NATURAL AND ARTIFICIAL RADIOACTIVITY IN SOME PROTECTED AREAS OF SOUTH EAST EUROPE

by

Jovana A. DŽOLJIĆ [1], ***Svetlana M. STEVOVIĆ*** [2], ***Dragana J. TODOROVIĆ*** [3], ***Svetlana M. POLAVDER*** [4], ***Milica M. RAJAČIĆ*** [3], ***and Jelena D. KRNETA NIKOLIĆ*** [3]

[1] Faculty of Ecology and Environmental Protection, University Union-Nikola Tesla, Belgrade, Serbia
[2] Innovation Centre, Faculty of Mechanical Engineering, University of Belgrade, Belgrade, Serbia
[3] Department of Radiation and Environmental Protection, Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia
[4] Mining Institute, L.t.d., Belgrade, Serbia

Scientific paper
http://doi.org/10.2298/NTRP1704334D

The primary aim of this research is the investigation of natural and artificial radioactivity in protected areas of Kopaonik, Vlasina, and Rila Mountains. Soil samples (including lake sediment), drinkable spring water and conifers at mentioned locations of Southeast Europe, are chosen as study objects due to their importance for people and the environment in global. Specific activities of ^{226}Ra, ^{232}Th, ^{40}K, ^{238}U, ^{235}U, ^{137}Cs, ^{210}Pb, and ^{7}Be are determined using gamma spectrometry and the obtained values compared with literature and mean world values. Risk assessment parameters and the soil-plant transfer factor were determined for ^{226}Ra, ^{40}K, ^{137}Cs, and ^{210}Pb. This is the first radioactivity study of high mountain areas of Vlasina and Kopaonik in Serbia and Rila in Bulgaria and as such a baseline measurement and foundation for future research.

Key words: gamma ray spectrometry, risk assessment, soil, Norway spruce, Kopaonik, Rila, Vlasina

INTRODUCTION AND BACKGROUND

Rapid industrialization and urbanization have increased the level of environmental pollution requesting metabolic adaptation of all ecosystem functions [1]. Once radioactive materials are incorporated into the ecosystem, they can be taken up by food or ingested by animals [2]. Levels of contaminants in environment affect the concentration and exposure to primordial radionuclides, enhancing the contact with living beings and increasing overall radioactivity exposure. Some radionuclides, such as long-lived ^{40}K, ^{232}Th, ^{238}U, ^{90}Sr, and ^{137}Cs, are metabolically incorporated into plant species by absorption from the soil through the root system. Others, such as ^{210}Pb and ^{7}Be, can be deposited on plant leaves [1]. Moreover, foliar deposition represents one way of radionuclide absorption from the air and is closely associated with the morphological characteristics of leaves and the local climate [3]. Measurements of specific activities of ^{7}Be in the environment, especially in soil or plants, are novel. The amount of ^{137}Cs in the environment and its radiological impact throughout Europe is the result of the Chernobyl accident in 1986 [4]. The most recent release of radionuclides, depleted uranium (DU), into the environment of Southeast Europe, precisely Serbia, occurred in 1999.

* Corresponding author; e-mail: jovana.dzoljic@pass.ac.rs

Radioactivity of soil, water and plants

The importance of investigating the radioactivity of soil, water and plants from selected protected areas of high mountain regions in Serbia and Bulgaria is based on their vicinity to terrains that were exposed to DU. These areas include places where people live, organized in different communities and municipalities. Norway spruce (*Picea abies* L.), is a perennial plant species, common in high mountain areas in this region, selected for estimating the beginning of radionuclide absorption by coniferous trees. Along with the research of specific activities and related ambient dose of radionucides, the soil-to-plant transfer factor is also considered.

Variations in specific activities of primordial radionuclides in soils around the world, related to geological and geographical conditions, may vary the public external dose from terrestrial radiation. The mean world values of radionuclides in the soils are in the range of 33-1000 Bqkg^{-1} for ^{238}U, 32 Bqkg^{-1} for ^{226}Ra, 45-360Bqkg^{-1} for ^{232}Th, and 420-3200 Bqkg^{-1} for ^{40}K [5]. Many studies of radionuclides in soil and water and their transfer to plants were done around the world, mostly for assessing the dose and the risks resulting from them [6, 7]. In terrestrial environment, the soil to plant relationship is considered very significant and widely used for estimating the amount of mineral materials uptake from the soil by plants.

The mean specific activities of ^{238}U, ^{232}Th, and ^{40}K in surface soils in Serbia are similar to equivalent values reported for soils in regions with a similar geological composition and geotectonic structure, as well as with worldwide average values. Obtained research results show mean values of 32.8 Bqkg^{-1} for ^{238}U, 37.8 Bqkg^{-1} for ^{232}Th, and 550 Bqkg^{-1} for ^{40}K in soils [8].

