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Correlation between Element and Radionuclide Activity Concentrations in Soil and Beech Forests Growth Potential

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Abstract: (1) Background: The main objective of this study was to determine the correlation between element and radionuclide activity concentrations and the growth potential of trees across European mountain beech forests; (2) Methods: As, Cd, Co, Cu, Ni, Pb, and Zn were determined using inductively coupled plasma–optical emission spectrometry (ICP/OES). Mercury was determined by Direct Mercury Analyzer DMA 80 Milestone. The Cr, Rb, Sr, Y, Zr, Sn, Ba, and W were determined by Spectro Xepos Energy Dispersive X-ray fluorescence spectrometry (EDXRF). Gamma spectrometry measurements of ^{22}Na, ^{40}K, ^{232}Th, ^{226}Ra, ^{238}U, ^{235}U, and ^{137}Cs were performed using a coaxial High-Purity Germanium (HPGe) detector; (3) Results: The median values of As for the upper and deeper soil horizon were lower, Ni, Pb, Rb, Sr, Y, Zr, Sn, and W were in the range, while the values of Cd, Co, Cr, Cu, Zn, Hg, and Ba were higher than median values given in the Geochemical Atlas of Europe (GAE) for the upper and deeper soil horizon. The radionuclide activity concentrations varied in approximately the same ranges. The production potential of forest trees ranged from 5262.67 for cambisol and umbrisol soil types on granite and limestone parent materials to 24490.78 for umbrisol and rendzina soil types on granite and dolomite parent materials; (4) Conclusions: Parent material had a significant role in the productivity of European mountain beech forests.

Keywords: element concentrations; radionuclide activity; beech forests; mountain; Europe

1. Introduction

Fagus silvatica L., or European beech, is one of the most important and widespread deciduous tree species in Europe [1]. According to pollen analyses this species has originally spread across Europe from a small, scattered population left after the last glaciation, and is currently in its maximum post-glacial spread [2]. European beech is distributed throughout Europe: from Sicily to Bergen in southern Norway [3,4], and from the Cantabrian Mountains in the west to the Carpathians and the Balkan Mountains in the east [5]. The primeval beech forests of the Carpathians and other regions of Europe are an outstanding example of an untouched forest complex in the temperate climate zone of Europe [5]. Beech shows a moderate ability to acidify the soil [6]. It grows well on soft soils in which the root system can easily penetrate. However, its optimal growth is in moist soils located on limestone or volcanic parent materials [7]. Soil quality plays an important role in the functioning of these forest ecosystems [7].

Soil is a multiphase system whose composition is a mixture of rock and mineral fragments, organic matter, water, and air [8]. The parent rock from which the soil is formed plays a crucial role in the pedogenetic processes [9]. Chemical reactions that take place in the pedosphere in the process of soil formation determine the mobilization and redistribution of elements in the soil profile, so there is a significant correlation between the total content of elements in the soil and the parent substrate [10,11]. Besides chemical elements being natural constituents of rocks and soils [12,13], natural radionuclides in soil or soil solutions continuously participate in biogeochemical processes [14–18].

In addition to the close connection between the parent material and the soil developed on it, the concentration of chemical elements and radionuclides activity in the soil is also associated with possible contamination from anthropogenic sources [19–23]. The circulation of chemical elements especially heavy metals and radionuclides in the biosphere has been increasing in recent decades, also with that the awareness of them as a potential risk to the environment is increasing [11].

In native forests, soils rarely experience significant disturbances, which are more common for other land-use systems. However, climate change, deforestation, and pollution can cause dramatic changes in forest soil quality. One of the most important consequences of climate change is the alteration of the quality or quantity of soil organic matter [24]. Deforestation and land degradation cause changes in hydrological processes, which can enhance soil erosion and surface runoff, increase the recharge of groundwater, and cause the reduction of organic carbon, phosphorus, nitrogen, and exchangeable potassium, calcium, and magnesium [25]. Pollution of forest soil especially by heavy metals can affect the physiological activity of roots and reduce forest productivity [26,27]. The rate of soil degradation in such changed conditions depends largely on the bedrock type, which was until recently considered of subordinate significance compared to climate and pedological characteristics [28]. Not only that bedrock have a significant role in vegetation growth by regulating physical and chemical properties in soils, but it can also change the response of vegetation to climate factors [28]. The main objective of this study was to determine the correlation between element and radionuclide activity concentrations in different soil types and the growth potential of trees across European mountain beech forests. We hypothesized that the soil type, geology, and environmental setting influence the element and activity concentrations of natural radionuclides in the soils of these mountain forests.

2. Materials and Methods

2.1. Study area

The dataset covered the European mountain beech forest region in Bosnia and Herzegovina (BA), Bulgaria (BG), Czech Republic (CZ), Germany (DE), Italy (IT), Poland (PL), Romania (RO), Serbia (RS), Slovakia (SK), Slovenia (SL), and Spain (ES) (Figure 1). All the study sites are in mountain regions, from the Southern Carpathians (Romania) in the east to the Picos de Europa (Spain) in the west, and from the Apennines (Italy) in the south to the Tatras (Poland) in the north.

In the studied area, five types of bedrock (carbonate (limestone and dolomite), sandstone, granite, conglomerate, and andesite) and four soil types (luvisol, cambisol, rendzina, umbrisol) were identified (Table 1). Elevations of plots vary from 400 to 1400 m a.s.l. (Table 1), with a wide range of climate conditions, i.e., annual precipitation of 517–2780 mm and mean temperatures of 2.6–10.2 °C.

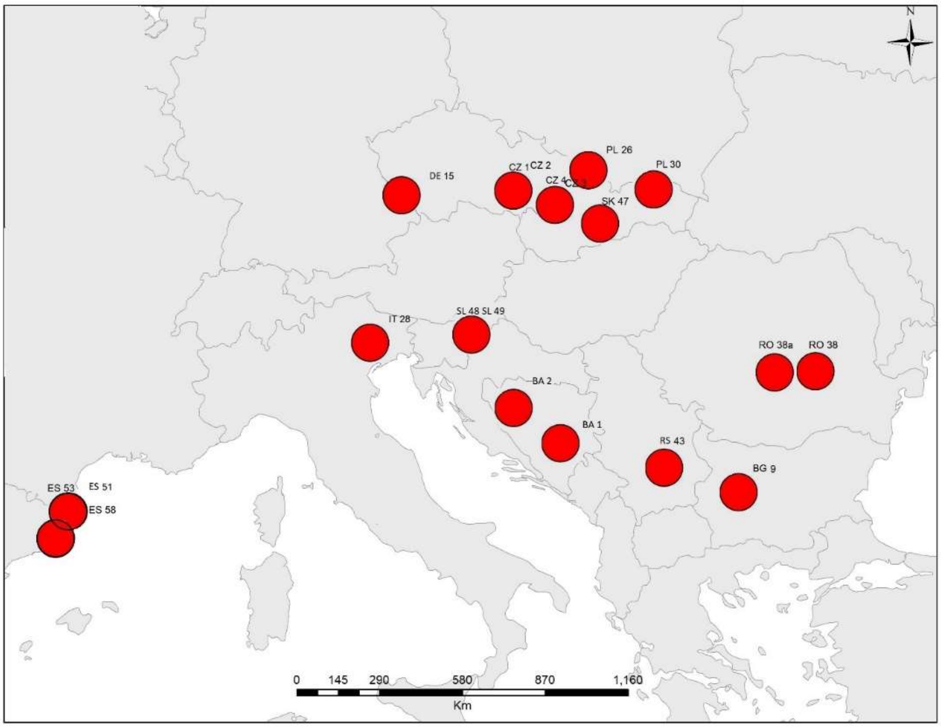

Figure 1. Soil sampling sites across European mountain beech forests.

