Energy and efficiency calibration of the gamma spectrometer was performed with the standard solutions type MBSS 2 (Czech Metrological Institute, Prague), which covers an energy range from 59.54 to 1836.06 keV. Geometry of calibration source was Marinelli (447.7±4.48 cm^3), with a density of 0.985±0.01 g/cm^3, containing ^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{137}Cs, ^{113}Sn, ^{85}Sr, ^{88}Y and ^{203}Hg. Geometry of sample container was Marinelli, 450 cm^3. Measuring process and analysis of spectra were computer controlled with use of the software GENIE 2000. The radiation spectrum was recorded during two days. The measurement uncertainty did not exceed 3%. All activities were expressed in Bq per kg of dry mass.

The samples were collected in forests situated along the roads from Złoty Stok to Hradec Králové. The samples of forest litter and then soil profiles from ground level down to 35–40 cm depth were taken. Each soil profile was separated into individual horizons.

Statistical methods

For statistical computations, the R language [15] was utilized. R is a free software environment for statistical computing and graphics.

To gain information about possible structures in our data clustering methods were used. These methods allow to assign objects to different groups, so that the data in each subset share some common trait. For our computation, the functions provided by the "cluster" library of R were used. Functions available in this library were described by Kaufman *et al.* [10]. For each variable, the data were standardized by subtracting the variable mean value and dividing by the variable mean absolute deviation, and then all of the pairwise dissimilarities between observations in the data set were computed. In our data the non-numeric parameter referring to soil type was included. Because of that, the general dissimilarity coefficients of Gover were computed. These coefficients enables, among others, dissimilarities calculation of points which are represented not only by numerical variables but also by the categorical ones.

The overviews of cluster existence in data were shown on dendrograms – a tree diagrams illustrating the arrangement of the clusters. Diagrams were constructed using "agnes" and "diana" functions from "cluster" library. Function "agnes" uses an agglomerative nesting procedure, while "diana" realizes divisive hierarchical clustering. To obtain more detailed information about possible clustering in our data, function "pam" was utilized. This function constructs a given number of cluster around medoids whose centers are computed by appropriate algorithm (PAM – partitioning arround medoids). In our data analysis weak separation of clusters was also considered. To assess existence of overlapping clusters in our data fuzzy clustering method provided by function "fanny" was utilized. Fuzzy methods are widely used in environmental data analysis [1].

Information about possible cluster existence in data, their number and structure, could be gained from the so-called silhouette coefficient (SC). This parameter is computed taking into account a number of clusters and average dissimilarities (distances) between them. For SC lower than 0.26, no substantial structure in data can be supposed. Weak and probably artificial structures can be observed for SC in the range 0.26–0.50. A reasonable structure is supposed for SC between 0.51 and 0.70 and strong structures for SC > 0.71 [10].

Similarity of variables distributions was verified using the Kolmogorov-Smirnov test. In this test quantiles of distributions of two data sets are compared. Pairwise tests of data distributions representing individual activities of radionuclides were performed.

Preliminary analysis of our results revealed possible problems due to outliers presence in data. Though, identification of outliers in *bi*-variate data seem not to be difficult, we decided to use methods dedicated to this problem. To avoid, or at lest to diminish influence of outliers on calculation results, the robust regression methods were used in computations. Correlations coefficients r between variables were computed using classical method and the robust ones. For robust correlation computations, the minimum covariance determinant (MCD) estimator of location was used (function "covMcd" from library "robustbase"). The MCD method looks for the subset of observations whose classical covariance matrix has the lowest possible determinant. The raw MCD estimate of location is then the average of these points, whereas the raw MCD estimate of scatter is their covariance matrix.

To assess interrelations between variables investigated the robust regression methods were used, which are forms of weighted least squares regression [7, 16,

Table 1. Parameters of: ^{214}Pb, ^{214}Bi, ^{231}Th, ^{235}U, ^{212}Pb, ^{212}Bi and ^{228}Ac activities in soil samples