During the UNEP DU mission, analysed soil samples from the Pcinja District, Southeast Serbia, and locations at Pljackovica, Vranje Garrison, Bratoselce, Borovac, Bukarevac, and Reljan (fig. 1.) confirmed the presence of various amounts of DU [9]. The reported mean specific activity of radionuclides in the soil of southern Serbia, from locations where DU was used, are 45 Bqkg^{-1} for ^{226}Ra, 50 Bqkg^{-1} for ^{232}Th, 651 Bqkg^{-1} for ^{40}K, 10 Bqkg^{-1} for ^{137}Cs, 3.4 Bqkg^{-1} for ^{235}U, and 57 Bqkg^{-1} for ^{238}U [10]. The importance of radioanalysis is also emphasised by considering the soil-cereals TF in the region of Pcinja, Serbia [11].

This is the first detailed research of radioactivity levels in soil, spring water and plants inside protected areas for possible establishment of monitoring points. Establishing high quality state monitoring of these areas is of importance. Risk assessments within protected areas of high mountains in this region are a pioneer research. The control of radiation levels is important not only for evaluating the effective annual dose in the place where one lives, but also for establishing baseline levels of environmental radioactivity for detecting any changes in future monitoring [12].

Study area

The study area covers Rila Mountain in Bulgaria and Kopaonik and Vlasina in Serbia as places with recognised natural, ecological, and cultural features. These are also tourist destinations and specific world rare areas, protected by the UN and national authorities. The terrains within them are used for agriculture, livestock breeding, mushrooms and forest fruit collection, traditional medical plant production and harvesting, this in part being the reason for authors selecting these sites for their study. The study area is presented in fig. 1.

Kopaonik mountain (NP Kopaonik) is the highest mountain in Central Serbia, direction NW-SE, with an eastern border between the Dinaric Alps and Rhodope. Outstanding natural features, diversity of terrain geology, geomorphology and biota, along with the importance of the area for conservation, resulted in designating it a National park in 1981. During the accident 1999, Kopaonik was under heavy and prolonged attack resulting in the destruction of the terrain and disruption of the forest ecosystem [13, 14].

Vlasina's plateau is situated in southeast Serbia, near the border with Bulgaria. A Landscape of Outstanding Features, Vlasina (LOF Vlasina) includes wetlands, a lake and the surrounding highland areas. The nearest high region is the Rila mountain range with the highest massif on the Balkans (Musala peak, 2925 m), located in Southwestern Bulgaria.

Rila Monastery Natural park (NP Rila Monastery) is a protected area having one of the highest degrees of naturalness, stability, typicality and representative values of ecosystems in Bulgaria. UNESCO World Cultural and Natural Heritage Conservation confirmed the national valorisation, identifying it as the second most visited protected area in Bulgaria.

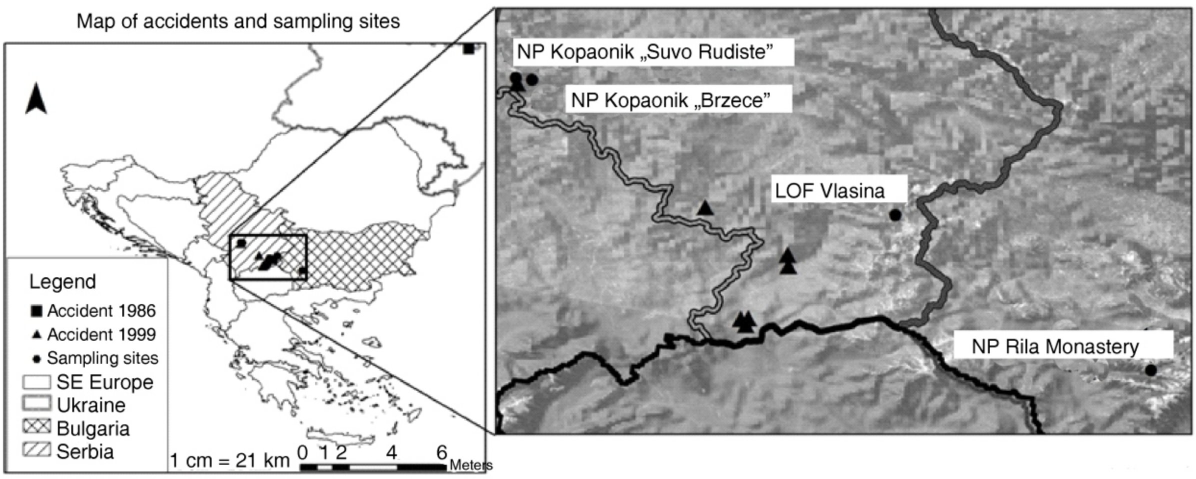

Figure 1. Map of accidents and sampling sitese

MATERIALS AND METHODS

Sampling sites from National park „Kopaonik", Landscape of Outstanding Features "Vlasina" in Serbia and National park „Rila" in Bulgaria, alongside Chernobyl and NATO bombing sites in Soutest Serbia, are marked on the Map, fig. 1, as accident locations.

Soil, water and plants were selected as samples for investigation since these are the media that first indicate and transfer radioactivity.