Table 1. Sampling site characteristics.

Country	Longitude	Latitude	Altitude (m a.s.l.)	Geological settings	Soil type
Bosnia and Herzegovina (BA)	18°15'44"E	43°42'25"N	1292	limestone	calci cambisol
	16°40'06.4"E	44°38'38.7"N	524	limestone	luvisol
Bulgaria (BG)	23°52'52"E	42°46'45"N	1350	sandstone	cambisol
Czech Republic (CZ)	16°44'21.4"E	49°17'06.6"N	490	limestone	rendzina modal
	16°44'24.3"E	49°17'05.1"N	485	limestone	rendzina modal
	18°01'07.5"E	49°02'08.3"N	415	sandstone, claystone	cambisol modal
	18°01'30.7"E	49°01'24.4"N	620	sandstone marlstone	cambisol modal
Germany (DE)	13°16'17.2"E	49°03'45.9"N	720	granite	cambisol
Italy (IT)	12°25'47"E	46°07'08"N	1090	limestone moraine	luvisol
Poland (PL)	20°54'11.2"E	49°25'58.7"N	830	magura sandstone	cambisol
	18°54'52.6"E	49°37'20.8"N	520	magura sandstone	cambisol
Romania (RO)	25°53'01.7"E	45°32'14"N	1277	conglomerate	eutric cambisol
	25°48'19.3"E	45°19'15.3"N	970	limestone	eutric cambisol
Serbia (RS)	21°22'41.7"E	43°24'22.5"N	695	granite	cambisol dystric
Slovakia (SK)	19°24'58.1"E	48°38'58.4"N	750	andesite	andic cambisol
Slovenia (SL)	15º03'42.8"E	46º06'56.1"N	600	dolomite	leptosol
	15º03'58.7"E	46º05'38.3"N	1070	dolomite	leptosol
Spain (ES)	2º43'19"E	42º12'05"N	1430	granite and granodiorite	umbrisol
	2º43'34"E	42º12'06"N	1430	granite and granodiorite	umbrisol
	2°27'24"E	41°46'32"N	1186	granite and granodiorite	umbrisol

2.2. Soil sampling

The dataset contains 37 soil samples from 20 beech forest stands. Monospecific beech stands were chosen, with similar stand ages for the dominant trees (between 70 and 100 years old). Beech forest management history includes unmanaged stands for at least 15 years. Management practices in forests can affect their natural features and processes and differences between managed and unmanaged forests depend strongly on the intensity of the forest management [29,30]. Magnitude and type of forest treatment can have different effects on the biodiversity as well as forest structure [30,31]. The plot size was a minimum of 0.1 ha with a minimum of 50 trees per plot. Soil sampling was done at two depths, the upper horizon of 0-40 cm and the deeper horizon of 40-80 cm in accordance with the recommendations of the Manual for Sampling and Analysis of Soil [32].

2.3. Soil chemical analyses

To determine the total content of As, Cd, Co, Cu, Ni, Pb, and Zn, soil samples were prepared by microwave digestion using the microwave system Milestone Ethos 1. Seven milliliters of concentrated HNO_3 and 2 ml of H_2O_2 were added into the vessels where previously measured 0.40 g of dried and ground soil samples. Element concentrations in samples were determined using inductively coupled plasma–optical emission spectrometry (ICP/OES system Thermo iCAP 6500 Duo). Total Hg content was quantitatively determined by Direct Mercury Analyzer DMA 80 Milestone. Quality assurance and quality control (QA/QC) for As, Cd, Co, Cu, Ni, Pb, and Zn evaluated with duplicate and blank samples and certified reference materials. Quality control was carried out with BCR reference materials CRM-141R - trace elements in calcareous loam soil and CRM-142R - light sandy soil. Recoveries were within ±10% of the certified values. For total Hg content, quality control was carried out with BCR reference materials CRM-143R - sewage sludge amended soil and deviations were within ±5% of the certified values. Reference materials provided by the Joint Research Centre, Ispra were purchased by Sigma-Aldrich Chemie GmbH (Buchs, Switzerland). The concentrations of Cr, Rb, Sr, Y, Zr, Sn, Ba, and W were determined by Spectro Xepos Energy Dispersive X-ray fluorescence spectrometry (EDXRF) with a binary cobalt/palladium alloy thick-target anode X-ray tube (50 W/60 kV) and combined polarized/direct excitation. After homogenized 4.00 g of soil samples and 20% weight (wt) of wax binder (Hoechst wax C micro powder, Merck, C.A.S. number: 110-30-5) samples were pressed into 32 mm diameter pellets using Retsch PP25 hydraulic press with an applied pressure of 15 tons for 5 minutes. The EDXRF is controlled by the Spectro XRF Analyzer Pro, Xepos C Software, and recording was performed using a standardless, FP oxides pellets (A) (JRRM) method.

To determine the radionuclide activity concentrations dried soil samples, were ground in a glass mortar, passed through a sieve, and then sealed in 450 mL Marinelli beakers for a month. Gamma spectrometry measurements of natural radionuclides (^{22}Na, ^{40}K, ^{232}Th, ^{226}Ra, ^{238}U, and ^{235}U) and ^{137}Cs were performed using a High-Purity Germanium (HPGe) detector (GEM30-70 ORTEC with 28% relative efficiency at 1.33 MeV) enclosed in a 10 cm thick lead shield to reduce the background. Based on the intensity of the gamma lines recorded in the measured spectra, the activity concentrations of ^{22}Na, ^{40}K, ^{137}Cs, ^{232}Th, ^{226}Ra, ^{238}U, and ^{235}U were calculated.

2.4. Data analyses

2.4.1. Indicators of soil pollution

To assess the degree of pollution and the environmental risk the Geoaccumulation (Igeo) [33] and the Ecological Risk Index (RI) were calculated [34]. The median value of element contents for the upper soil horizon given in the Geochemical Atlas of Europe (GAE) [35] was selected as the background concentration. The background concentration values were (in mg kg^{-1}): 7.03 (As), 0.14 (Cd), 8.00 (Co), 60.00 (Cr), 12.90 (Cu), 18.00 (Ni), 22.60 (Pb), 52.00 (Zn), and 0.04 (Hg).