		^{214}Pb	^{214}Bi	^{231}Th	^{235}U	^{212}Pb	^{212}Bi	^{228}Ac
Min	(Bq/kg)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
q_1	(Bq/kg)	2.6	6.7	0.0	1.4	7.6	0.0	0.0
ME	(Bq/kg)	13.1	12.1	7.6	2.3	15.5	9.3	16.3
q_3	(Bq/kg)	20.6	19.0	12.9	3.5	31.7	19.5	32.5
Max	(Bq/kg)	44.9	36.1	22.0	6.2	49.6	29.2	50.2
$\bar{x}$	(Bq/kg)	14.2	12.9	7.9	2.6	19.9	11.2	19.1
SD	(Bq/kg)	11.8	9.9	6.6	1.7	15.7	9.5	16.5
g_1	(–)	0.66	0.46	0.42	0.5	0.32	0.24	0.26
g_2	(–)	–0.21	–0.66	–0.76	–0.68	–1.23	–1.31	–1.31
RVC	(–)	3.2	2.8	2.8	2.4	2.5	2.6	2.6

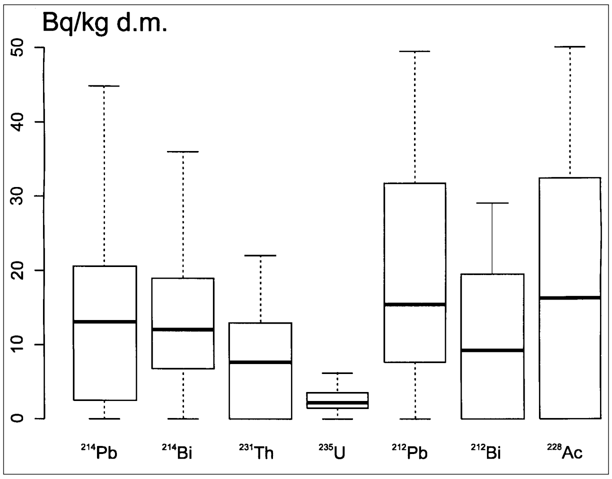

Fig. 1. Boxplots of ^{214}Pb, ^{214}Bi, ^{231}Th, ^{235}U, ^{212}Pb, ^{212}Bi and ^{228}Ac activities in soil.

18]. Recently, we have utilized these methods in analysis of ^{137}Cs and ^{239,240}Pu distribution in forest soils [21]. From a variety of robust regression methods for our computations, we chose regression based on MM-estimators (a type of maximum likehood estimators). This method is resistant on outliers in explanatory variables (leverage points) as well as outliers in the response variable [7, 16, 18]. In our computations we used a function "rlm" (library "MASS") with default values of the controlling parameters.

Results and discussion

In Table 1 statistical parameters of ^{214}Pb, ^{214}Bi, ^{231}Th, ^{235}U, ^{212}Pb, ^{212}Bi and ^{228}Ac activities in soil horizons are listed. The following parameters of our data are shown: minimal value (min), lower quartile (q_1), median (ME), upper quartile (q_3), maximal value (max), mean value ($\bar{x}$), standard deviation (SD), skewness (g_1), kurtosis (g_2) and relative variability coefficient (RVC) – ratio of difference between maximal and minimal values to mean value.

Distributions of the activities were positively skewed. The lowest activity was found for ^{235}U (median value was 2.25 Bg/kg) and the highest one for ^{228}Ac (16.26 Bg/kg in median). In organic horizons activities of radioisotopes were lower than in inorganic ones.

In Fig. 1 the box plots showing: ^{214}Pb, ^{214}Bi, ^{231}Th, ^{235}U, ^{212}Pb, ^{212}Bi and ^{228}Ac activities distributions in soil are drawn. In these plots lower base of the rectangle is a lower quartile, upper base is an upper quartile and a horizontal line dividing the rectangle is a median. Whiskers are formed by connecting the formed box with short horizontal lines drawn for quantile $q = 0.95$ (upper whisker) and quantile 0.05 (lower whisker).