A total of 5 soil samples from a depth of 0-10 cm were collected. Two samples were collected at National park "Kopaonik", at the locality of Suvo Rudiste, 1700 m a. s. l.(E20°49'0.09", N43°17'33.24"), and at a lower altitude of 1100 m, near the village Brzece (E20°52'49.85", N43°17'6.48"). One soil sample and one sample of river sediment were extracted at LOF-Vlasina (E22°19'26.67", N42°44' 54.55"), at 1219 m of altitude and one soil sample was taken at Nature park "Rila Monastery" (E23° 20' 20.59", N42°7'57.35"). At each sampling site, about 1.5-2 kg of soil was collected from the surface of approximately 1 m^2.

Spring water samples were taken from fountains marked as a source of drinkable water. One spring water sample was taken at each location, namely from the "Marine vode" fountain (E20°49'2.1", N43°17'30.48") at National park "Kopaonik", LOF Vlasina (E22°19'55.61", N42°43'57.31"), and from Nature park "Rila Monastery"(E23°20'25.72", N42°8'0.08"). At all sampling sites, 15 L of water were collected.

Twigs and needles of young species of perennial, coniferous trees of Norway spruce, *Picea abies* L.,were sampled. At each location, 1 kg of twigs and 1kg of needles were collected from the same locality as the soil samples.

Sample preparation

Sample preparation and radioactivity analysis were done at the Vinča Institute of Nuclear Sciences Radiation and Environmental Protection Department. After removing biota and stones, the soil samples were dried at a temperature of 105 ºC to a constant weight, then homogenized and approximately 500 g of each sample were stored in Marinelli beakers. The beakers were sealed using bee wax and left in the laboratory for 28 days to achieve radioactive equilibrium between radon and its progenies.

Water samples were acidified and then evaporated to dry residue under a IR lamp. The residue was collected and mineralized at a temperature of 450 ºC. The whole amount of mineralised residue (1-2 g) is then transferred to cylindrical polystyrene containers of 120 ml covering only the bottom with a thin layer of sample.

After cleaning off soil and litter, the plant samples are dried at room temperature, mineralized at 450 ºC and transferred to 120 ml cylindrical polystyrene containers. The masses of the samples were about 20-30 g. Upon this, they are sealed with bee wax and stored for 28 days to achieve radioactive equilibrium between radon and its progenies. Specific activities of radionuclides ^{226}Ra, ^{232}Th, ^{40}K, ^{238}U, ^{235}U, ^{210}Pb, and ^{7}Be were determined by gamma spectrometry measurements using three HPGe spectrometers produced by CANBERRA, with relative efficiencies of 18 %, 20 %, and 50 %.These spectrometers are readily used in the Laboratory for measurement of environmental samples. Time of measurements for all samples was 60 000 s.

Detector efficiency calibration for different geometries and different matrices was done in accordance with the measured sample type [15].

Calibration for soil samples was performed using referent radioactive material, matrix of silicone resin, Czech Metrological Institute, Praha, 9031-OL-420/12, total activity of 41.48 kBqat 31.08.2012 (^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{203}Hg, ^{88}Y, ^{113}Sn, ^{85}Sr, ^{137}Cs).

For plant and water samples, secondary reference material, produced by spiking the mineralized plant matrix with the primary referent material, *Czech Metrological Institute, Praha*, 9031-OL-427/12, type ERX, total activity of 72.40 kBq at 31.08.2012 (^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{203}Hg, ^{88}Y, ^{113}Sn, ^{85}Sr, ^{137}Cs, ^{210}Pb) was used. The secondary reference material was placed in polystyrene cylindrical containers of 120 ml [15].

Risk assessment

Absorbed dose rate ($\dot{D}$)

Using results of radionuclide specific activity measurements in the soil samples and following eq. (1), the intensity of the absorbed rate of gamma radiation was calculated

$$\dot{D}(\mathrm{nGyh}^{-1}) = 0.462C_{\mathrm{Ra}} + 0.604C_{\mathrm{Th}} + 0.0417C_{\mathrm{K}} \quad (1)$$

where C_{Ra}, C_{Th}, and C_{K} represent the specific activity of the radionuclides [11].

Annual effective dose (D_E)

Also, the annual effective dose of gamma radiation was calculated following eq. (2)

$$D_{\mathrm{E}}\,(\mathrm{mSv}) = 0.7(\mathrm{SvGy}^{-1}) \times 365\,(\mathrm{d}) \times 24(\mathrm{h}) \times \dot{D}(\mathrm{nGyh}^{-1}) \times 0.2 \quad (2)$$

The estimation of annual effective doses includes the conversion coefficient from absorbed dose in the air to effective dose (0,7 SvGy^{-1}) and the outdoor occupancy factor, 0.2 [16].