2.4.2. Indicators of activity concentration of radionuclides

The activity concentrations of ^{40}K, ^{238}U, and ^{232}Th measured in each of the studied samples indicate the amount of radioactivity present but do not provide a measure of radiation risk in the form of the rate of absorbed dose. The absorbed dose D (nGy h^{-1}) in the air at 1 m above ground level in the study samples at each study site was calculated using the equation recommended by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) [36]. According to UNSCEAR [36], the world value of D ranges from 59 nGy h^{-1}/Bk kg^{-1}. To estimate the annual effective doses, the conversion coefficient from the absorbed dose in the air to the effective dose (0.7) and the outdoor occupancy factor (0.2) proposed by UNSCEAR [36] were used. The average annual effective dose worldwide according to UNSCEAR [36] is approximately 0.5 mSv. The equivalent activity of Ra (Ra_{eq}) is the weighted sum of the activities of ^{226}Ra, ^{232}Th, and ^{40}K based on the assumption that 10 Bk kg^{-1} of ^{226}Ra, 7 Bk kg^{-1} of ^{232}Th or 130 Bk kg^{-1} of ^{40}K produce the same gamma-ray dose rates [37]. The maximum value of Ra_{eq} must be < 370 Bk kg^{-1} [38] to keep the external dose at < 1.5 mGy/y [37]. The modified amount of Ra_{eq} is the external hazard index (H_{ex}) [37]. The H_{ex} value must be ≤ 1 to maintain the radiation hazard.

2.4.3. Site Index

According to Nyland [39], the Site Index (SI) is the potential of forest trees to grow on a particular site. In addition to measuring site productivity, the SI is also used in the forest site management system. In this study, SI was calculated to measure site productivity following equation:

$$SI = \frac{a_2(T^2 - T_0^2) + b_2(T - T_0) + T_0^2}{T^2/H - a_1(T^2 - T_0^2) + b_1(T - T_0)}$$

where: H – tree height, T – year, TO – 25, a1, a2, b1, and b2 are constants 0.032, 0.60, 4, and 44, respectively.

2.4.4. Principal component analysis

To test the correlation between element and radionuclide activity concentrations and site productivity, the principal component analysis (PCA) was applied. The task of the PCA method was to determine linear combinations of the original variables, whereby the loss of information contained in the initial data set was minimized. By reducing the original data set, the analysis was simplified and thus the interpretation of the results was facilitated. The original, correlated data set was transformed into a set of uncorrelated variables (principal components (PCs)), with decreasing variance values. The total variance is the sum of the variances of all source variables. Part of that total variance is explained by one main component called an eigenvalue. The eigenvalue of the vector α_i is the largest for the first PC, and its value decreases for each subsequent component. According to Kaiser's criterion, only those PCs with eigenvalues greater than the unity were retained. The correlation coefficients (loadings) connecting the original and derived variables were the basis for the interpretation of the main components. The values of the coefficients were obtained using the rotation procedure (Varimax method), by which the obtained values of the coefficients were transformed to facilitate the interpretation of the results.

3. Results

3.1. Element concentrations

The element concentrations in soils from mountain beech forests across Europe are given in Table 2. Figures 2 and 3 show the sum of elements (As, Cd, Co, Cr, Cu, Ni, Pb, Zn, Hg, Rb, Sr, Y, Zr, Sn, Ba, and W) concentrations in the upper and deeper soil horizons.

Table 2. Element concentrations (in mg kg^{-1}) in soil samples from mountain beech forests across Europe and their median values in the upper and deeper soil horizons, according to the GAE.

Elements	Range	Median	Standard deviation	Upper GAE	Deeper GAE

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As	0.01 – 22.9	5.35	5.71	7.03	6.02
Cd	0.99 – 6.03	2.99	1.22	0.14	0.09
Co	2.51 – 26.0	11.1	4.53	8.00	8.97
Cr	14.2 – 335	86.2	48.7	60.0	62.0
Cu	11.3 – 39.8	22.1	7.79	12.9	13.9
Ni	4.79 – 56.3	22.5	13.3	18.0	21.8
Pb	1.38 – 91.8	13.6	18.0	22.6	17.2
Zn	51.0 – 361	111	57.3	52.0	47.0
Hg	0.20 – 5.07	2.09	1.41	0.04	0.02
Rb	16.6 – 156	89.7	37.1	79.5	83.0
Sr	45.4 – 371	61.8	65.7	89.0	95.0
Y	3.90 – 53.93	26.7	10.3	21.0	23.0
Zr	76.7 – 416	240	86.6	230	220
Sn	0.30 – 7.00	3.70	1.43	3.00	3.00
Ba	94.0 – 830	484	174	380	390
W	2.67 – 9.20	6.00	1.52	< 5.00	< 5.00

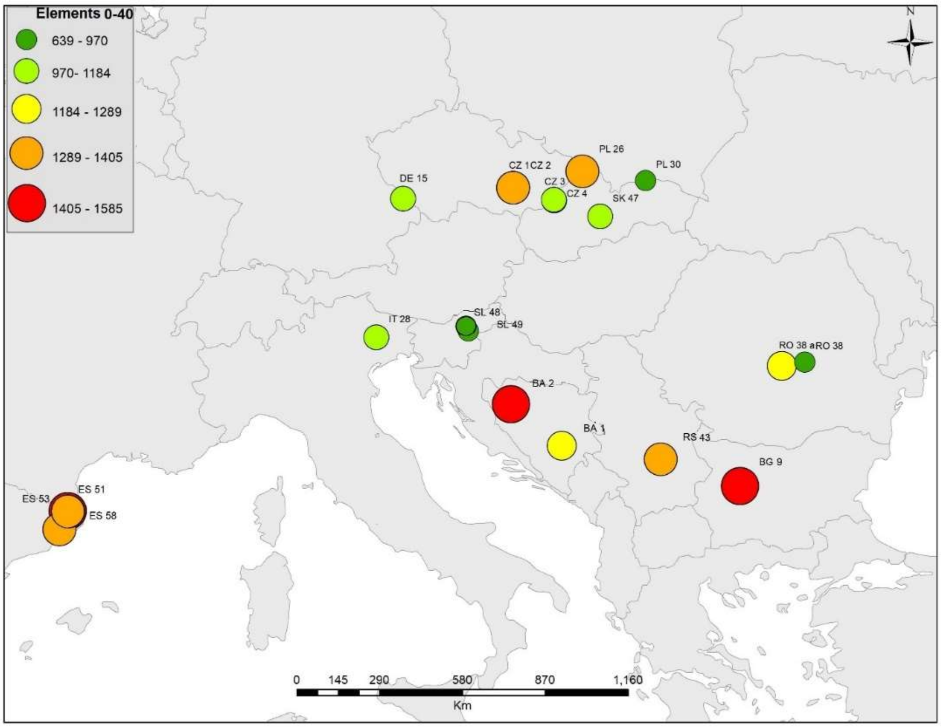

Figure 2. The sum of element (As, Cd, Co, Cr, Cu, Ni, Pb, Zn, Hg, Rb, Sr, Y, Zr, Sn, Ba, and W) concentrations (in mg kg^{-1}) in the upper soil horizon samples from mountain beech forests across Europe.

