Mosses as bioindicators of radionuclide and metal pollution in northern Kosovo and Metohija mountain region

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Abstract

The study investigates mosses (*Hypnum cupressiforme* Hedw.) as bioindicators of pollution in three non-urban mountain areas of northern Kosovo and Metohija regions. Concentrations of radionuclides and metals were measured in moss and soil samples. ^{137}Cs specific activities in soil were strongly correlated with organic matter content. ^{137}Cs in mosses was significantly higher in coniferous than in deciduous forests. ^{7}Be measured in moss samples was increasing with altitude. Concentrations of Ni, Cr, Cu and Zn exceeded regulatory limits in many soil samples from two mountains (Kopaonik and Rogozna). However, concentrations of elements in mosses were weakly correlated with those in soil.

Keywords

moss; soil; radioactivity; metal; enrichment factor; contamination factor

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Introduction

Primordial radioactivity related to ^{238}U (^{226}Ra), ^{235}U and ^{232}Th series and ^{40}K are present in all environments. Due to their long half-lives, these radionuclides are the source of permanent exposure of various biological species. Artificial radionuclide ^{137}Cs occurs in the environment in significant amounts as a consequence of nuclear tests and accidents, particularly the Chernobyl accident; it is radiologically very important due to its half-life of 30.07 y. Production of cosmogenic radionuclide ^{7}Be occurs in spallation processes by cosmic rays in the upper troposphere and lower stratosphere; it is partially important in atmospheric transport processes due to relatively short half-life of 53.3 days [1].

Both, radionuclides and metals have a radioecological impact on the biosphere through the food chain since plants mainly absorb nutrients from the soil. Uptake also occurs from soil particles suspended in air, transported by wind and precipitated by rainfall. Metals occur naturally in all soils, waters, and living organisms. Besides, they can be released from fossil fuel combustion, traffic, industrial and residential activities. Several metals are marked as potentially toxic in low concentration; among them Cd, Hg, As, Cr and Pb have strongly toxic properties. They can pose a significant threat to ecosystems and public health due to their toxicity and persistence in nature.

The changes in the ecological status of an area can be monitored by bio-indicators such as mosses because of their ability to accumulate trace elements. Mosses are a group of specific organisms (bryophytes) which are sensitive to ambient changes in the environment. These changes, particularly climatic variations, affect their growing, physiological activity, uptake and retention of elements [2-4]. Mosses have been proven to be useful predictor of environmental pollution due to high surface/volume ratio, lack of root system, "evergreen phase" during the year, slowly growing with minimal morphological changes during the lifespan, resistance in dry weather conditions, the absence or thin water-repellent cuticle on the surface, high cation exchange capacity, and widespread geographical distribution [5-7]. Besides, using moss tissue as a bio-monitor is well established and efficient technique for monitoring atmospheric deposition of trace elements (atmospheric pollution) and for assessing the environmental quality in an inexpensive and easy way. Mosses have also been used as monitors of harmful gases (sulfur dioxide) in indoor and outdoor environments [8]. Bioaccumulation of trace elements in moss tissue depends on the

atmospheric concentrations of pollutants, the uptake of pollutants, elevation, climatic conditions, vegetation cover, and topography of sampling sites.

Several moss species have been adopted for the indication of environmental pollution, but carpet-forming mosses are most often used. Carpet-forming moss species absorb water and nutrients as well as other trace elements primarily from precipitation and deposition of airborne particles rather than from direct uptake from soil [9]. However, they can still be correlated with soil pollution based on resuspension and transport of contaminants by wind.

In recent years mosses have been extensively investigated as bio-indicators in many studies, with particular interest focused on radionuclides [10-13], metals [14-17], persistent organic pollutants [18-20], etc. Few studies that dealt with radioactivity and metals in moss in mountain regions of Serbia were conducted over the past ten years [13, 21-24].

This is the first environmental study which used mosses as indicators of pollution in non-urban, mountain area of North Kosovo and Metohija, aiming to determine specific activities of radionuclides (^{226}Ra, ^{232}Th, ^{40}K, ^{7}Be and ^{137}Cs) and metal contents (Mn, Ni, Ca, Mg, Fe, Zn, Cr, Cu, Cd and Pb) in soil and moss samples, therefore this study may bring new data about the radionuclide and metal contents in soil and moss in the area of northern Kosovo.

Materials and Methods

Characteristics of the study area

This study deals with the investigation of radioactivity levels and metals in the presumably unpolluted mountain region of the northern part of Kosovo and Metohija, along the borders with the Republic of Serbia and Montenegro (Figure 1).

Kopaonik Mountain is one of the largest mountains of the Republic of Serbia and the largest mountain in Central Serbia. It stretches 100 km in length, 40 km in width and has a surface area of about 120 km^2 in total. The climate is subalpine with an average annual air temperature of 3.7 °C. According to Annual report of Hydrometeorology Service of Serbia [25], the average annual precipitation for Kopaonik Mountain was 1082.2 mm and 1064.4 mm in 2017 and 2018, respectively. The relief contours of the Kopaonik Mt. were created when older sedimentary rocks were affected by powerful tectonic movements and pierced by volcanic activity with indentation

and intrusion of magmatic rock complexes. Because of this, Kopaonik Mt. is characterized by a diverse geological structure with rocks of different origin and age (granite, serpentinite, shale, marble, andesite, limestone).

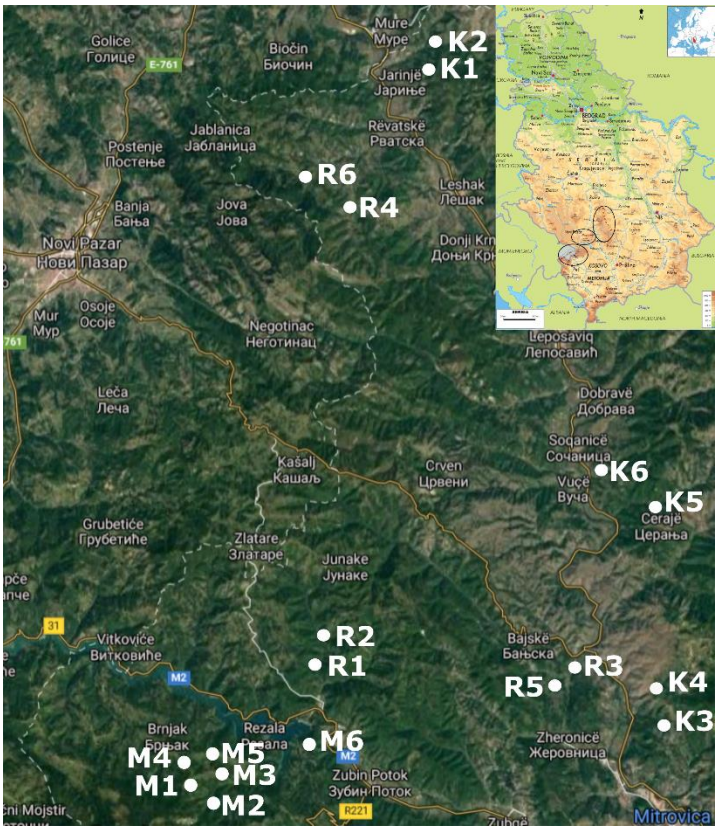

Fig. 1 Map of the study area

Rogozna Mountain is about 20 km long and is a natural border between central Serbia and Kosovo and Metohija. Rogozna Mt. is made up mostly of volcanic rocks. It is rich in minerals composed of Miocene sediments, Tertiary volcanoes, Jurassic and Cretaceous flysch, peridotites, Triassic and Paleozoic metasediments. Rogozna Mountain has characteristics of moderately continental climate, and an average annual precipitation of about 900 mm [26].

Mokra Gora Mountain belongs to the Dinaric mountain system, more precisely to the mountain range of Prokletije. The climate is moderately continental with slightly warmer summers and cold and wet winters [27]. The amount of precipitation ranges from 757 mm (620 m a.s.l.) to 900 mm (1120 m a.s l.); going upwards the mountain peaks, precipitation is increasing, but does not exceed 1050 mm [26]. The relief of Mokra Gora Mt. is related to the karst process in the carbonate rocks with the tectonic movements. The Middle and Upper Triassic carbonate complex form the highest

parts of the Mokra Gora Mt. and is the most widespread geological formation. Affected by tectonic movements, the limestones are intersected by numerous fissures and cracks. The mainly sedimentary, but magmatic and metamorphic rocks consist of shales, serpentinite, gabbro amphibolite, andesites and pyroclastic quartz latites.