Calculation of soil-to-plant transfer factor (TF)

The soil-to-plant transfer factor (TF) was calculated for ^{226}Ra, ^{40}K, ^{137}Cs, and ^{210}Pb using eq. (3)

given by the International Atomic Energy Agency (1994)

$$TF = \frac{\text{radionuclide activity per unit of plant dry mass [Bgkg}^{-1}]}{\text{radionuclide activity per mass unit of dry soil [Bqkg}^{-1}]} \quad (3)$$

RESULTS AND DISCUSSION

Results of radionuclide specific activity measurements in samples of soil, plant and water are presented in tabs. 1, 3, and 4.The results are presented with expanded uncertainty with coverage factor $k = 2$, giving a confidence level of 95 % for normal distribution.

The uncertainty budget includes uncertainty arising from counting statistics, measurement of mass and efficiency calibration. The uncertainty budget of efficiency calibration covers the uncertainties of the counting statistics from reference material measurements, uncertainty of reference material activity and the uncertainty of the coincidence summing correction factors [15].

Radionuclide specific activities in soil samples from all locations are presented in tab. 1. It should be noted that the specific activity of ^{137}Cs detected in all samples is a result of the nuclear accident in Chernobyl in 1986.

The lithological composition of LOF Vlasina is determined as a metamorphic complex of shale and, specifically, at the sampling site of the "Vlasina" complex, as albite-chlorite muscovite schists and (dotted) gneisses [17]. Soil samples from the Vlasina site have lower specific activities of measured radionuclides than values measured at Borovac in the Pcinja District, South Serbia [18] and global values (tab. 2) and correspond to the natural radionuclide distribution [16]. The investigation of ^{235}U and ^{238}U specific activities in soils and their ratio is used to indicate the presence of DU. The difference between natural and depleted uranium is in isotopic composition which, in DU, changes by removing ^{234}U and ^{235}U fractions, leading to an increment of ^{238}U. The value of the activity ratio of ^{235}U and ^{238}U of 0.045 noticed at this location is similar to the ratio in natural uranium of 0.047.

The geological background of National park „Kopaonik", Serbia, is represented by contact-metamorphic rocks and occurrences and, specifically, in the case of site "Suvo Rudiste" determined as granodiorite transition to quartz monzonite [19]. Wherever the geology of the terrain is represented by granite, higher specific activity of U and Th is expected. Comparing radionuclide specific activities in the soil of "Suvo Rudiste" and Borovac in southern Serbia, the terrain contaminated by DU [18] shows similar radionuclide distribution. The same values of specific activities of ^{235}U and ^{238}U ratio are found at Kopaonik and the previously mentioned location, recording values of 0.055 at "Suvo Rudiste" and 0.056 at Borovac[18], which is slightly higher than the ratio in natural uranium. The obtained results of radionuclide specific activities are in agreement with literature values reported for Kopaonik, and are a common characteristic for the area [14].

At lower altitudes of NP Kopaonik, at sampling site "Brzece", lower values of all radionuclide specific activities except for ^{137}Cs are detected, compared to the sampling site "Suvo Rudiste". A different geological background for this site is determined, represented

Table 1. Specific activities of natural and artificial radionuclides in samples of soil from protected areas

		Samples	^{226}Ra [Bqkg^{-1}]	^{232}Th [Bqkg^{-1}]	^{40}K [Bqkg^{-1}]	^{238}U [Bqkg^{-1}]	^{235}U [Bqkg^{-1}]	^{137}Cs [Bqkg^{-1}]	^{210}Pb [Bqkg^{-1}]
"Rila monastery" Natural park	1	Mountain soil	29 2	35 3	370 25	30 6	1.5 0.2	49 3	50 10
National park "Kopaonik"	2	Mountain soil Suvo Rudište	88 6	111 7	780 50	93 8	5.1 0.4	9.8 ± 0.8	64 7
	3	Mountain soil Brzece	30 3	41 3	650 40	37 5	1.8 0.2	89 5	52 5
Landscape of outstanding features "Vlasina"	4	Mountain soil	19 2	16 1	300 20	25 6	1.2 0.1	30 2	37 9
	5	Sediment from Vlasina lake	34 3	36 3	510 30	50 10	2.3 0.2	1.0 0.2	50 20

Table 2. Mean radionuclide specific activities in the world and some countries in the region, (UNSCEAR, 2000)

Countries	Specific activities of radionuclides							
	^{40}K [Bqkg^{-1}]		^{238}U [Bqkg^{-1}]		^{226}Ra [Bqkg^{-1}]		^{232}Th [Bqkg^{-1}]	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Albania	360	15-1150	23	6-96	–	–	24	4-160
Bulgaria	400	40-800	40	8-190	48	12-210	30	7-160
Greece	360	12-1570	25	1-240	25	1-240	21	1-190
Croatia	490	140-710	110	83-180	54	21-77	45	12-65
Hungary	370	79-570	29	16-66	33	14-76	28	12-45
Global value	400	140-850	35	16-110	35	17-60	30	11-64

by sandstone, marl and alveolite of the Fleece middle part [19]. The maximal value of ^{137}Cs -specific activity, 89 Bqkg^{-1}, can be explained by terrain geology and higher soil erosion.