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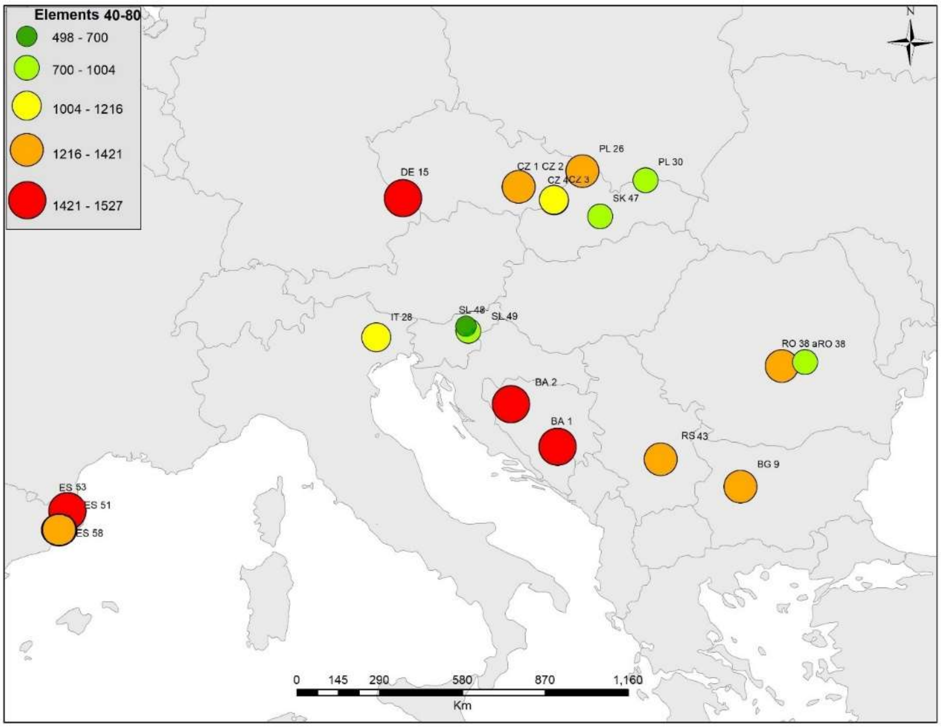

Figure 3. The sum of element (As, Cd, Co, Cr, Cu, Ni, Pb, Zn, Hg, Rb, Sr, Y, Zr, Sn, Ba, and W) concentrations (in mg kg^{-1}) in the deeper soil horizon samples from mountain beech forests across Europe.

The median values of As for the upper and deeper soil horizons were lower, those of Ni, Pb, Rb, Sr, Y, Zr, Sn, and W were in the range, while the values of Cd, Co, Cr, Cu, Zn, Hg, and Ba were higher than median values given in the GAE for the upper and deeper soil horizons (Table 2).

A concentration ratio < 1 for the upper/deeper horizon was observed for Cd, Co, Cu, Ni, and Rb. Anomalies in concentrations in the upper horizon of the soil in relation to the deeper horizon were expressed in soil samples from SK and SL.

For As, Cr, Sr, Y, Zr, Ba, and W the upper/deeper horizon concentration ratio was ≈ 1. Above As values in the upper horizon compared to the deeper horizon were observed in samples from SK and DE. Anomalies of Cr values in the upper soil horizon compared to the deeper one were expressed in samples from SK, RO, BG, and SL, of Ba from SL, and of W in samples from BG and SL. Anomalies in the concentrations of Sr in the upper horizon compared to the deeper horizon were expressed in soil samples from IT, Y from RS and SL, and Zr in samples from IT, SL, and DE.

The concentration ratio of the upper/deeper horizon was > 1 for Pb, Zn, Hg, and Sn. Values for Pb < 1 were present in soil samples from SK, RO, and SL. After Pb, Hg showed the strongest enrichment in the upper soil horizon compared to the deeper horizon. Higher contents of Hg in the upper soil horizon in comparison with the deeper were expressed in samples from CZ, RO, BG, DE, and ES. Higher concentrations of Zn in the upper soil horizon were expressed in the samples from SK and SL in comparison with the deeper one, and of Sn in the samples from CZ, RO, BG, SL, and DE.

Accumulation of toxic elements and their negative impact on forest soil results in a decrease in overall soil quality [40]. First, the negative impact is reflected in the reduction of soil resources [40], causing its acidification [41], thereby, indirectly affecting the vigour of vegetation [42]. In soil samples from mountain beech forests across Europe, the total chalcophile elements, which have an affinity for sulfur content (Cu, Pb, Zn, Hg, As, Cd), was in the range of 81.5–473 mg kg^{-1}. The position of the ΣCu+Pb+Zn+Hg+As+Cd in soil samples from mountain beech forests across Europe in relation to the median values in the upper soil horizon according to the GAE is presented in Figure 4. All the studied

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sites (except samples from PL and RS) had a content of ΣCu+Pb+Zn+Hg+As+Cd higher than 94.7 mg kg^{-1} (ΣCu+Pb+Zn+Hg+As+Cd in the upper soil horizons, according to the GAE), with the highest values in samples developed on limestone parent material. Soil samples developed on limestone parent material contained the highest average concentrations of As, Cd, Co, Cr, Cu, Ni, Pb, Zn, and Hg in the samples at a depth of 40-80 cm. The exception was represented by the samples from BA and SL, which had the highest content in surface samples.

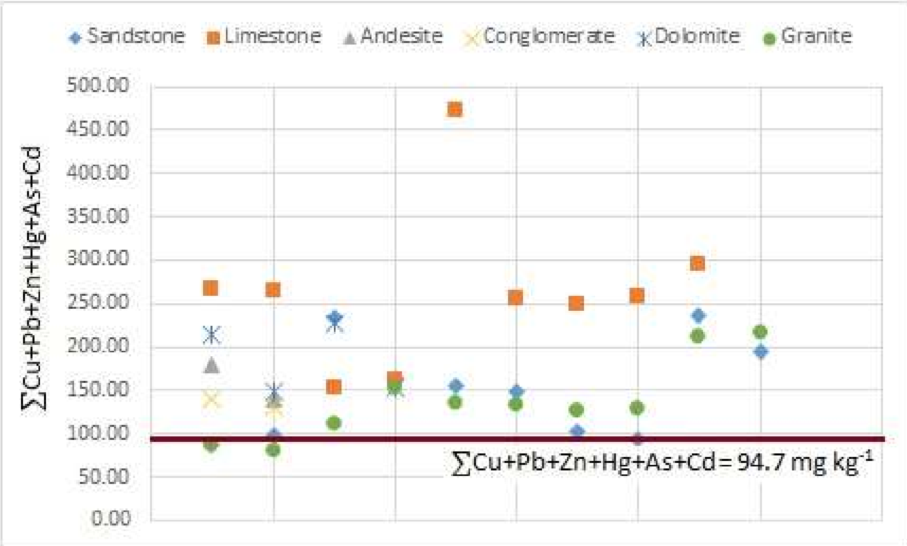

Figure 4. ΣCu+Pb+Zn+Hg+As+Cd in soil samples from mountain beech forests across Europe in relation to ΣCu+Pb+Zn+Hg+As+Cd in the upper soil horizons, according to the Geochemical Atlas of Europe (GAE).

Surface soil samples developed on carbonate parent material can be enriched in toxic elements. In addition to the parent material, the accumulation of these elements in the upper soil horizon can also be the result of anthropogenic activities [43–45]. Atmospheric deposition is one of the possible sources. Atmospheric deposition increases the concentration of elements in the upper horizon of the forest soil, due to the adsorption potential of the humus layer, which is present in northernmost European forests [46,47].

To assess the degree of pollution and the environmental risk of As, Cd, Co, Cr, Cu, Ni, Pb, Zn, and Hg in the upper soil horizons from mountain beech forests across Europe, Igeo and RI were calculated. According to the content of As, Co, Cr, Cu, Ni, and Pb, the largest number of samples belonging to the class of uncontaminated to moderately contaminated soils (Table 3). According to the Zn content, the samples belonged to the class from unpolluted to heavily polluted soils, and according to the Cd and Hg content, to the class from moderately to extremely contaminated soils (Table 3).