Sample collection and preparation

Moss samples of *Hypnum cupressiforme* Hedw. and underlying soil samples were collected from 18 locations - 6 from each mountain. The size of the field coincidence with a collection of six representative samples was chosen due to mosses' abundance in the mountain area. It approximately occupied 400 km^2 for all samples. *Hypnum cupressiforme* Hedw. (Hypnaceae) or hypnum moss is a cosmopolitan species that has a wide variety of habitats in different climatic zones. The species prefers acidic environments and it grows on tree trunks, rocks, ground and other surfaces [28].

Sampling was performed during the spring of 2018. Six representative samples of moss and soil from each mountain are collected. In Table 1 position and elevation of each location from Kopaonik Mt., Rogozna Mt. and Mokra Gora Mt. are marked by K1-K6, R1-R6 and M1-M6, respectively. Ambient dose equivalent rate (ADER) at 1 m height was measured at each location by Geiger counter Radex 1503^+.

Sampling was carried out in open areas away from trees. All the sampling sites were far from towns, single houses, motorways, small industries or other forms of human activities. The collected moss samples were of carpet-forming growth types. Five to ten sub-samples were collected within the site and mixed in one compound sample. Samples were stored in plastic bags to protected samples from potential accidental contamination and transferred to the laboratory. They have been cleaned from litter and dead leaves and only green and greenish-brown parts of the moss were used for further analysis. These moss parts represent 3-5 years of plant growth. Samples have not been washed or treated on any other way. Disposable polyethylene gloves have been used to prevent any kind of contamination. Mosses were cleaned from adherent soil and dried. Underlying topsoil samples (0-15 cm in depth) were also collected, cleaned from stones and roots, dried to constant weight, pulverized and passed through a 2-mm stainless steel sieve. All samples were packed in

Marinelli beakers (450 mL), sealed, and left aside for a month to ensure equilibrium between ^{226}Ra and its progeny.

Gamma spectrometry

Coaxial HPGe detector (GEM30-70 ORTEC) of 30% relative efficiency and 1.65 keV FWHM at 1.33 MeV (^{60}Co) and 717 eV at 122 keV (^{57}Co) was used for measuring specific activities of ^{226}Ra, ^{232}Th, ^{40}K, ^{137}Cs and ^{7}Be in samples. In order to reduce the background, the detector was shielded with 10 cm of lead. A standard mixture of gamma-emitting isotopes (MBSS 2) provided by the Czech Metrology Institute was used for system calibration for soil measurements. The laboratory for gamma spectrometry participates in world-wide proficiency tests organized by IAEA Reference Materials Group, Terrestrial Environment Laboratory. Detector efficiency for moss samples was estimated using a software.

Gamma spectrometric measurements of soil and moss samples were performed for 21600 s and 172800 s, respectively. The specific activity of ^{226}Ra was obtained using three gamma lines of its progeny, ^{214}Pb (351.9 keV) and ^{214}Bi (609.3 keV and 1764.5 keV). The specific activity of ^{232}Th was estimated by the gamma lines at 338.3 keV, 911.1 keV, 968.9 keV (^{228}Ac) and 583.0 keV (^{208}Tl). The gamma lines at 661.6 keV and 1460.7 keV were used for evaluating the activities of ^{137}Cs and ^{40}K, respectively. The specific activity of ^{7}Be was determined by the visible peak at 477.6 keV, considering a decay correction to the time of sampling. Minimum detectable activities (MDAs) of radionuclides in moss samples were calculated using Currie's method: 0.58 for ^{226}Ra, 0.67 for ^{232}Th, 7.84 for ^{40}K, 0.39 for ^{137}Cs and 3.89 for ^{7}Be [29,30].

Determination of metals in soil and plant

The quantification of elements (Mn, Ni, Ca, Mg, Fe, Zn, Cr, Cu, Cd, and Pb) in soil and moss samples was performed using the atomic absorption spectrometric method (AAS). The grain-size fraction of the soil and moss samples were 0.2 mm to ensure better detection of the element content. The reagents used for quantification of elements are the products of "Sigma-Aldrich Company" 65% HNO_3, 35% H_2O_2 and 70% HClO practical grade (P.A.) purity. Standard solutions

elements "Acros Organics Standard (USA)", containing 1000 mg mL/L were used for the determination of the calibration graph of the elements as well as for the determination of elements from the samples. The standard reference materials are products of "LGC standards" and "National Research Council Canada".

For the determination of the quantity of elements in the soil, 1 g of soil sample previously dried in a microwave was dissolved by HNO_3 and $HClO_4$ and evaporated to a certain volume. After cooling, 12 mL of distilled water was added. The mixture was filtrated and placed in sample vials. The quantity of elements in the moss sample was determined using 1 g of the prepared moss material which was afterward dissolved by HNO_3 and H_2O_2. The mixture was evaporated to a certain volume. After cooling, 12 mL of distilled water was added. Thus, the prepared mixture was filtrated and placed in sample vials [31].

An atomic absorption spectrophotometer Perkin Elmer Company Model 3300/96 with MHS-10 hydride system was used to determine the quantity of elements such as Mn (λ = 279.8 nm), Ca (422.7 nm), Mg (285.2 nm), Fe (248.3 nm), Zn (213.9 nm), Cu (324.8 nm), Cd (228.8 nm), and Pb (283.3 nm). Standard solutions of appropriate concentrations were used to prepare the calibration diagrams. The range of concentrations of the standard solutions was 0.5-2.0 mg dm^{-3} for Cu, Zn, Mg, and 1.0-5.0 mg dm^{-3}, for Mn, Fe, Ca. All sample solutions were analyzed by AAS using an air-acetylene flame (2.0:10.0) for Cu, Zn, Mg, Mn, Fe and (3.8:10.0) for Ca. Blanks and standard reference materials: MEES-3 (Trace elements in sediments) and LGC7173 for moss material were used to verify the accuracy of the used method. The obtained values ranged from ± 5% of the certified values. Each measurement was performed in triplicate after which the mean values were calculated. The quantity of metals in the analyzed samples was expressed in terms of mg kg^{-1} of dry material.

Determination of organic matter in soil was based on wet burning of a soil sample using $K_2Cr_2O_7$ in an acidic medium. Colour change is used for spectrophotometric determination of organic carbon at a wavelength of 585 nm.

Enrichment and pollution assessment

Enrichment factors (EFs) were calculated in order to determine the maximum levels of elements potentially available to mosses from soil, as well as to evaluate the contribution from other sources

mainly induced by anthropogenic activities. EF relates the concentration of particular element of interest (X) to the concentration of a conservative soil element abundant in the Earth's crust (such as Ti, Al, Fe, etc.) in moss versus local parent material [32,33] as follows:

$$EF = \frac{\left(\frac{X}{reference\ element}\right)_{in\ moss}}{\left(\frac{X}{reference\ element}\right)_{in\ soil}} \quad (1)$$

Iron was used as the reference element for the calculation.

Besides, pollution level was also estimated by calculating contamination factor (CF) of each element. CF was determined as the ratio of the concentration of an element in moss samples to its background level in that moss. Calculation and the categorization of pollution levels have been done using the scales proposed by Fernández and Carballeira [34].

Statistical analysis

According to Shapiro-Wilk normality test, the variables do not meet the assumptions of normal distribution. Therefore, the differences between radionuclides and metal concentrations in the soil and the moss samples between localities were tested with Kruskal-Wallis nonparametric test. Correlations between radionuclides and other elements were tested through Spearman's coefficient. Multivariate statistic method (PCA - Principal component analysis) was used to reveal the relationship of the radionuclides, other elements, and localities. Statistical analysis was performed using the Statistica software package (version 10, 2010).