Research results of radioactivity in soil samples from Central Serbia, NP Kopaonik, "Suvo Rudiste", even though higher than the global average (tab. 2), are considered a general characteristic for the area. Similar results of radionuclide specific activities in the soil of Kopaonik, especially at Pancic's peak, are noted by other authors [14]. At lower altitudes of the same mountain, at sampling site "Brzece", except for ^{40}K, all other natural radionuclides show a lower value than at "Suvo Rudiste" (tab. 1).

Rila Mountain and its surroundings are largely made up of various amphibolite-facies gneisses intruded by granitic bodies. The geological background of the sampling site inside the Natural Park is represented by biotite and amphibole-biotite gneisses [20]. Obtained results of radionuclide specific activities are characteristic for terrain formed of gneisses. At this sampling site, the specific activity of ^{137}Cs, 50 Bqkg^{-1}, is in accordance with data cited in literature [16].

In soil samples from Nature park "Rila Monastery", the detected specific activities of radionuclides correspond to the global average and are characteristic for the terrain.

The highest values of all natural radionuclides in the different soil samples are detected at site "Suvo Rudiste" in NP Kopaonik (tab. 1). The ratio of specific activity of ^{235}U and ^{238}U in soil samples from different locations is in the range of 0.045 to 0.055 which corresponds to the ratio in natural uranium, indicating its natural origin.

Results of radionuclide specific activities in the perennial spruce species *Picea abies* L., presented in tab. 3, show different accumulation values in twigs (diameter less than 1 mm) and needles, with spatial variation observed as well.

Comparing radionuclide specific activities in spruce needles from Kopaonik mountain, Vlasina, and Rila, the minimal values noted are 2.2 Bqkg^{-1} for ^{226}Ra at NP Rila Monastery and 86 Bqkg^{-1} for ^{40}K at LOF-Vlasina site. Detected specific activities of ^{238}U and ^{235}U in spruce needles at all sampling sites are lower than the minimal detectable activity (MDA), (tab. 3). In the needles from „Suvo Rudište" the detected specific activity of ^{232}Th is 4.5 Bqkg^{-1}, representing the maximal value. A maximal value of 8.8 Bqkg^{-1} for ^{226}Ra was detected at NP Kopaonik, a maximal value of 22 Bqkg^{-1} for ^{40}K has been detected at NP-Rila Monastery, while the maximal value of 6.9 Bqkg^{-1} for ^{137}Cs has been observed at samples from NP Kopaonik. The highest value for ^{210}Pb was found in samples from NP Kopaonik, with a similar value found in needles from NP Rila Monastery.

The specific activity of ^{40}K in spruce needles from LOF-Vlasina and NP-Rila Monastery is lower than previously mentioned results found in literature [21, 22].

Research results show various specific activities of ^{226}Ra in spruce needles. The amount of ^{226}Ra in spruce needles depends on the age of the plant, with the lowest amount found in the younger species [23]. The results obtained in this research also show a very low value of ^{226}Ra in spruce twigs (tab. 3).

Specific activities of ^{137}Cs in needles are similar to data previously cited in literature [22, 24].

Incorporation of ^{210}Pb into plants through the root system shows that almost 98 % of lead is atmospheric in origin [25]. The maximal detected specific activity of this radionuclide was noticed in the samples of the older plants (45 Bqkg^{-1}), confirming that the atmosphere is the origin of deposition [23]. In this research, the maximal detected specific activity of ^{210}Pb was 90 Bqkg^{-1}, found in samples from NP-Kopaonik „Suvo Rudište". This locality is a very popular tourist destination in Serbia with a well-developed infrastructure. Higher values of ^{210}Pb in the spruce may be a result of air pollution from the traffic and foliar deposition.

Except for the samples of spruce needles from Rila and Kopaonik and twig samples from Vlasina, the specific activity of ^{7}Be at all other locations was below minimum detectable activity. ^{7}Be concentrations in the vegetation reflected the changing atmospheric conditions, mainly precipitation [26] that, along with

Table 3. Natural and artificial specific activities of radionuclides in the samples of spruce* from protected areas

		Samples	^{226}Ra [Bqkg^{-1}]	^{232}Th [Bqkg^{-1}]	^{40}K [Bqkg^{-1}]	^{238}U [Bqkg^{-1}]	^{235}U [Bqkg^{-1}]	^{137}Cs [Bqkg^{-1}]	^{210}Pb [Bqkg^{-1}]	^{7}Be [Bqkg^{-1}]
"Rila monastery" Natural park	1	Spruce needles (*Piceaabies*) "Suvo Rudiste"	2.2 0.3	<0.5	220 10	<3	<0.2	1.0 0.2	82 8	4.1 0.9
	2	Spruce twigs (*Piceaabies*) "Suvo Rudiste"	<1	<1	45 6	<5	<0.4	<0.3	200 10	<2
National park "Kopaonik"	3	Spruce needles (*Piceaabies*)	8.8 ± 0.9	4.5 ± 0.7	140 ± 10	<2	<0.1	6.9 ± 0.5	90 ± 10	3.0 ± 0.7
Landscape of outstanding features "Vlasina"	8	Spruce needles (*Piceaabies*)	4 1	<2	80 9	<10	<0.4	<0.4	<12	<2
	9	Spruce twigs (*Piceaabies*)	<5	<2	110 10	<10	<0.7	0.5 0.2	130 20	30 10