Table 3. Assessment of the pollution degree of elements in soil samples from mountain beech forests across Europe using Igeo.

Heavy metals	Range Igeo values	Igeo class	Pollution Level
As	-10.04 - 1.12	0 - 2	Uncontaminated - moderately contaminated
Cd	2.24 - 4.84	3 - 5	Moderately to heavily - heavily to extremely contaminated
Co	-2.24 - 0.39	0 - 1	Uncontaminated - uncontaminated to moderately contaminated
Cr	-2.36 - 0.82	0 - 1	Uncontaminated - uncontaminated to moderately contaminated
Cu	-0.78 - 1.04	0 - 2	Uncontaminated - moderately

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			contaminated
Ni	-2.50 - 1.02	0 - 2	Uncontaminated - moderately contaminated
Pb	-4.62 - 1.44	1 - 2	Uncontaminated to moderately - moderately contaminated
Zn	-0.40 - 2.21	0 - 3	Uncontaminated - moderately to heavily contaminated
Hg	1.75 - 6.40	2 - 6	Moderately - extremely contaminated

The RI was calculated as the sum of the ecological risk factors (Er) of individual elements. The values of Er for As, Co, Cr, Cu, Ni, Pb, and Zn were lower than 40, which indicates a low ecological risk of these elements in soil samples from mountain beech forests across Europe (Table 4). Among the investigated elements, Cd and Hg exhibited a high environmental risk (Table 4). The values of RI in the analyzed samples were 600 ≤ RI in the largest number of samples, which indicates that the soil from mountain beech forests across Europe in the investigated areas presented a high ecological risk to the surrounding environment (Table 4). Determination of the percentage contribution of individual elements to the total environmental risk indicated that the greatest contribution to the total risk derived from Hg and Cd.

Table 4. Assessment of the environmental risk of elements in soil samples from mountain beech forests across Europe, using Er and RI.

Heavy metals	Range Er values	Scope of Er	Ecological risk Level of Er	Range RI values	Scope of RI	General level of potential ecological risk
As	0.01 - 32.69	< 40	low			
Cd	212.21 - 1291.71	160 ≤ E*f* < 320 320 ≤ E*f*	high - serious			
Co	1.59 - 9.81	< 40	low			
Cr	0.59 - 5.28	< 40	low			
Cu	4.36 - 15.41	< 40	low	708.52 - 6419.19	600 ≤ RI	serious
Ni	1.33 - 15.16	< 40	low			
Pb	0.31 - 20.30	< 40	low			
Zn	1.14 - 6.95	< 40	low			
Hg	201. 57 - 5070.19	160 ≤ E*f* < 320 320 ≤ E*f*	high - serious			

3.2. Radionuclide activity concentrations

The activity concentrations of ^{22}Na, ^{40}K, ^{137}Cs, ^{232}Th, ^{226}Ra, ^{238}U, and ^{235}U in soil samples from mountain beech forests across Europe are shown in Table 5. Figures 5 and 6 show the sum of radionuclide activity (^{22}Na, ^{40}K, ^{137}Cs, ^{232}Th, ^{226}Ra, ^{238}U, and ^{235}U) concentrations measured in the upper and deeper soil horizons.

Table 5. Radionuclide activity concentrations (in Bq kg^{-1}) in soil samples from mountain beech forests across Europe.

Radionuclide	Range	Median	SD
^{22}Na	0.50-4.99	2.15	0.79
^{40}K	10.0-1049	94.0	258
^{137}Cs	0.40-204	3.90	38.9
^{232}Th	3.30-50.8	14.7	7.67
^{226}Ra	16.2-85.4	43.0	15.1
^{238}U	21.0-150	54.0	24.3
^{235}U	1.00-7.71	3.00	1.25

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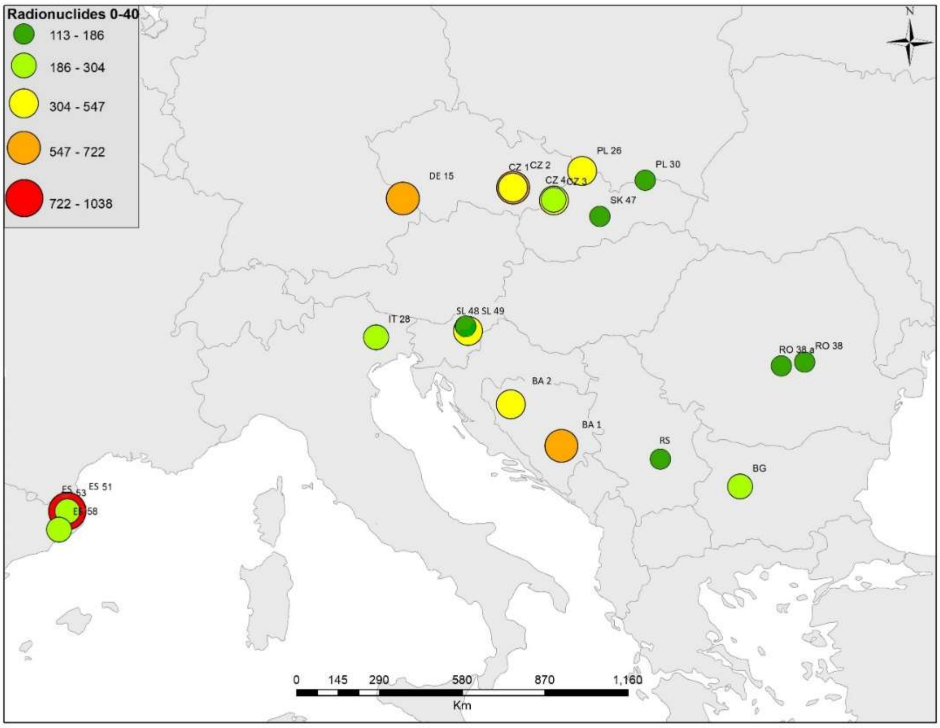

Figure 5. The sum of radionuclide activity (^{22}Na, ^{40}K, ^{137}Cs, ^{232}Th, ^{226}Ra, ^{238}U, and ^{235}U) concentrations (in Bq kg^{-1}) in the upper soil horizons from mountain beech forests across Europe.