Results and discussion

Radioactivity

Specific activities of radionuclides in soil and moss samples are presented in Table 1, a wide spanning of values is obvious. Table 1 also presents the values of ambient dose equivalent rate (ADER) measured in the air, as well as the annual effective dose (D_E) calculated based on the specific activities of ^{226}Ra, ^{232}Th, ^{40}K, and ^{137}Cs in soil [35,36]. Specific activities of radionuclides in soil and moss samples were ordered in the following way: ^{40}K > ^{137}Cs > ^{232}Th > ^{226}Ra. The

mean specific activities of ^{226}Ra, ^{232}Th and ^{40}K in soil are similar to the worldwide averages of 32, 45 and 412 Bq kg^{-1}, respectively [35]. Activity concentrations of primordial radionuclides in moss are mostly comparable to the results of previous studies conducted in Serbia (Table S1). The highest levels of natural radionuclides were observed in sample K3 taken from the southern slopes of the Kopaonik mountain. The highest value of ADER in air was also measured at the same location. This can be related to geomorphology of the location i.e. to the presence of granite rocks which are known to exhibit an enhanced radioactivity due to the partial melting and fractional crystallisation of magma, which enables terrestrial radionuclides (such as uranium and thorium) to be concentrated in the liquid phase and become incorporated into silica-rich products [37,38].

Coefficients of variance obtained for ^{226}Ra, ^{232}Th, ^{40}K, ^{137}Cs, and ^{7}Be in mosses were mainly the lowest in Mokra Gora Mt. (48%, 50%, 24%, 68%, and 19%, respectively) in comparison to Rogozna (86%, 83%, 34%, 114% and 36%, respectively) and Kopaonik (112%, 131%, 20%, 108%, and 56%, respectively). The range of ^{137}Cs activity concentration in moss is lower than most of the results presented in Table S1. Čučulović et al. [39] reported ^{137}Cs activity concentrations from 16 to 384 Bq kg^{-1} in the region of Stara Planina Mountain for the period of 1996 - 1998. However, the mean value ± standard deviation (43.7±51.3) obtained in our study is higher than the value of 23±43 Bq kg^{-1} obtained in a recent study conducted in the whole country [12]. This could be explained by the fact that flat, mostly cultivated areas usually have lower ^{137}Cs activity concentration than mountain areas.

Kruskal-Wallis test showed that there was no significant difference among the mountains with regard to radionuclide concentrations in soil and mosses samples. However, the highest concentrations of ^{137}Cs were measured in soil and moss samples from Mokra Gora Mt. This can be related to vegetation features that might have affected the deposition, retention, migration, and absorption of this artificial radionuclide. It was observed that the samples with highest ^{137}Cs concentrations were collected in coniferous forests. According to Mann Whitney U test, the difference between ^{137}Cs in moss collected in deciduous forests and coniferous (or mixed) forests was statistically significant ($p=0.001$). It is probably related to acidic conifer needles that retain the soil moisture and make different substrate. Low pH leads to accumulation of organic matter due to inhibition of microbial activity [40]. ^{137}Cs fixation increases with moisture content and organic matter. Besides, it is typical that with the altitude increase, coniferous forests prevail and the precipitation regime becomes stronger.

A mean value of ^{7}Be concentration in mosses was 400.4 Bq kg^{-1}. The range values are lower than those obtained for eastern Serbia [41] and in good agreement with the range reported by Krmar et al. [12] for the whole country (Table S1). A great variation in ^{7}Be concentrations was observed. This could be explained by fluctuation in air currents, precipitations or some local factors which have an impact on ^{7}Be deposition. The medians of ^{7}Be specific activities were 281, 318 and 554 Bq kg^{-1} in moss samples from Kopaonik, Rogozna and Mokra Gora, respectively. ^{7}Be specific activity was shown to be correlated with altitude ($p < 0.05$). The highest concentrations of ^{7}Be in Mokra Gora Mt. are probably related to increased elevation, precipitation, atmospheric movements, prevailing wind direction and topography of the sampling sites.

Although mosses have no developed roots, they uptake natural radionuclides from soil by resuspension on the surface or transporting of soil particles by water, wind and gravity. ^{7}Be is a cosmogenic radionuclide; therefore it is directly obtained through atmospheric deposition. Even though ^{137}Cs is usually not precipitated through atmospheric deposition nowadays, it exists in soil and therefore, ^{137}Cs uptake is similar to the uptake of natural radionuclides. Physiological and morphological features (different growing ages of moss tissue, different proportion of sections that have different dynamic processes of biosorption and accumulation potential etc.) of the same moss species may vary in different localities, affecting the accumulation of airborne radionuclides [7, 42].

Metals

The results of measuring concentrations of metals in soil and moss samples are given in Table 2. The mean values of the metal concentrations in soil samples were ordered as follows: Fe > Ca > Mg > Mn > Cr > Zn > Ni > Cu, and for the moss samples, Ca > Mg > Fe > Be > Mn > Zn > Ni > Cu > Cr. Concentrations of Cd and Pb were below detection limit (1 mg kg^{-1}) in all samples. The examined species absorb higher concentrations of macroelements such as Ca and Mg as opposed to microelements such as Fe, Mn, Zn, Ni, Cu, and Cr which are present in lower concentrations in the substrate. Cr was not detected in most of the moss samples; Ni was only detected in moss samples from Kopaonik Mt. Comparing to results in the close neighborhood these values are similar to other studies (Table S1). Low concentrations of metals may be related to dilution due to

frequent precipitation and intensive biomass growing in the sampling period [3]. Trace elements are required by moss in low concentrations for certain metabolic functions and maintenance of homeostasis [43].

According to Harmens et al. [44] who summarized the results of measuring metal concentrations in mosses across Europe, the highest median concentration of Fe and Cr were reported in neighboring countries – Romania, Macedonia, Albania, and Bulgaria. The median of Fe concentration obtained in our study (1177 mg kg^{-1}) was slightly lower than those, but much higher than the value reported for Kosovo (312 mg kg^{-1}). On the contrary, the same study [44] identified Albania, Kosovo and Macedonia as the countries with lowest median concentrations of Cu measured in mosses (3.96, 3.04, and 3.54 mg kg^{-1}, respectively). The median of Cu concentration obtained in our study was 5.4 mg kg^{-1}.

The Kopaonik Mt. localities have the highest concentrations of metals like Mn, Ni, Ca, Mg, Zn and Cu in soil samples, comparing to the other two mountains. Also, Kopaonik Mt. is distinguished by increased concentrations of Mn, Ni, Mg, Fe, Zn, Cr, and Cu in the moss samples. The differences in the concentrations of metals among localities depend on the type of soil, the geological substrate on which it was formed, and the chemical and physical characteristics that differ due to the different influences of environmental factors on habitat [45].

Using the Kruskal-Wallis test, it was shown that there is a significant difference between the tested localities depending on the concentration of metals in soil samples and moss. For soil samples, it was shown that there was a statistically significant difference between the amount of Mn ($p = 0.003$), Ni ($p = 0.003$), Mg ($p = 0.011$), Cr ($p = 0.032$) and Cu ($p = 0.047$) between the Mokra Gora locality and the other two localities. Also, Kopaonik locality differs from the other two localities by the amount of Ca ($p = 0.003$) and Zn ($p = 0.005$). The localities do not differ significantly in the amount of Fe in the soil samples.

For moss samples, it was shown that there was a statistically significant difference between the amount of Mg ($p = 0.003$), Cu ($p = 0.017$) and Fe ($p = 0.025$) between Mokra Gora locality and the other two. Also, locality Kopaonik differs from the other two localities by the amount of Ni ($p = 0.001$) and Cr ($p = 0.029$), while locality Rogozna differs from the locality Mokra Gora and Kopaonik by the amount of Ca ($p = 0.003$) and Zn ($p = 0.007$). The localities do not differ significantly in the amount of Mn in the moss samples.

According to Serbian Soil Quality Regulation, regulatory limits for Cr, Cu, Ni, and Zn in the soil are 100, 36, 35, and 140 mg kg^{-1}, respectively [46]. These regulatory limits were exceeded in many soil samples from Kopaonik and Rogozna (Table 2), indicating the level of contamination that distorts ecological balance and implies further investigation as well as limitations in the soil management. Nevertheless, no high contamination by metals could be observed in moss samples collected at these locations. This fact indicates that metals in the soil samples are probably of natural origin rather than the result of wet and dry deposition. Therefore, this moss species cannot be considered as a reliable indicator of the presence of potentially toxic elements in the underlying soil. According to the soil samples analyzed in this study, Mokra Gora Mt. appeared to have the healthiest environment with regard to metals contamination. However, this conclusion should be taken with caution since the samples from Mokra Gora Mt. were collected at higher altitudes than others (Table 1).