*Specific activity in plant samples expressed as [Bqkg^{-1}] of plant mass dried at room temperature

Table 4. Radionuclide activity concentration in spring water

	Samples	^{226}Ra [mBqL^{-1}]	^{232}Th [mBqL^{-1}]	^{40}K [mBqL^{-1}]	^{238}U [mBqL^{-1}]	^{235}U [mBqL^{-1}]	^{137}Cs [mBqL^{-1}]	^{210}Pb [mBqL^{-1}]
1	Spring water Rila Monastery fountain	12 2	<3	70 10	60 10	2.5 0.5	<0.5	<50
2	Spring water "Marine vode", Kopaonik "Suvo Rudiste"	46 6	<5	<30	<30	<2	<2	<20
3	Spring water LOF "Vlasina"	<30	<10	<70	<70	<4	<4	<40

its short half-life, can explain lower values of ^{7}Be in a temperate climate.

Results of radionuclides in water samples from all loctions are presented in tab. 4.

Various concentrations of radionuclide activity were found in spring water samples. Research results show that in samples from LOF Vlasina all radionuclides show a value of activity concentration lower than MDA.

Radio analysis of water samples from all sampling sites showed that activity concentrations of ^{226}Ra, ^{232}Th, ^{238}U, and ^{137}Cs (tab. 4) are significantly lower than the guidance level [2]. Activity concentrations of ^{137}Cs and ^{210}Pb in spring water were below minimum detectable activity.

Previous studies of radioactivity in water were carried out for samples of water of different origin [27]. Drinking water in Serbia contains less than 70 mBqL^{-1} of ^{226}Ra, less than 250 mBqL^{-1} of ^{40}K and less than 50 mBqL^{-1} of ^{232}Th [27]. Results obtained in this study show significantly lower values than previously presented. At the same time, activity concentrations of the studied samples are notably lower than the maximal allowed activity concentration for ^{226}Ra and ^{232}Th in drinking water of 490 mBqL^{-1} and 590 mBqL^{-1} respectively, defined by the national legislation [28].

Based on the results of natural and artificial radionuclide specific activities in the soil (tab. 1), risk assessment results are presented in the tab. 5.

The absorbed dose rate is found to be in the range of 31 nGyh^{-1} at LOF Vlasina to 140 nGyh^{-1} at NP Kopaonik "Suvo Rudište". An almost twice higher value, compared to that of LOF Vlasina (66 nGyh^{-1}), was determined at site "Brzece" NP Kopaonik, which is to be expected regarding the results of radionuclide specific activities. At the same mountain, at higher altitudes and that of site "Suvo Rudiste", the absorbed dose rate shows a maximal value that is higher than the global average of 58 nGyh^{-1} [5], due to the geological background in the form of granodiorite.

The minimal value of the annual effective dose of 0.04 mSv was obtained at LOF Vlasina, while the maximal value of 0.17 mSv was determined at "Suvo Rudiste", NP Kopaonik (tab. 5). The annual dose at NP "Rila Monastery" and LOF Vlasina is lower than the global average value of 0.07 mSv given for outdoor environment [5], while site "Suvo Rudiste" at Kopaonik has higher values (tab. 5).

Table 5. Risk assessment results from different localities

Sampling sites	Altitude [m]	$\dot{D}$ [nGyh^{-1}]	D_E [mSv]
NP Rila monastery	1147	50	0.06
NP Kopaonik "Suvo Rudiste"	1735	140	0.17
NP Kopaonik "Brzece"	1100	66	0.08
LOF Vlasina	1242	31	0.04

The quantification of radionuclide uptake from soil-to-leaf using transfer factors (TF) was determined for radionuclides ^{226}Ra, ^{40}K, ^{137}Cs, and ^{210}Pb and the results presented in tab. 6.

Research results of the transfer factor for ^{40}K are higher than for ^{226}Ra and correspond to values in literature. The maximal value for TF-^{40}K is found in samples from NP Rila Monastery, for TF-^{226}Ra in samples from LOF Vlasina, and for TF-^{137}Cs in spruce samples from NP Kopaonik "Suvo Rudiste".

Obtained higher values for the ^{210}Pb transfer factor correspond to the fact that besides root absorption, these radionuclides can be absorbed through foliar deposition. In spruce needles from NP Kopaonik and NP Rila Monastery a similar value of TF-^{210}Pb,that of 1.42 and 1.67, respectively, is detected, while the TF-^{210}Pb for twigs shows a value higher than 3.51 in the samples from LOF Vlasina and that of 4.08 at NP Rila Monastery.