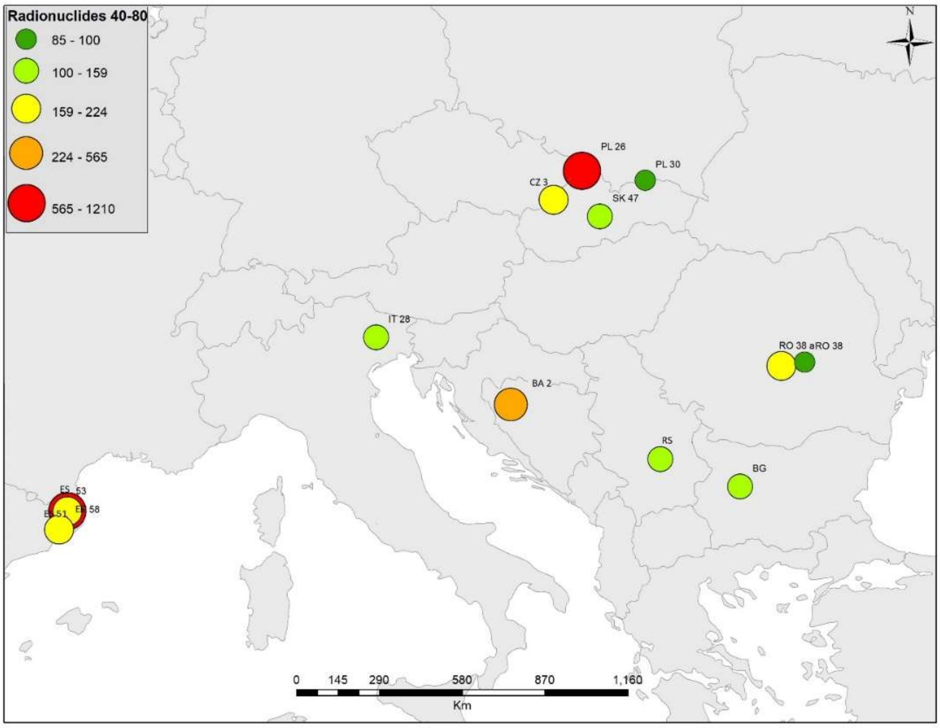

Figure 6. The sum of radionuclide activity (^{22}Na, ^{40}K, ^{137}Cs, ^{232}Th, ^{226}Ra, ^{238}U, and ^{235}U) concentrations (in Bq kg^{-1}) in the deeper soil horizon from mountain beech forests across Europe.

The specific activity of ^{22}Na ranged from 0.50 to 2.67 Bq kg^{-1} in the upper horizon, and from 1.15 to 4.99 Bq kg^{-1} in the deeper horizon (Table 5). In soil samples from mountain beech forests across

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Europe, ^{40}K ranged from 10.0 to 889 Bq kg^{-1} in the upper horizon, and from 21.0 to 1049 Bq kg^{-1} in the deeper horizon (Table 5). The highest concentrations of 889 Bq kg^{-1} and 1049 Bq kg^{-1} were measured in soil samples from ES developed on the granite parent material. These values were within the limits of the activity concentration (1290 Bq kg^{-1}) of this radionuclide for granite rocks (Table 6). According to UNSCEAR [36], the average activity concentration of ^{40}K in the world soil is 400 Bq kg^{-1}. Radionuclide ^{137}Cs originates from the accident of the "Lenin" nuclear power plant in Chornobyl in 1986. Given that the half-life of this radionuclide is 30.1 y. [48], it is assumed that it will be redistributed by the processes of relocation and leaching, but it will be present for a long time in ecosystems. The activity concentration of ^{137}Cs in the soil samples from mountain beech forests across Europe ranged from 0.50 to 204 Bq kg^{-1} in the upper horizon, and from 0.40 to 43.5 Bq kg^{-1} in the deeper horizon (Table 5). The highest concentrations of 106 and 204 Bq kg^{-1} were measured in soil samples from IT and BA developed on the limestone parent material. The specific activity of ^{232}Th ranged from 6.20 to 24.0 Bq kg^{-1} in the upper horizon and from 3.30 to 50.8 Bq kg^{-1} in the deeper horizon (Table 5). Compared to activity concentrations of ^{232}Th for granite rocks (87.5 Bq kg^{-1}; Table 6), the obtained median value was lower. According to UNSCEAR [36], the average activity concentration of this radionuclide in the world soil is 30 Bq kg^{-1}. The ^{226}Ra ranged from 16.2 to 63.1 Bq kg^{-1} in the upper horizon, and from 17.2 to 85.4 Bq kg^{-1} in the deeper horizon in soil samples from mountain beech forests across Europe (Table 5). Activity concentrations of ^{238}U ranged from 23.5 to 150 Bq kg^{-1} in the upper horizon, and from 21.0 to 96.5 Bq kg^{-1} in the deeper horizon (Table 5). According to UNSCEAR [36], the average activity concentration of this radionuclide in the world soil is 35 Bq kg^{-1}. Activity concentrations of ^{235}U ranged from 1.21 to 7.71 Bq kg^{-1} in the upper horizon, and from 1.00 to 4.95 Bq kg^{-1} in the deeper horizon (Table 5).

In the soil, activity concentrations of natural radionuclides primarily depend on their concentration in the rocks from which the soil was developed [23]. In soil samples from mountain beech forests across Europe, the radionuclide activity concentrations varied in approximately the same ranges, with the observed deviations between soils that were developed on different parent rocks. The measured activity concentration of natural radionuclides was slightly higher in soil samples developed on the sandstone, limestone, and granite parent material, while the activity concentration of ^{137}Cs was slightly higher in soil samples developed on the carbonate parent rock (limestone and dolomite).

Table 6. Activity concentrations of ^{40}K, ^{232}Th, and ^{238}U in different rocks (in Bq kg^{-1}).

Radionuclide	Basalt	Syenite	Granite	Limestone	Sandstone
^{40}K	210	1400	1290	89.0	370
^{232}Th	6.50	69.2	87.5	7.00	11.0
^{238}U	5.30	102	59.7	28	19.0

In the analyzed samples, a disequilibrium between the two radionuclides was observed in the U-series, the activity ratio $^{238}U/^{226}Ra$ was > 1 with a mean value of 1.51 and ranged from 0.63 to 3.42. This is a consequence of the differences in the geochemical properties between the two radionuclides [49]. The ^{238}U has greater mobility than ^{226}Ra in the environment, and it is more rapidly transferred to a deeper horizon where it accumulates [50]. This disequilibrium in the U-series is the reason for a moderate correlation of ^{226}Ra and ^{238}U (R^2 = 0.3), as indicated by Figure 7.

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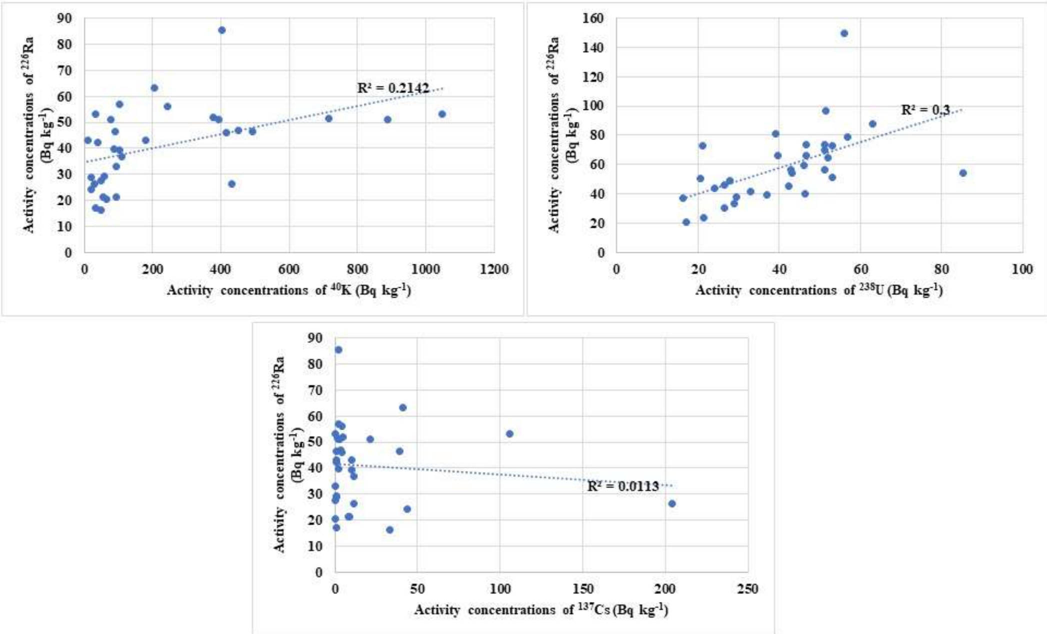

Figure 7. Correlation of activity concentrations of ^{226}Ra with natural ^{40}K and ^{238}U, and artificial ^{137}Cs.