Enrichment and contamination factors

Table 3 presents the results of calculating EFs of elements analyzed in moss samples. In theory, there is no enrichment of particular element in moss if EF=1, while any value greater than 1 indicates enrichment of the element relative to its level in soil [47]. However, in order to avoid possible errors in calculating EFs, it was suggested that elements should be considered as enriched when the average EF is greater than 3. For a greater significance, EF > 3 should be observed in at least 30% of the analyzed samples [48]. Accordingly, EFs of almost all elements presented in Table 3 indicate that there are sources of contamination other than soil in these locations. The lowest values of EFs were obtained for Cr and this result is in agreement with the findings of Fernández and Carballeira [47]. High values of EFs for Mn were obtained in all samples from Mokra Gora. Previous studies suggested that Mn may be introduced into mosses by leaching from higher plants rather than from anthropogenic sources [33]. Therefore, significantly higher values of EFs for Mn observed in Mokra Gora (in comparison to other two mountains) are probably caused by high precipitation and the type of vegetation that prevails in this mountain (coniferous or mixed forests).

Table 3 also presents contamination factors calculated for moss samples. According to the scale proposed by Fernández and Carballeira [34], following categories were established based on

the values of CF: CF<1 no contamination; 1–2 suspected; 2–3.5 slight; 3.5–8 moderate; 8–27 severe, and >27 extreme contamination. According to Table 3, most of the samples fall into the first three categories. Severe contamination by Ni was observed in three samples (K3, K4 and K6) from Kopaonik Mt. Sample K3 was also severely contaminated by Cr. The rest of the locations from Kopaonik were moderately contaminated by Ni, Fe or Cr. These results are in agreement with the study of Maxhuni et al. [49] who also reported high levels of Ni and Cr in northern areas of Kosovo (Mitrovica). The authors assumed that these elements mainly originated from the industrial emission of the refinery of "Trepča" and other mining activities. Although the sampling sites in our study are located in uninhabited mountain regions, relatively far from towns, high-traffic routes, and industrial areas, contaminants and pollutants can be transported to these locations by wet and dry deposition. Particularly, sampling sites K3 and K4 are located approximately 15 km northward from flotation tailings of "Trepča" mining complex, so the contamination is probably influenced by wind-blown dust from several slag dumps. However, according to CF, extreme contamination was not observed in any of the analyzed locations.

Correlation analysis

The results of the correlation analysis are presented in Tables 4 and S2. It has been shown that there are significant correlations between certain elements in the samples. According to Ajmone-Marsan et al. [50] a high positive correlation between the concentrations of Cr and Ni in analyzed soils (Spearman's rho=0.958) indicates their natural origin. This assumption is supported by the fact that Ni was positively correlated with altitude. On the contrary, strong negative correlations of Mn, Zn, Cr, and Cu with altitude were observed. Some of the possible reasons could be found in increasing precipitation trends with elevation, as well as in decreasing the effects of pollution caused by anthropogenic activities. Besides, soil pH was strongly negatively correlated with altitude. According to Caporale and Violante [51], pH affects the sorption of metal cations on variable charge minerals either by changing the number of sites available for sorption or by changing the concentration of cation species, while sorption of anions usually decreases with increasing pH due to decrease in positive charge of minerals.

Strong positive correlations between the pairs of natural radionuclides (^{226}Ra, ^{232}Th, and ^{40}K) in the soil as well as in moss samples can be explained by similar geochemical behavior which influences radionuclide distribution based on the topography and environmental processes such as

weathering. Ambient dose equivalent rate measured in air was moderately correlated with the annual effective dose calculated from the specific activities of radionuclides in soil (Spearman's rho = 0.514). ^{137}Cs in soil was strongly correlated with organic matter content (Spearman's rho = 0.840). This result supports the findings of previous studies suggesting that organic matter affects the mobility, adsorption to soils and biological availability of radionuclides in the environment [52,53].

Other researchers also confirmed the existence of a synergistic and antagonistic relationship between individual elements [43, 54]. The results of the correlation between certain elements show that there is an antagonistic effect. Also, some authors report that certain synergistic effects have been observed for antagonist pairs of elements, which largely depend on the corresponding reaction of the plant species [43].

The last row of Table 4 presents the Spearman's correlation coefficient between the elements in soil and moss samples. The result indicates mainly weak correlations (except for Ni and Mg) which is in agreement with the assumption that these moss species absorb water and nutrients as well as other trace elements primarily through wet and dry deposition.

Principal component analysis

The data obtained for radionuclides and other elements in the soil and moss samples from three different mountains were studied by multivariate component statistics. Figure 2A shows the bi-plot of the analysis of the activity concentration of radionuclides and elements in the soil and moss samples.

PC analysis was performed by extracting the first four PC axes which explain 53.86% of the total variation, with the first axis (PC-I) describing 27.87%, while the second PC axis (PC-II) describes 25.99% of the total variation. The first two components separate the activity concentration of radionuclides and other elements in soil and moss samples. The highest load on the first PC axis (PC-I) is shown by the characters ThS (-0.942), RaS (-0.938), D_E (-0.870), ThM (-0.849), RaM (-0.821), ADER (-0.815) had negative values, while the lowest load are by the characters ZnM (0.045) and ZnS (-0.029). Different loads in value and sign occur for all components, which indicate that the type of variation includes changes that depend on the locality. On the PC-II axis, the characters CuM (0.834), MnS (0.823) and MgM (0.822) and ZnS (0.803)

had positive values and show the highest load (Table S3). According to the factor structure of the correlation matrix, the contributions of the characters along the PC-I and PC-II axes show that the characters with the highest load contribute to the difference in the amount of elements between the localities. Screen plot and PC loadings of the localities relative to the activity concentration of the radionuclides and other elements in the soil and moss samples are shown in Figure 2B.

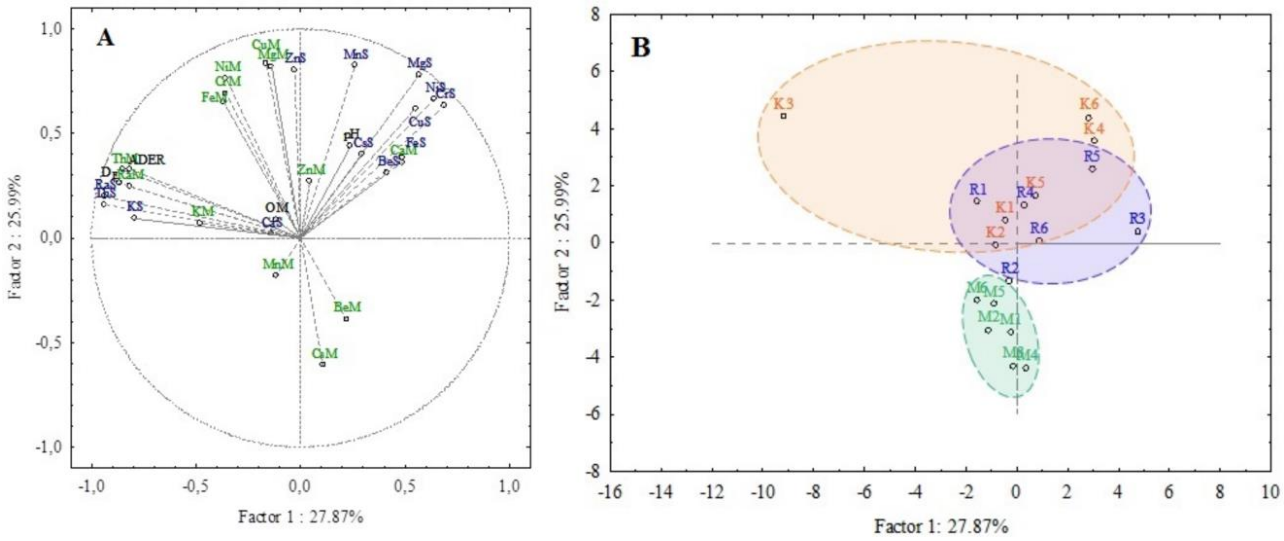

Fig. 2 A - Biplot for PCA-soil and moss model for dependence of nuclides and elements contents from different sampling locations; B - Principal components of localities based for nuclides and element content in soil and moss samples

The PCA showed that the investigated samples tended to form two groups. Based on the contribution vector of the locality elements, the graph of the population practice along the PC-I and PC-II axes (Fig. 2B) shows that the localities Kopaonik and Rogozna differ from Mokra Gora Mt. with an activity concentration of radionuclides and other elements. Samples from Mokra Gora Mt. are distinguished by the highest values of Mn, Be and Cs in moss samples. Therefore, moss samples from Mokra Gora Mt. are characterized by a higher presence of ^{137}Cs (Fig. 2B). The elements contributing to the highest variability of Kopaonik and Rogozna localities along the PC-I axis are Mg, Ni and Cr in the soil samples. Based on the obtained results, it can be concluded that the concentration of certain radionuclides and other elements in the soil and moss samples depends on concentration of the same in the substrate. Therefore, environmental factors could influence the radionuclides and metal contents of the populations.