CONCLUSIONS

The main conclusion of this research is that accident situations in the immediate vicinity of investigated areas in Southeast Europe did not affect the natural spatial distribution of radionuclides. As the first radioactivity investigation of mentioned areas, it

Table 6. Transfer factor soil-to-leaf in plants from the analysed study area

Sample		TF-^{226}Ra	TF-^{40}K	TF-^{137}Cs	TF-^{210}Pb
NP Rila monastery	Norway spruce twigs	–	0.12	–	4.08
	Norway spruce needles	0.08	0.60	0.02	1.67
NP Kopaonik	Norway spruce needles "Suvo Rudiste"	0.10	0.18	0.70	1.42
LOF Vlasina	Norway spruce twigs	–	0.37	0.02	3.51
	Norway spruce needles	0.21	0.27	–	–

should be viewed as a starting point and basis for future investigation.

In comparison to other sampling locations, higher specific activities of all radionuclides were found at both sampling sites on Kopaonik. The conclusion is that the obtained specific activities of radionuclides from these sampling sites are typical and expected for said soil samples, due to the geological characteristics of the terrain. They are within UNSCEAR reported values of natural radionuclide distribution. Higher specific activity of ^{137}Cs in the soil samples, detected at lower altitudes near the inhabited areas, can be explained by soil erosion and geological characteristics. Specific activities of natural and anthropogenic radionuclides in plant samples are low and in accordance with literature, as well.

The detected specific activities of all radionuclides in soil samples from LOF "Vlasina" were below world average values. The specific geomorphological history of this place and climate changes resulted in low radioactivity that is also in accordance with reported UNSCEAR values.

This is the first detailed investigation of radioactivity in soil, spring water and spruce samples from protected high mountain areas in Serbia and Bulgaria. The measured activity concentrations in the water samples from all three localities are very low, lower than guidance levels recommended by WHO (2011). The amount of ^{137}Cs and ^{210}Pb is below MDA.

Samples from "Rila monastery" Nature park, Bulgaria, were taken for comparison since it is one of the nearest high mountain regions eastward. Risk assessment in the area is insignificant, implying that regarding radiological safety, the areas are safe for human activities.

Further research and monitoring of radioactivity of high mountain areas in Serbia and Bulgaria is highly recommended as part of regular monitoring of the environment.

ACKNOWLEDGEMENTS

The authors wish to thank the employees of the Nuclear and Environmental Protection Laboratory, Vinča Institute of Nuclear sciences , Belgrade, for the contribution to this paper. This research did not receive any specific grants from public or commercial funds or the non-profit sector, but The Ministry of Science and Technological Development of the Republic of Serbia supported this work under Project III43009.

AUTHORS' CONTRIBUTIONS

The theoretical analysis was carried out by J. A. Džoljić, S. M. Stevović, D. J. Todorović, and S. M. Polavder, experimental work by M. M. Rajačić, J. D. Krneta-Nikolić, and J. A. Džoljić. The credit for the concept of the research goes to S. M. Stevović. All authors were included into result analysis and discussion, while manuscript and figures' preparation was done by J. A. Džoljić.

REFERENCES

[1] Nikolić, M., Stevović, S., Family *Asteraceae* as a Sustainable Planning Tool in Phytoremediation and its Relevance in Urban Areas, *Urban Forestry & Urban Greening, 14* (2015), 4, pp. 782-789

[2] ***, WHO, Guidelines for Drinking-Water Quality 4th ed., World Health Organization Geneva, 2011, p. 541

[3] Todorović, D., *et al*., Leaves of Higher Plants as Biomonitors of Radionuclides (^{137}Cs, ^{40}K, ^{210}Pb, and ^{7}Be) in Urban Air, *Environmental Science and Pollution Research, 20* (2013), 1, pp. pp. 525-532

[4] ***, US Department of Health and Human Services, Toxicological Profile for Cesium, Agency for Toxic Substances and Disease Registry, Atlanta, USA, 2001, p. 306

[5] ***, United Nations Scientific Committee on the Effects of Atomic Radiation,UNSCEAR 2008 Report Vol. I: Sources and Effects of Ionizing Radiation, United Nations, New York, 2010, p. 245

[6] ***, IAEA, Quantification of Radionuclide Transfer in Terrestrial and Freshwater Environments for Radiological Assessments, IAEA-TECDOC-1616, International Atomic Energy Agency, Vienna, 2009, p. 616

[7] ***, IAEA, Handbook of Parameter Values for the Prediction of Radionuclide Transfer in Terrestrial and Freshwater Environments, Technical Reports Series No. 472, International Atomic Energy Agency, Vienna 2010, USA, p. 208

[8] Dragović, S., *et al*., Lithogenic Radionuclides in Surface Soils of Serbia: Spatial Distribution and Relation to Geological Formations, *Journal of Geochemical Exploration, 142* (2014), July, pp. 4-10

[9] ***, UNEP, Depleted Uranium in Serbia and Montenegro, Post-Conflict Environmental Assessment in the Federal Republic of Yugoslavia, United Nations Environment Programme, Geneva, USA, 2002, p. 200