Investigation of clustering in data was performed for ^{214}Pb, ^{214}Bi, ^{231}Th, ^{235}U, ^{212}Pb, ^{212}Bi and ^{228}Ac activities. Application of both agglomerative and divisive methods leads to a similar structure of dendrogram. Figure 2

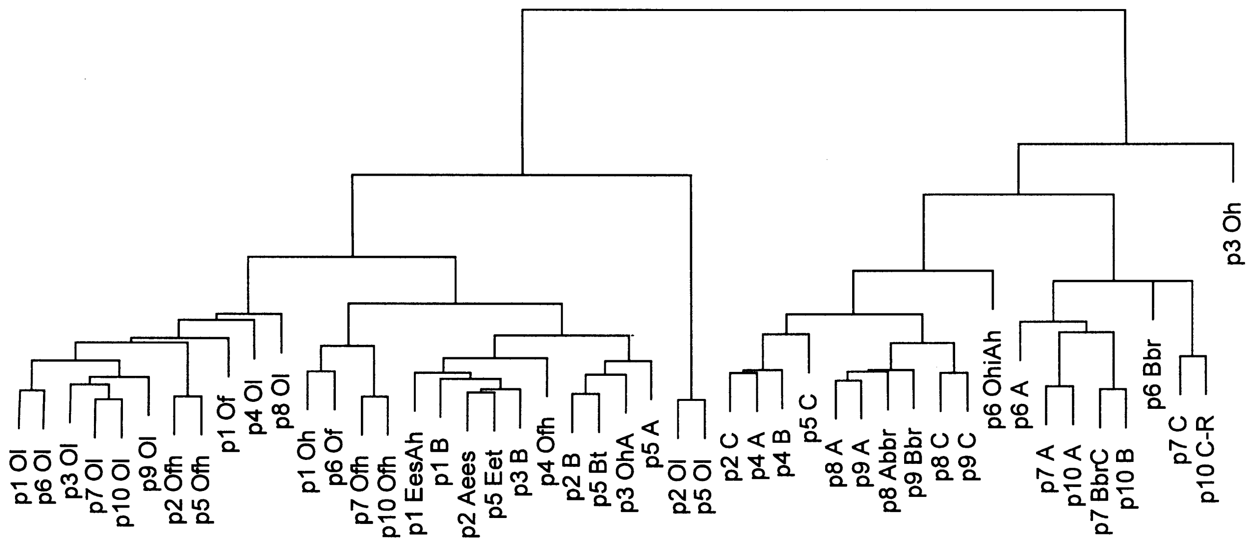

Fig. 2. Dendrogram constructed using divisive algorithm for points from 7D space, whose coordinates were determined by the radioisotopes activities.

Table 2. Contribution in (%) of each point in two clusters for which the SC was found

Soil horizon	Oh/Ah	Abbr	Of	Ofh	C	B	A	Oh	A	C	AEes	B	A	C	C	Bbr	B	Bt	B	OhA	A	A	EesAh
Cluster 1	32	32	33	33	34	34	34	34	34	34	34	35	35	36	36	36	37	37	39	49	53	53	54
Cluster 2	68	68	67	67	66	66	66	66	66	66	66	65	65	64	64	64	63	63	61	51	47	47	46

Soil horizon	C-R	C	Eet	A	Ol	Bbr	B	Ofh	Ofh	Ofh	Ol	Oh	Ol	BbrC	Ol	A	Of	Ol	Ol	Ol	Ol	Ofh	Ol	Ol
Cluster 1	55	55	55	56	56	57	59	61	61	61	61	62	62	67	67	67	67	68	70	70	70	70	71	71
Cluster 2	45	45	45	44	44	43	41	39	39	39	39	38	38	33	33	33	33	32	30	30	30	30	29	29

shows the dendrogram constructed using divisive algorithm. Additionally, the horizon or subhorizon type and sample identifier were marked.

No clear patterns could be observed in Fig. 2. However, in the left branch of dendrogram most of the points are from organic horizon, whereas in right branch points from inorganic horizons are mainly represented.

The SC computed with PAM algorithm was 0.323 for 2 clusters. This value suppose no reliable clustering in data. Using fuzzy clustering method the SC value computed was only a little bigger than the one computed using PAM. The SC was found also for 2 clusters and its value was 0.393. In Table 2 contributions of points in 2 clusters are listed. Additionally, for each point the soil horizon type is shown. The values are expressed in (%) and rounded to integer.

Data in Table 2 confirm poor separation of clusters. Inorganic soil horizons belong rather to the second cluster, whereas the organic ones are well represented in the first one. But ratio of contributions do not significantly exceed 1:2. This conclusion supports dendrogram structure observed in Fig. 2.

In Fig. 3 an example of histogram of activity distribution density (for ^{214}Pb) is shown. Positions of individual points are marked with vertical dashes above the horizontal axis. In upper part of the plot description of soil horizon or subhorizon type is shown for each point. Low activities observed on the left side of histogram are described by upper organic subhorizons, in center and on the right side are located points representing lower organic and inorganic horizons.