Conclusions

The mean specific activities of ^{226}Ra, ^{232}Th and ^{40}K measured in soil samples were comparable to the worldwide averages. However, wide ranges of values were observed. Strong correlations were found between the pairs of natural radionuclides (^{226}Ra, ^{232}Th and ^{40}K) in soil as well as in moss samples. The difference among three mountains with regard to radionuclide concentrations was not statistically significant. However, the highest concentrations of ^{137}Cs were measured in soil and moss samples from Mokra Gora Mt. probably due to elevation and vegetation features. ^{137}Cs in mosses collected in coniferous (or mixed) forests was significantly higher than that in deciduous forests indicating that vegetation has an important role in ^{137}Cs deposition, retention, migration, and absorption in the environment. ^{137}Cs in soil was strongly correlated with organic matter content. ^{7}Be specific activity in moss samples was positively correlated with altitude.

There is a significant difference among the localities with regard to the concentration of metals measured in soil and moss samples. The concentrations of Ni, Cr, Cu and Zn exceeded regulatory limits in many soil samples from Kopaonik and Rogozna, while Mokra Gora Mt. appeared to have the healthiest environment with regard to heavy metal concentrations in soil. Strong negative correlations of Mn, Zn, Cr, and Cu in soil with altitude were observed. The highest values of potentially toxic elements in mosses were also detected in the samples from Kopaonik Mt (severe contamination was observed in some samples). EFs of almost all elements in mosses indicate that there are sources of contamination other than soil in these locations. The highest values of EFs for Mn obtained in the samples from Mokra Gora might be associated with the vegetation type. The studied species grown on the different substrate type on different localities could accumulate analyzed metals in different amounts.

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Compliance with ethical standards

Conflicts of interest: There are no conflicts to declare

References

1. UNSCEAR (2000) Sources and effects of ionizing radiation, Report to General Assembly, with Scientific Annexes. United Nations, New York
2. Boquete MT, Fernandez JA, Aboal JR, Carballeira A, Martínez-Abaigar J, Tomas-Las-Heras R, Núnez-Olivera E (2016) Trace element concentrations in the moss *Hypnum cupressiforme* growing in a presumably unpolluted area. Chemosphere. 158:177–183
3. Dolegowska S, Migaszewski ZM (2019) Biomonitoring with mosses: Uncertainties related to sampling period, intrasite variability, and cleaning treatments. Ecol Indic. 101:296–302
4. Zechmeister HG (1995) Growth rates of five pleurocarpous moss species under various climatic conditions. J Bryol. 18:455–468
5. Aceto M, Abollino O, Conca R, Malandrino M, Mentasti E, Sarzanini C (2003) The use of mosses as environmental metal pollution indicators. Chemosphere. 50:333–342
6. Fernandez JA, Carballeira A (2000) Evaluation of contamination by different elements in terrestrial mosses. Arch Environ Contam Toxicol 40:461–468
7. Kılıç Ö, Belivermiş M, Sıkdokur E, Sezer N, Erentürk SA, Haciyakupoglu S, Madadzada A, Frontasyeva M (2019) Assessment of ^{210}Po and ^{210}Pb by moss biomonitoring technique in Thrace region of Turkey. J Radioanal Nucl Chem. 322:699–706
8. Qin X, Zhu Y, Yu J, Xian X, Liu C, Yang Y, Tao N (2018) Chemical sensing in real time with plants using a webcam. Anal Chem. 90:13030–13035
9. Schnyder E, Štrok M, Kosonen Z, Skudnik M, Mazej D, Jeran Z, Thöni L (2018) Lead concentrations and stable lead isotope ratios in moss in Slovenia and Switzerland. Ecol Indic. 95:250–259
10. Ivanić M, Fiket Ž, Medunić G, Furdek Turk M, Marović G, Senčar J, Kniewald G (2019) Multi-element composition of soil, mosses and mushrooms and assessment of natural and artificial radioactivity of a pristine temperate rainforest system (Slavonia, Croatia). Chemosphere. 215:668–677
11. Krmar M, Mihailović D, Arsenić I, Radnović D, Pap I (2016) Beryllium-7 and ^{210}Pb atmospheric deposition measured in moss and dependence on cumulative precipitation. Sci Total Environ. 541:941–948

12. Krmar M, Radnović D, Hansman J, Mesaroš M, Betsou C, Jakšić T, Vasić P (2018) Spatial distribution of ^{7}Be and ^{137}Cs measured with the use of biomonitors. J Radioannal Nucl Chem. 318:1845–1854
13. Mitrović B, Ajtić J, Lazić M, Andrić V, Krstić N, Vranješ B, Vićentijević M (2016) Natural and anthropogenic radioactivity in the environment of Kopaonik mountain, Serbia. Environ Pollut. 215:273–279
14. Ajtić JV, Sarvan DZ, Mitrović BM, Čučulović AA, Čučulović RD, Frontasyeva MV (2018) Elemental composition of moss and lichen species in Eastern Serbia. Nucl Technol Radiat Prot. 33:275-285
15. Aničić Urošević M, Vuković G, Vasić P, Jakšić T, Nikolić D, Škrivanj S, Popović A (2018) Environmental implication indices from elemental characterisations of collocated topsoil and moss samples. Ecol Indic. 90:529–539
16. Barandovski L, Frontasyeva VM, Stafilov T, Šajn R, Ostrovnaya MT (2015) Multielement atmospheric deposition in Macedonia studied by the moss biomonitoring technique. Environ Sci Pollut Res. 22:16077–16097
17. Lazo P, Steinnes E, Qarri F, Allajbeu S, Kane S, Stafilov T, Frontasyeva MV, Harmens H (2018) Origin and spatial distribution of metals in moss samples in Albania: a hotspot of heavy metal contamination in Europe. Chemosphere. 190:337–349
18. Augusto S, Máguas C, Branquinho C (2013) Guidelines for biomonitoring persistent organic pollutants (POPs), using lichens and aquatic mosses – A review. Environ Pollut. 180:330–338
19. Harmens, H., Norris, D., Mills, G., and the participants of the moss survey (2013). Heavy metals and nitrogen in mosses: spatial patterns in 2010/2011 and long-term temporal trends in Europe. ICP Vegetation Programme Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK
20. Wu Q, Wang X, Zhou Q (2014) Biomonitoring persistent organic pollutants in the atmosphere with mosses: Performance and application. Environ Int. 66:28–37
21. Dragović S, Mihailović N (2009) Analysis of mosses and topsoils for detecting sources of heavy metal pollution: multivariate and enrichment factor analysis. Environ Monit Assess 157:383–390
22. Dragović S, Mihailović N, Gajić B (2010) Quantification of transfer of ^{238}U, ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs in mosses of a semi-natural ecosystem. J Environ Radioactiv. 101:159–164