The ^{226}Ra also showed a moderate correlation with ^{40}K (R^2 = 0.21) and a weak correlation with ^{137}Cs (R^2 = 0.0113) (Figure 7). Furthermore, a moderate correlation was established between ^{232}Th and ^{40}K (R^2 = 0.3509) (Figure 8). A moderate correlation indicates that the individual results for any of the activity concentrations of radionuclides in each pair are a good predictor of the individual values for the others [49]. A weak correlation between ^{238}U and ^{232}Th (R^2 = 0.0182) was revealed due to the higher concentration of activity of ^{238}U than ^{232}Th and due to the higher mobility of ^{238}U than ^{232}Th in the analyzed soils (Figure 8).

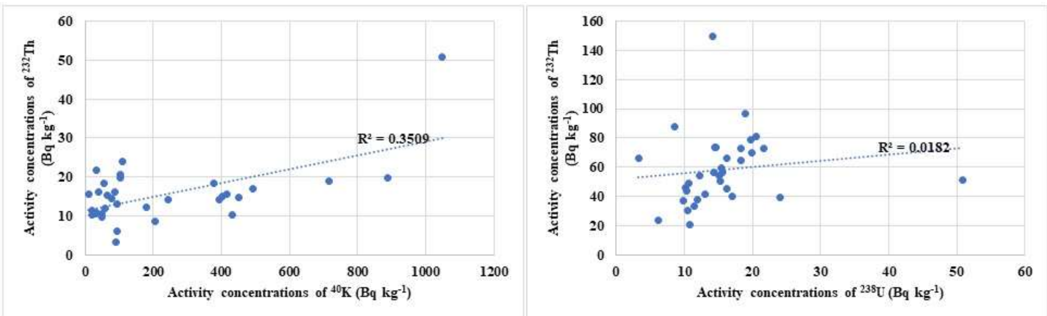

Figure 8. Correlation of activity concentrations of ^{232}Th with natural ^{40}K (left) and ^{238}U (right).

In soil samples from mountain beech forests across Europe, D ranged from 17.47 to 97.63 nGy h^{-1} with an average of 44.73 nGy h^{-1}, which is in line with the global value (59 nGy h^{-1}) (UNSCEAR, 2000). The average annual effective dose was 0.05 mSv, with a range of 0.02 to 0.12 mSv. Worldwide, the average annual effective dose is 0.5 mSv (UNSCEAR, 2000). The Ra_{eq} ranged from 33.99 to 206.42 Bk kg^{-1} with an average of 80.40 Bk kg^{-1}, which is lower than the recommended threshold value. The calculated value of the H_{ex} ranged from 0.09 to 0.56, with an average of 0.22, and the samples met the condition for $H_{ex} \leq 1$.

3.3. Analysis of site productivity

The edaphic characteristics of the investigated area depend on the action and interaction of the pedogenetic factors. The main feature of the land cover of the research area is given by soils developed on limestone, dolomite, sandstone, granite, andesite, and conglomerates parent materials. On limestone-dolomite parent material, three soil types were defined: rendzina, cambisol, and

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luvisol, while cambisol and umbrisol soil types were developed on the other parent materials. The production potential of trees from mountain beech forests across Europe based on SI values ranged from 5262.67 for cambisol and umbrisol soil types on granite and limestone parent materials in samples from ES and RO to 24490.78 for umbrisol and rendzina soil types on granite and dolomite parent materials in samples from ES and SL. Figure 9 shows a 3D surface plot with a clear separation of three peaks for SI values.

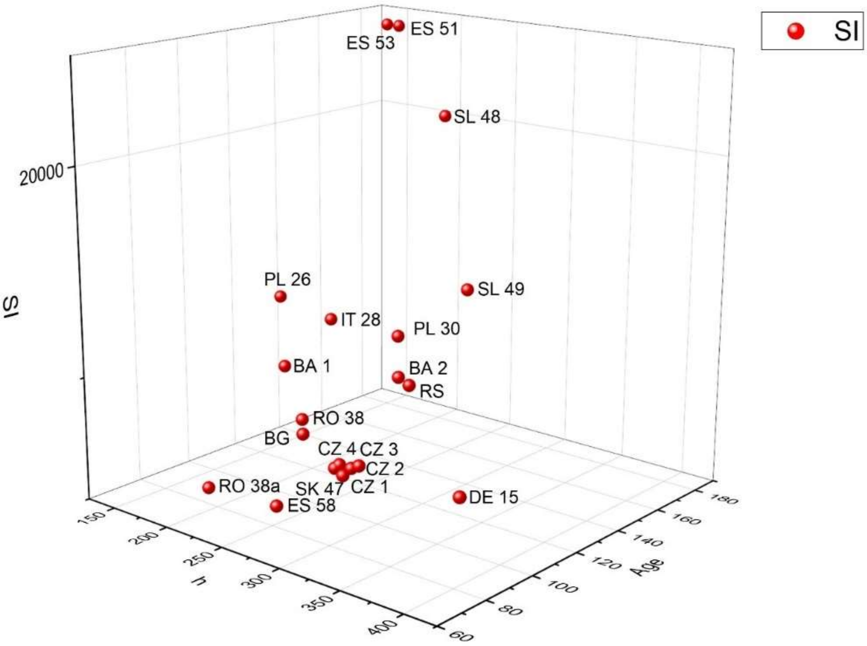

Figure 9. 3D surface plot: the x-axis is tree height (h), the y-axis is tree age (Age), and the z-axis is site index (SI).

Rendzina is the dominant soil type developed on dolomite and limestone parent materials, which are prone to mechanical disintegration [51]. The studied rendzina was classified into two subtypes: leptosol developed on dolomite parent material in samples from SL, and rendzina modal developed on limestone parent material on gentle slopes up to 4° in the CZ and a steep slope up to 32° in BA. The higher content of clay fraction in this type of soil was due to topography, abundant wetting, high precipitation, and low evapotranspiration [52]. Dolomite and limestone parent materials cause a neutral to moderately alkaline soil reaction (pH 7–8). According to Kašanin-Grubin et al. [52], in the investigated sites, the content of organic matter was higher in soils developed on dolomite parent material and was characterized by a decrease in depth. In this study, rendzina was on average a medium-productive forest soil with a higher productive potential on the dolomite parent material in SL (SI = 20901). According to Hristov et al. [53], the rendzina soil type on calcareous rocks has a favorable impact on the soil structure and vegetation and represents a biologically active soil type with a high number of stable forms of humus. Also, rendzina has a high potential for organic carbon sequestration [53].