Distributions of the remaining activities are also positively skewed and similar to each other. To verify the supposition that these distributions belong to the same family and differences between them are results only of different expected values and spreads, radionuclides activities a_{nuc} were transformed using the following formula:

$$a^{t}_{nuc} = \frac{a_{nuc} - \min(a_{nuc})}{\max(a_{nuc}) - \min(a_{nuc})} \quad (1)$$

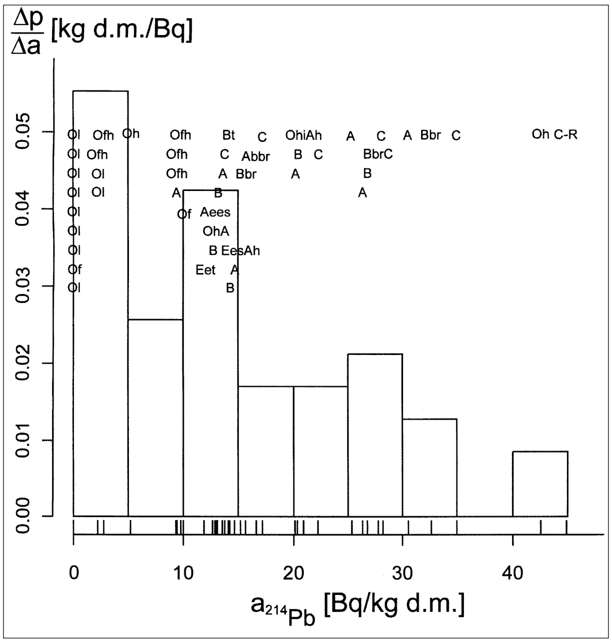

Fig. 3. Histogram of activity density of ^{214}Pb.

Table 3. Correlation coefficients between activities of radionuclides computed with standard (r_s) and robust MCD (r_r) methods

	r_r						
	^{214}Pb	^{214}Bi	^{231}Th	^{235}U	^{212}Pb	^{212}Bi	^{228}Ac
^{214}Pb	1.000	0.994	0.739	0.893	0.950	0.942	0.946
^{214}Bi	0.972	1.000	0.702	0.881	0.940	0.935	0.937
^{231}Th	0.385	0.357	1.000	0.716	0.858	0.854	0.852
^{235}U	0.698	0.666	0.694	1.000	0.880	0.894	0.877
^{212}Pb	0.947	0.944	0.472	0.674	1.000	0.995	0.999
^{212}Bi	0.789	0.778	0.520	0.535	0.871	1.000	0.995
^{228}Ac	0.809	0.808	0.556	0.544	0.885	0.974	1.000
	r_s						

where a^t_{nuc} is the transformed activity of a certain nuclide. Values of a^t_{nuc} are limited in the range from 0 to 1. Distributions of all pairs of the transformed activities were compared using the Kolmogorov-Smirnov test to verify supposition concerning statistically significant differences in their distributions. But the smallest p-value computed in this test was 0.15. All others were bigger than 0.2 and some of them exceeded 0.8. Rejection the null hypothesis is usually recommended when p-value is smaller than at least 0.05. The conclusion is that in our samples distributions of activities are of the same type and activity of specific radionuclide could be turned into activity of the other one by simple linear transformation. This conclusion enables utilization of linear correlation coefficients for investigations of interrelation between radionuclides activities.

Linear correlation coefficients between the investigated radionuclides activities were computed. The calculated results are shown in Table 3. The data below the table diagonal (composed of ones) show correlation coefficients r_s computed using the standard method and the parameters r_r above diagonal were computed with the robust method.

Regardless of computation method, all of the correlation coefficients were significantly bigger than zero. Utilization of the MCD method caused for some pairs of variables a significant increase in r value, e.g. a correlation coefficient between ^{214}Bi and ^{231}Th increased nearly two times when it was computed with the robust method. This observation supposed existence of outliers in our data.