23. Grdović S, Vitorović G, Mitrović B, Andrić V, Petrujkić B, Obradović M (2010) Natural and anthropogenic radioactivity of feedstuffs, mosses and soil in the Belgrade environment, Serbia. Arch Biol Sci. 62:301–307
24. Mitrović B, Vitorović G, Vitorović D, Pantelić G, Adamović I (2009) Natural and anthropogenic radioactivity in the environment of mountain region of Serbia. J Environ Monit. 11:383–388
25. Republic hydrometeorological service of Serbia, Republic of Serbia, Annual report for 2018. Belgrade (2019)
http://www.hidmet.gov.rs/latin/meteorologija/klimatologija_godisnjaci.php
26. Ivanović R, Ivanović M, Đokić M (2011) Hydrographic resources of Ibarski Kolašin in the function of tourism development. Bulletin of the Serbian Geographical Society XCI-1
27. Radak ĐB, Bokić SB, Preljević FN, Rat MM, Janjić BĐ, Knežević MJ, Ančkov TG (2016) Vascular flora of the Prometanj site (Mokra Gora, northern Prokletije Mt.). Zbornik Matice Srpske za prirodne nauke 130:53–73 (In Serbian)
28. Frahm JP (2009) A preliminary study of the infraspecific taxa of *Hypnum cupressiforme* in Europe. Archive for Bryology 40:1–10
29. Currie LA, 1968. Limits for qualitative detection and quantitative determination. Application to radiochemistry. Anal Chem. 40:586–593
30. Done L, Ioan M-R, 2016. Minimum Detectable Activity in gamma spectrometry and its use in low level activity measurements. Appl Radiat Isotopes. 114:28–32
31. Shah A, Niaz A, Ullah N, Rehman A, Akhlaq M, Zakir M, Khan MS (2013) Comparative study of heavy metals in soil and selected medicinal plants. J Chem. 2013:1–5
32. Puxbaum H (1991). Metal compounds in the atmosphere. In E. Merian (Ed.), Metals and their Compounds in the Environment. Occurrence, Analysis and Biological Relevance, pp. 176–257.
33. Dragovic S, Mihailovic N (2008). Analysis of Mosses and Topsoils for Detecting Sources of Heavy Metal Pollution: Multivariate and Enrichment Factor Analysis. Environ Monit Assess. 157:383–90.
34. Fernández JA, Carballeira A (2001) Evaluation of Contamination, by Different Elements, in Terrestrial Mosses. Arch Environ Contam Toxicol. 40:461–468

35. UNSCEAR (2008) Exposure of the public and workers from various sources of radiation. United Nations, New York
36. Kapdan E, Varinlioglu A, Karahan G (2011) Radioactivity levels and health risks due to radionuclides in the soil of Yalova, northwestern Turkey. Int J Environ Res. 5:837–846
37. Buket C, Füsun Çam N, Günseli Y, Osman C (2010) Natural radioactivity (^{226}Ra, ^{232}Th and ^{40}K) and assessment of radiological hazard in the Kestanbol granitoid, Turkey. Radiat Prot Dosim. 141:192–198
38. El-Taher A, Uosif MAM, Orabi AA (2007) Natural radioactivity levels and radiation hazard indices in granite from Aswan to Wadi El-Allaqi southeastern desert, Egypt. Radiat Prot Dosim. 124:148–154
39. Čučulović A, Popović D, Čučulović R, Ajtić J (2012) Natural radionuclides and ^{137}Cs in moss and lichen in Eastern Serbia. Nucl Technol Radiat. 27:44–51
40. Maly S, Fiala P, Reininger D, Obdrzalkova E (2014) The relationships among microbial parameters and the rate of organic matter mineralization in forest soils, as influenced by forest type. Pedobiologia 57: 235–244
41. Čučulović A, Čučulović R, Sabovljević M, Radenković MB, Veselinović D (2016) Natural radionuclide uptake by mosses in eastern Serbia in 2008-2013. Arh Hig Rada Toksikol. 67:31–37
42. Długosz-Lisiecka M (2017) Kinetics of ^{210}Po accumulation in moss body profles. Environ Sci Pollut R. 24:20254–20260
43. Kabata-Pendias A (2011) Trace elements in soils and plants, fourth ed. CRC Press, Taylor and Francis Group, Boca Raton, New York, London
44. Harmens H, Norris DA, Sharps K, Mills G, Alber R, Aleksiayenak Y, et al. (2015) Heavy metal and nitrogen concentrations in mosses are declining across Europe whilst some "hotspots" remain in 2010. Environ Pollut. 200:93-104
45. Zlatić NM, Stanković MS (2019) Effects of calcareous and serpentinite parent material on the mineral characteristics of soils and plant material of *Teucrium montanum* L. (Lamiaceae). Environ Monit Assess. 191:564
46. Official Gazette of the Republic of Serbia 30/2018 (In Serbian)

47. Fernández JA, Carballeira A (2001) A comparison of indigenous mosses and topsoils for use in monitoring atmospheric heavy metal deposition in Galicia (northwest Spain). Environ Pollut. 114::431–441
48. Dongarrà G, Varrica D (1998) The presence of heavy metals in air particulate at Vulcano island (Italy). Sci Tot Environ. 212:1–9
49. Maxhuni A, Lazo P, Kane S, Qarri F, Marku E, Harmens H (2016). First survey of atmospheric heavy metal deposition in Kosovo using moss biomonitoring. Environ Sci Pollut Res. 23:744–755
50. Ajmone-Marsan F, Biasioli M, Kralj T, Grcman H, Davidson CM, Hursthouse AS, et al. (2008) Metals in particle-size fractions of the soils of five European cities. Environ Pollut. 152:73–81
51. Caporale AG, Violante A (2016) Chemical Processes Affecting the Mobility of Heavy Metals and Metalloids in Soil Environments. Curr Pollution Rep. 2:15–27
52. Dragović S, Gajić B, Dragović R, Janković-Mandić L, Slavković-Beškoski L, Mihailović N, Momčilović M, Ćujić M (2012) Edaphic factors affecting the vertical distribution of radionuclides in the different soil types of Belgrade, Serbia. J Environ Monit. 14:127–137
53. Koarashi J, Nishimura S, Atarashi-Andoh M, Muto K, Matsunaga T (2019) A new perspective on the ^{137}Cs retention mechanism in surface soils during the early stage after the Fukushima nuclear accident. Sci Rep. 9:7034
54. Gonneau C, Genevois N, Frérot H, Sirguey C, Sterckeman T (2014) Variation of trace metal accumulation, major nutrient uptake and growth parameters and their correlations in 22 populations of *Noccaea caerulescens*. Plant Soil. 384:271–287
55. Lazo P, Stafilov T, Qarri F, Allajbeu S, Bekteshi L, Frontasyeva M, Harmens H (2019) Spatial distribution and temporal trend of airborne trace metal deposition in Albania studied by moss biomonitoring. Ecol Indic. 101:1007–1017
56. Stafilov T, Šajn R, Barandovski L, Bačeva AK, Malinovska S (2018) Moss biomonitoring of atmospheric deposition study of minor and trace elements in Macedonia. Air Qual Atmos Hlth. 11:137–152
57. Harmens H, Norris DA, Steinnes E, Kubin E, Piispanen J, Alber R et al. (2010) Mosses as biomonitors of atmospheric heavy metal deposition: spatial patterns and temporal trends in Europe. Environ Pollut. 158:3144–3156

Table 1 Characteristics of the sampling locations (attitude, vegetation, soil pH, and organic matter content), specific activities of radionuclides in soil and moss samples, ambient dose equivalent rates (ADER), and annual effective doses calculated from terrestrial radionuclides (D_E)