Cambisol is the dominant soil type developed on both limestone and the other parent materials. Calcicambisol and eutheric cambisol are present on limestone, while on sandstone and claystone is present cambisol modal, eutheric cambisol on conglomerates, dystric cambisol on granites and granite monocytes, and andic cambisol on andesite pyroclastic rocks. Its formation is related mainly to moderate slopes up to 25°. These soils characterized a higher percentage of clay fraction in soil samples from BA and CZ developed on limestone and sandstone marlstone parent materials, respectively [52]. On granite, andesite, and conglomerate parent materials, a highly acidic reaction enables a certain destructive decomposition of clay minerals in the soil, so the percentage of clay is somewhat lower in the soil developed on this parent material [54]. The richness of organic matter is an important chemical characteristic of this type of soil [55]. However, according to Kašanin-Grubin et al. [52], in the investigated sites, in soils developed on sandstones, granite, andesite, and conglomerates parent materials, the content of organic matter was relatively low, and with depth, their content decreased significantly. Cambisol of the investigated sites was characterized by lower to moderate site productivity (SI from 5402 to 14295). Moderate productivity was related to limestone (SI = 12027) and magura sandstone (SI = 14295) from PL. To some degree, a limiting factor could be the content of the skeletal fragments [56]. The productivity of cambisol was a function of depth and skeletal fragment content on almost all parent materials [56]. Deeper soils with fewer skeletal fragments have a higher ecological production value. The increase in rock fragment content could be conducive to soil nutrient accumulation and soil water storage and circulation and change certain features of plants, contributing to plant growth [57].

Relief plays a crucial role in the formation of luvisol [58]. This soil type appeared in IT and BA in combination with calcicambisol. Luvisol was developed on the limestone parent material, covering parts of the terrain whose morphology is characterized by a low energy relief, mainly plains and mild forms of meso-relief with up to 5° slope. According to Kašanin-Grubin et al. [52], in the investigated sites, textural differentiation was pronounced, and clay content increased with depth. With depth, the participation of the sand fraction generally decreases, and the fraction of colloidal clay increases. The highest content of clay was at a depth of 40 – 80 cm [52]. Luvisol developed on limestone parent material had a slightly lower acidity and the pH value ranged from moderately acidic to neutral [52]. The high content of organic matter decreased sharply with depth [52]. The main carrier of adsorptive capacity is the humus [59]. The productive capacity of luvisol on limestone parent material is moderate. Approximate values of SI 10000. In conditions of humid mountain climate, the luvisol subtype on limestone rocks also represents a highly productive environment of mixed communities of fir-spruce-beech forest [60].

Umbrisols have a very limited range. Developed on granite and granite and granodiorite parent material, only in ES, on moderate to steep slopes of up to 30°. According to Kašanin-Grubin et al. [52], in the investigated sites, the dominant grain size fraction was sandy-clay. The clay content increased with depth [52]. The chemical properties were characterized by a moderately acidic reaction, and the content of organic matter gradually decreased with depth [52]. The productivity of the umbrisol ranged from extremely low (SI 5262.67) in soil samples on moderate slopes to extremely high (SI 24490.78) in soil samples on steep slopes of up to 30°.

3.4. Principal component analysis

To determine the correlation between element and radionuclide activity concentrations in different soil types and the growth potential of trees across European mountain beech forests, PCA was performed (Figure 10). The obtained correlation agreed with the 3D surface plot (Figure 9). SI values in soil samples developed on granite and granodiorite parent material were correlated with concentrations of ^{232}Th, ^{226}Ra, ^{40}K, ^{238}U, ^{235}U, Rb, and Zr, and soil samples developed on the limestone-dolomite substrate were correlated with Cu, Ni, Co, As, Cd, Hg, Zn, and ^{137}Cs. Štrbac et al. [61] determined the highest concentrations of heavy metals in soil samples from BA, BG, SL, and IT. Soil samples from BA, SL, and IT belong to luvisol and rendzina soil types developed on limestone parent material.

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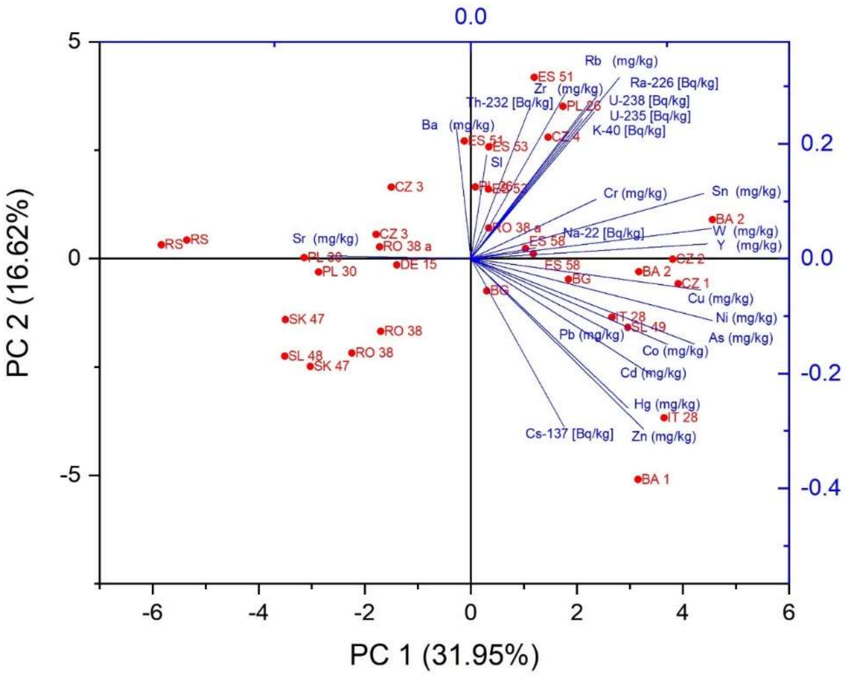

Figure 10. Principal Component Analysis of element and radionuclide activity concentrations in soils from European beech forests.

4. Conclusions

Bedrock had a significant role in the productivity of European mountain beech forests, regulating the physical and chemical properties of soils, providing mineral nutrients, influencing soil texture characteristics controlling the water and nutrient retention capacity, but supplying heavy metals that might have an adverse influence on tree growth. In conclusion, the production potential of trees in mountain beech forests across Europe was highest for umbrisol and rendzina soil types developed on granite and dolomite parent materials on steep slopes of up to 30°. Soil samples developed on granite and granodiorite parent material were correlated with concentrations of ^{232}Th, ^{226}Ra, ^{40}K, ^{238}U, ^{235}U, Rb, and Zr, while soil samples developed on the limestone-dolomite substrate were correlated with Cu, Ni, Co, As, Cd, Hg, Zn, and ^{137}Cs. The highest average concentrations of As, Cd, Co, Cr, Cu, Ni, Pb, Zn, and Hg were found in the soil samples developed on limestone parent material at a depth of 40-80 cm. Furthermore, higher ΣCu+Pb+Zn+Hg+As+Cd content was also found in soil samples developed on limestone parent material. The exception was the samples from BA and SL, which had the highest content in surface samples. Although the accumulation of these elements in the upper soil horizon, because of anthropogenic activities, especially through atmospheric deposition, could potentially reduce forest productivity, soil types developed on limestone and dolomite parent material showed moderate productivity. Overall, comparing the radionuclide activity concentrations of these mountain forests to the internationally recommended values, it is possible to conclude that these soils are safe for residents and those involved in forest activities.

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