As it could be expected, good correlations were observed for the radionuclides belonging to the same decay chain. But activities of radionuclides from different decay chains were also correlated. To explain this observation a similar source of radionuclides on the investigated area might be supposed. The same existence of minerals in bedrock might explain the results obtained. Even if minerals comprised of radionuclides detected in our investigations are hardly soluble in water, some amounts of them might be transported from deeper regions to the earth surface via plants root system, and in this way they start circulation in ecosystem. On the areas where bedrock is exposed to atmosphere, weathering processes cause rock dispersion to mineral dust which then is carried by winds to distant places. Long term occurrence of these processes might cause homogenization of mineral (and radionuclides) composition on large areas.

Table 4. Parameters and their standard deviations of linear equation describing relationship between ^{214}Pb and ^{214}Bi activities. The t test values were computed to verify $b_{0Ra} = 0$ and $b_{1Ra} = 1$

	Value	Standard deviation	t
b_{0Ra}	0.060	0.350	0.17
b_{1Ra}	1.097	0.021	4.60

To compare activities of nuclides from the same decay chain, parameters of linear equation were computed. Because of outliers presence in data, the robust linear regression method was used.

In Table 4 parameters of linear equation $a_{Pb\text{-}214} = b_{0Ra} + b_{1Ra} \times a_{Bi\text{-}214}$ (radium series) are shown.

Supposition that the b_{0Ra} parameter is zero cannot be rejected. In this way relationship between ^{214}Pb and ^{214}Bi activities simplifies to the ratio. The b_{1Ra} parameter value is very close to 1, but the t value is big enough to reject the assumption.

In Table 5 parameters of linear equation $a_{Th\text{-}231} = b_{0Ac} + b_{1Ac} \times a_{U\text{-}235}$ (actinium series) are shown.

Similarly, like for radionuclides from the radium series the zero value of the intercept can be accepted. The b_{1Ac} parameter is significantly different than one.

In Table 6 parameters of equations describing the relationships between activities of radionuclides from the thorium series are shown. The first equation $a_{Pb\text{-}212}$

Table 5. Parameters and their standard deviations of linear equation describing relation between ^{231}Th and ^{235}U activities. The t test values were computed to verify $b_{0Ac} = 0$ and $b_{1Ac} = 1$

	Value	Standard deviation	t
b_{0Ac}	0.00	1.10	0.0
b_{1Ac}	3.09	0.37	5.7

Table 6. Parameters and their standard deviations of linear equation describing relation between radioactivities of ^{228}Ac, ^{212}Pb and ^{212}Bi from the thorium decay chain. The t test values were computed to verify $b_{0Th} = 0$, $b_{3Th} = 0$, $b_{1Th} = 1$ and $b_{4Th} = 1$

	Value	Standard deviation	t
b_{0Th}	1.02	0.33	3.1
b_{1Th}	0.935	0.013	–4.9
b_{3Th}	–0.04	0.40	–0.1
b_{4Th}	0.596	0.016	–25

$= b_{0Th} + b_{1Th} \times a_{Th\text{-}228}$ describes the relationship between ^{212}Pb and ^{228}Ac activities. In the second $a_{Bi\text{-}212} = b_{3Th} + b_{4Th} \times a_{Pb\text{-}212}$ the relationship between successive radionuclides activities, i.e. ^{212}Bi and ^{212}Pb, is considered.

In the relationship between ^{212}Pb and ^{228}Ac activities, the intercept value cannot be assumed to be zero. Also the slope, though only somewhat smaller than 1, cannot be regarded as insignificantly different than one. In the relationship between ^{212}Bi and ^{212}Pb the intercept value is not significantly different than zero, but the slope value is considerably smaller than 1.

Conclusions

Mean and median activities of the radionuclides investigated were somewhat similar, ranging from several to nearly 20 Bq/kg d.m. Variabilities of activities (RVC) were similar, they were limited in the range from 2.4 to 3.2. Distributions of radionuclides activities were not normal (Gaussian), but they were similar to each other. Only poor clustering in data was observed. Properties of soil horizon samples described by horizon type and radionuclide activities were changed rather continuously, without clear breakpoints. The changes in activities of all radionuclides determined were well correlated. Good correlation between radionuclides activities from different decay chains might be a result of long term processes which are responsible for elements transport in environment. Additionally, similarity of bedrocks geochemical compositions on the investigated area might be supposed. Most of slopes and intercepts values in linear relationships between radionuclide activities from the same decay chain suppose low deviations from radiochemical equilibrium state in the samples investigated. The biggest deviation from equilibrium was observed for radionuclides from the actinium decay chain.

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