		Latitude/Longitude		ALT. [m]	Vegetat.	pH	OM [%]	ADER [μSv h^{-1}]	^{226}Ra [Bq kg^{-1}]		^{232}Th [Bq kg^{-1}]		^{40}K [Bq kg^{-1}]		^{137}Cs [Bq kg^{-1}]		^{7}Be [Bq kg^{-1}]		D_E [μSv y^{-1}]
		N	E						soil	moss	soil	moss	soil	moss	soil	moss	soil	moss	
Kopaonik	**K1**	43°13.347'	20°41.870'	571	D	6.95	12.24	0.13	24.3	3.8	38.2	4.0	393	198	88.0	19.9	nd	282	75.6
	K2	43°13.223'	20°41.755'	478	D	7.41	6.01	0.10	33.7	2.4	50.4	4.9	562	157	47.3	10.5	nd	280	92.4
	K3	42°55.802'	20°51.234'	808	D	4.90	7.85	0.29	118.4	13.1	143.4	27.1	1236	170	51.6	5.2	nd	333	244.4
	K4	42°57.344'	20°50.128'	489	D	6.26	5.75	0.11	14.4	1.9	14.8	3.4	160	118	119.3	63.8	7.8	717	45.5
	K5	43°01.700'	20°50.531'	673	D	6.71	0.68	0.12	17.6	1.9	33.0	3.3	418	139	nd	20.9	nd	248	55.8
	K6	43°00.814'	20°49.072'	495	D	7.09	9.51	0.11	13.5	1.2	19.6	1.8	244	124	167.8	3.8	nd	187	60.2
Rogozna	**R1**	42°57.530'	20°37.964'	782	D	7.61	2.15	0.15	37.0	6.5	65.1	10.1	1130	235	nd	11.1	nd	238	127.0
	R2	42°58.437'	20°37.377'	920	D	4.03	7.41	0.11	28.2	1.9	49.6	4.5	450	114	52.8	4.5	nd	358	83.8
	R3	42°56.524'	20°45.979'	629	D	6.74	0.88	0.10	1.9	nd	1.6	nd	22	79	16.4	4.9	3.5	508	5.9
	R4	43°11.165'	20°42.286'	489	D	7.75	4.18	0.09	29.3	2.4	51.7	4.2	737	162	30.8	20.5	nd	278	97.3
	R5	42°57.818'	20°48.435'	514	D	5.03	9.07	0.12	17.3	1.0	22.3	0.8	161	120	443.4	68.8	nd	505	102.1
	R6	43°09.995'	20°39.218'	614	D	6.02	3.90	0.09	9.9	7.3	17.5	11.20	174	183	15.1	8.9	nd	192	29.8
Mokra Gora	**M1**	42°53.489'	20°34.842'	1669	CF	6.12	7.15	0.14	17.9	5.0	19.0	6.3	213	205	138.2	126.2	nd	593	56.2
	M2	42°52.215'	20°31.798'	1691	M	4.41	8.21	0.12	33.9	2.9	47.0	4.4	590	158	91.5	101.3	nd	556	98.1
	M3	42°54.617'	20°33.715'	1348	M	4.18	8.02	0.08	31.3	2.7	39.3	1.6	364	118	20.5	114.4	nd	555	68.6
	M4	42°55.060'	20°34.407'	1104	M	4.98	5.51	0.12	20.8	1.1	31.9	2.9	241	106	19.8	168.1	nd	553	50.8
	M5	42°54.453'	20°34.404'	952	D	6.04	3.42	0.12	40.6	1.8	65.8	2.3	1034	133	14.6	33.2	nd	507	126.9
	M6	42°56.099'	20°38.812'	702	D	5.79	0.82	0.16	35.1	3.6	54.8	6.1	760	149	0.8	1.0	nd	319	99.5

D – deciduous forest; M – mixed (coniferous and broad leaved) forest; CF – coniferous forest; nd – not detected

Table 2 Metals content in soil and moss samples (mg kg^{-1} d.w.)

		Mn		**Ni**		**Ca**		**Mg**		**Fe**		**Zn**		**Cr**		**Cu**	
		[mg kg^{-1}]															
		soil	moss	soil	moss	soil	moss	soil	moss	soil	moss	soil	moss	soil	moss	soil	moss
Kopaonik	**K1**	602.9	110.4	**40.5***	7.51	11459	4929	4686	1492	33654	1315	**168.3***	70.2	55.4	nd	23.4	5.46
	K2	485.7	106.4	**65.5***	12.1	21288	3843	2604	1176	33936	1361	80.6	79.8	52.1	nd	15.2	5.71
	K3	466.6	76.0	29.27	48.6	7301	3668	2918	3941	22547	1702	**148.4***	28.1	34.4	8.34	10.7	9.18
	K4	541.3	59.6	**190.7***	33.5	8143	5431	8568	4260	50305	1285	127.8	26.3	**187.8***	5.12	**43.1***	5.62
	K5	484.7	107.9	**101.5***	16.5	6545	5513	6435	3103	26313	1069	75.7	34.6	**135.8***	4.74	31.4	8.14
	K6	526.7	62.1	**166.6***	26.4	10750	5405	9255	2385	48050	1037	**217.1***	88.1	**161.5***	2.42	**122.4***	7.92
Rogozna	**R1**	339.4	97.8	**79.7***	nd	5961	7003	4640	1828	64100	1653	59.4	18.3	**120.3***	nd	30.4	5.61
	R2	346.5	66.7	27.7	4.35	1785	5792	3541	1241	29527	1325	29.2	19.0	81.9	nd	9.08	4.82
	R3	585.9	87.1	**197.2***	nd	2035	7339	7620	1170	47437	1014	53.1	17.0	**160.1***	nd	**60.4***	3.11
	R4	590.4	61.6	**48.7***	8.54	3416	8595	4368	2752	28561	1026	108.3	28.9	90.7	nd	**48.8***	7.57
	R5	638.7	89.1	**203.1***	7.26	3267	8232	6651	2439	56225	1391	110.7	22.6	**189.0***	2.51	**45.2***	5.43
	R6	390.1	56.3	**38.2***	nd	2121	6361	5513	1088	55968	1380	35.0	10.2	**115.8***	nd	33.9	5.81
Mokra Gora	**M1**	60.4	72.8	5.81	nd	2054	5411	1452	1148	34135	946	25.1	23.1	37.5	nd	9.57	2.34
	M2	285.1	106.1	11.9	nd	34352	5563	1106	1026	22548	779	44.2	35.8	41.9	nd	11.0	3.04
	M3	70.8	83.2	14.5	nd	1926	3776	927	884	26082	716	20.9	24.4	38.6	nd	11.3	1.92
	M4	88.9	89.7	11.7	nd	2211	3510	1019	821	32760	669	21.8	33.1	51.5	nd	7.88	1.95
	M5	206.5	67.8	24.6	nd	2548	4509	3428	972	36948	811	73.4	19.45	63.4	nd	20.1	1.62
	M6	152.6	85.3	20.5	nd	2041	3351	3198	951	33404	1329	58.4	25.1	64.2	nd	14.2	nd

*exceeding regulatory limits
nd – not detected

Table 3 Enrichment factors (EF) and contamination factors (CF) of elements in mosses compared to the respective soils

		EF							***CF***							
	Sample	**Mn**	**Ni**	**Ca**	**Mg**	**Zn**	**Cr**	**Cu**	**Mn**	**Ni**	**Ca**	**Mg**	**Fe**	**Zn**	**Cr**	**Cu**
Kopaonik	**K1**	11.5	11.6	26.9	19.9	26.1	-	14.6	1.23	3.13	1.95	1.05	4.20	1.76	-	0.96
	K2	13.7	11.6	11.3	28.3	62.0	-	23.5	1.18	5.04	1.52	0.83	4.35	2.00	-	1.00
	K3	10.2	104.0	31.5	84.6	11.9	15.2	53.7	0.84	**20.25***	1.45	2.77	5.44	0.70	**9.70***	1.61
	K4	6.9	11.0	41.8	31.1	12.9	1.7	8.2	0.66	**13.96***	2.15	2.99	4.10	0.66	5.95	0.99
	K5	13.9	10.2	52.7	30.2	28.6	2.2	16.2	1.20	6.88	2.18	2.18	3.42	0.87	5.51	1.43
	K6	7.4	9.9	31.5	16.1	25.4	0.9	4.1	0.69	**11.00***	2.14	1.67	3.31	2.20	2.81	1.39
Rogozna	**R1**	18.0	-	73.6	24.7	19.3	-	11.6	1.09	-	2.77	1.28	5.28	0.46	-	0.98
	R2	12.1	9.8	203.1	22.0	40.7	-	33.2	0.74	1.81	2.29	0.87	4.23	0.48	-	0.85
	R3	9.3	-	225.8	9.6	20.0	-	3.2	0.97	-	2.90	0.82	3.24	0.43	-	0.55
	R4	6.5	11.0	157.5	39.5	16.7	-	9.7	0.68	3.56	3.40	1.93	3.28	0.72	-	1.33
	R5	8.7	2.2	157.8	23.0	12.8	0.8	7.5	0.99	3.03	3.25	1.71	4.44	0.57	2.92	0.95
	R6	9.0	-	187.8	12.4	18.2	-	10.7	0.63	-	2.52	0.76	4.41	0.26	-	1.02
Mokra Gora	**M1**	75.5	-	165.0	49.5	57.6	-	15.3	0.81	-	2.14	0.81	3.02	0.58	-	0.41
	M2	23.3	-	10.1	58.1	50.7	-	17.3	1.18	-	2.20	0.72	2.49	0.90	-	0.53
	M3	73.6	-	122.8	59.7	73.1	-	10.6	0.92	-	1.49	0.62	2.29	0.61	-	0.34
	M4	63.2	-	99.4	50.5	95.1	-	15.5	1.00	-	1.39	0.58	2.14	0.83	-	0.34
	M5	20.6	-	110.8	17.8	16.6	-	5.0	0.75	-	1.78	0.68	2.59	0.49	-	0.28
	M6	35.0	-	102.8	18.6	26.9	-	-	0.95	-	1.32	0.67	4.25	0.63	-	-

*severe contamination

Table 4 The Spearman correlation matrix for elements measured in soil samples and correlation coefficients between the elements in soil and moss (the last row)

Metals	^{226}Ra	^{232}Th	^{40}K	^{137}Cs	Mn	Ni	Ca	Mg	Fe	Zn	Cr	Cu	pH	OM	ALT.
^{226}Ra	1	0.948**	0.915**	-0.284	-0.412	-0.470*	0.137	-0.631**	-0.445	-0.022	-0.600**	-0.531*	-0.174	-0.032	0.384
^{232}Th		1	0.967**	-0.350	-0.240	-0.309	-0.123	-0.463	-0.416	0.108	-0.434	-0.377	-0.063	-0.092	0.208
^{40}K			1	-0.382	-0.259	-0.313	0.222	-0.408	-0.430	0.139	-0.422	-0.335	0.024	-0.141	0.222
^{137}Cs				1	0.315	0.095	0.308	0.116	0.061	0.321	0.008	0.031	-0.134	0.840**	-0.154
Mn					1	0.843**	0.422	0.742**	0.280	0.759**	0.626**	0.734**	0.488*	0.203	-0.823**
Ni						1	0.282	0.868**	0.529*	0.649**	0.845**	0.841**	0.540*	-0.069	0.787**
Ca							1	0.164	-0.028	0.686**	0.028	0.216	0.410	0.346	-0.381
Mg								1	0.608**	0.602**	0.903**	0.847**	0.480*	-0.096	-0.677**
Fe									1	0.189	0.657**	0.548*	0.434	-0.127	-0.424
Zn										1	0.395	0.564*	-0.513*	0.269	-0.703**
Cr											1	0.816**	0.401	0.228	-0.633**
Cu												1	0.643**	-0.125	-0.736**
pH													1	-0.255	-0.659**
OM														1	0.007
ALT.															1
Soil/Moss	0.446	0.399	0.445	0.194	0.042	0.530*	-0.038	0.633**	0.329	0.463	0.114	0.447	-	-	-

**Correlation is significant at the 0.01 level

*Correlation is significant at the 0.05 level

Supplementary information

Table S1 Comparison with data from neighboring countries, regions and mountain areas of Serbia

Serbia	^{226}Ra	^{232}Th	^{40}K	^{137}Cs	^{7}Be	
			[Bq kg^{-1}]			Reference
Whole country	-	-	128-2235	BDL-296	60-666	[12]
Eastern Serbia	1.1-41	1.4-28	64-484	-	88-227	[41]
Mt. Kopaonik	nd-39	nd-37	104-386	9.4-228	-	[13]
Mt. Zlatibor	0.9-25.8	0.8-13.7	44.5-692	112-1248	-	[22]
Mt. Tara	-	<0.8-7.2	21.1-197.7	574-836	-	[24]
Mt. Maljen	-	6.4*	191.2*	1200*	-	[24]
Mt. Kosmaj	75*	18.4*	370*	99*	-	[23]
Mt. Kopaonik	1.2-13.1	1.8-27.1	118.4-197.7	3.8-63.8	186.7-717.4	This study
Mt. Rogozna	nd-7.3	nd-11.20	79.4-235.0	4.5-68.8	191.6-508.1	
Mt. Mokra Gora	1.1-5.0	1.6-6.3	105.8-204.6	1.0-168.1	319.2-592.6	

Country/region/ mountain area	Mn	Ni	Ca	Mg	Fe	Zn	Cr	Cu	
					[mg kg^{-1}]				Reference
Albania	-	5.81	-	-	1629	13.8	4.83	3.96	[19]
	63.2	7.6	6509	1550	1735	18	9.3	10.0	[55]
Northern Macedonia	-	3.45	-	-	1490	19.9	3.48	3.54	[19]
	160	3.5	6900	1900	1700	30	5.7	4.6	[56]
Serbia	-	4.43	-	-	2267	29.0	6.44	11.1	[57]
	-	4.7	-	-	2250	33	7.1	12	[14]
Kosovo and Metohija	86.2	2.0	-	-	312	38.5	2.63	3.04	[19]
	360	5.4	-	-	2484	36.8	6.83	25.61	[15]
Mt. Zlatibor	80.8	11.9	-	-	-	42.4	7.10	7.30	[21]
Mts. Kopaonik, Rogozna, Mokra Gora	84.2	2.2	5420	1208.5	1177.0	25.7	0.0	5.4	This study

*mean value

nd – not detected

BDL – below detection level

Table S2 The Spearman's correlation coefficients in the moss samples

Metals	^{226}Ra	^{232}Th	^{40}K	^{137}Cs	^{7}Be	Mn	Ni	Ca	Mg	Fe	Zn	Cr	Cu	pH	OM	ALT.
^{226}Ra	1	0.857**	0.831**	-0.103	-0.201	-0.010	-0.069	-0.174	0.005	0.397	-0.054	-0.039	0.171	-0.028	0.041	0.210
^{232}Th		1	0.740**	-0.259	-0.261	-0.100	0.014	-0.112	0.082	0.529*	-0.086	0.085	0.249	0.001	-0.131	0.108
^{40}K			1	-0.040	-0.381	0.115	0.012	0.073	0.181	0.408	0.075	-0.027	0.302	0.366	0.032	-0.009
^{137}Cs				1	0.620**	0.185	-0.246	-0.028	-0.220	-0.560*	0.088	0.014	-0.327	-0.220	0.179	0.403
^{7}Be					1	-0.022	-0.279	-0.176	-0.296	-0.534*	-0.127	0.017	-0.608**	-0.515*	0.166	0.496*
Mn						1	-0.080	-0.168	-0.108	0.007	0.375	0.161	-0.106	0.090	0.034	0.130
Ni							1	-0.017	0.843**	0.391	0.548*	0.705**	0.784**	0.279	0.292	-0.625**
Ca								1	0.410	0.170	-0.404	-0.103	0.309	0.302	-0.090	-0.286
Mg									1	0.531*	0.189	0.594**	0.812**	0.408	0.112	-0.593**
Fe										1	-0.187	0.490*	0.517*	0.164	-0.022	-0.465
Zn											1	0.276	0.304	0.224	0.412	-0.241
Cr												1	0.508*	0.051	0.074	0.447
Cu													1	0.439	0.086	-0.595**
pH														1	-0.255	-0.659**
OM															1	0.007
ALT.																1

**Correlation is significant at the 0.01 level

*Correlation is significant at the 0.05 level

Table S3 Factor loading for elements in plants and mosses, soil characteristics and doses

Variable	PC-I	PC-II
RaS	-0.938	0.198
RaM	-0.821	0.247
ThS	-0.942	0.161
ThM	-0.849	0.323
KS	-0.796	0.092
KM	-0.476	0.070
CsS	0.296	0.402
CsM	0.106	-0.609
BeS	0.418	0.311
BeM	0.219	-0.389
MnS	0.260	0.823
MnM	-0.116	-0.181
NiS	0.639	0.664
NiM	-0.357	0.764
CaS	-0.142	0.017
CaM	0.487	0.363
MgS	0.567	0.779
MgM	-0.138	0.822
FeS	0.491	0.384
FeM	-0.368	0.649
ZnS	-0.029	0.803
ZnM	0.045	0.271
CrS	0.688	0.633
CrM	-0.357	0.691
CuS	0.550	0.620
CuM	-0.164	0.834
D_E	-0.870	0.261
pH	0.241	0.441
OM	-0.120	0.087
ADER	-0.815	0.327
% Total variance	27.87	25.99