[10] Sarap, N. B., *et al*., Environmental Radioactivity in Southern Serbia at Locations where Depleted Uranium was Used, *Archives of Industrial Hygiene and Toxicology, 65* (2014), 2, pp. 189-197

[11] Marković, J., *et al*., Transfer Factors for the "Soil-Cereals" System in the Region of Pcinja, Serbia, *Nucl Technol Radiat, 31* (2016), 4, pp. 376-381

[12] ***, IAEA, Safety Reports Series 64: Programmes and Systems for Source and Environmental Radiation Monitoring,International Atomic Energy Agency, Vienna, USA, 2010, p. 248

[13] ***, UNEP/UNCHS Balkans Task Force (BTF), Assessment of the Damage to Biodiversity in Protected Areas of the Federal Republic of Yugoslavia (1999), Technical mission. Available online.http://www.grid.unep.ch/btf/missions/september/biodiversity.pdf (last accessed 17.12.2016.)

[14] Mitrović, B., *et al*., Natural and Anthropogenic Radioactivity in the Environment of Kopaonik Mountain, Serbia, *Environmental Pollution, 215* (2016), Aug., pp. 273-279

[15] Nikolić, J., *et al.*, Application of GEANT4 Simulation on Calibration of HPGe Detectors for Cylindrical Environmental Samples, *Journal of Radiological Protection, 34* (2014), 2, pp. 47-55
[16] ***, United Nations Scientific Committee on the Effects of Atomic Radiation,UNSCEAR 2000 Report vol. I: Sources, UN, New York, 2000, p. 654
[17] Petrović, B., *et al*., Basic Geological Map of SFRY 1:100000, the Vlasotince Sheet (in Serbian), Federal Geological Institute, Beograd, 1966
[18] Popović, D., *et al*., Radionuclides and Heavy Metals in Borovac, Southern Serbia, *Environmental Science and Pollution Research, 15* (2008), 6, pp. 509-520
[19] Urošević, M., *et al*., Basic Geological Map of SFRY 1:100000, the Novi Pazar Sheet (in Serbian), Federal Geological Institute, Beograd, 1970
[20] Sarov, S., *et al*., Geological Map of the Republic of Bulgaria 1:50000, the Rila Monastery Sheet (in Bulgarian), Ministry of Environment and Water, Bulgarian National Geological Survey, Sofiya, 2010
[21] Mietelski, J. W, *et al*., ^{137}Cs, ^{40}K, ^{90}Sr, $^{238,\ 239+240}$Pu, ^{241}Am and $^{243+244}$Cm in Forest Litter and Their Transfer to Some Species of Insects and Plants in Boreal Forests: Three Cases Study, *Journal of Radioanalytical and Nuclear Chemistry, 262* (2004), 3, pp. 645-660
[22] Tomankiewicz, E., *et al*., Accumulation Properties of Norway Spruce (Piceaabies) for Different Radionuclides, *Nukleonika, 51* (2006), Suppl. 2, pp. 59-67
[23] Seidel, C., Artificial and Natural Radionuclides in Spruce Needles in Upper Austria from 1983 to 2008 - an Application for Radioecological Monitoring, Universität für Bodenkultur Wien, Dissertation, 2010
[24] Jasinska, M., *et al*., Radioactive Contamination of the Forest of Southern Poland and Finland, *Journal of Radioanalytical and Nuclear Chemistry, 146* (1990), 1, pp. 1-13
[25] Hovmand, M. F., *et al*., Root Uptake of Lead by Norway Spruce Grown on ^{210}Pb Spiked Soils, *Environmental Pollution, 157* (2009), 2, pp. 404-409
[26] Poschl, M., *et al*., Seasonal and Inter-Annual Variation of Beryllium-7 Deposition in Birch-Tree Leaves and Grass in the Northeast Upland Area of the Czech Republic, *Journal of Environmental Radioactivity, 101* (2010), 9, pp. 744-750
[27] Janković, M. M., *et al.*, Natural Radionuclides in Drinking Waters (in Serbia), *Applied Radiation and Isotopes, 70* (2012), 12, pp. 2703-2710
[28] ***, Official Gazette of the Republic of Serbia, 2011, Regulation on Limits of Radionuclide Content in Drinking Water, Foodstuffs, Feeding Stuffs, Drugs, Items of General Use, Building Materials and Other Goods to be Placed on the Market, Serbia, no. 86. Andno. 97 from 2013

Received on January 9, 2017
Accepted on August 28, 2017

Јована А. ЏОЉИЋ, Светлана М. СТЕВОВИЋ, Драгана Ј. ТОДОРОВИЋ, Светлана М. ПОЛАВДЕР, Милица М. РАЈАЧИЋ, Јелена Д. КРНЕТА НИКОЛИЋ

ПРИРОДНА И ВЕШТАЧКА РАДИОАКТИВНОСТ У ЗАШТИЋЕНИМ ПОДРУЧЈИМА ЈУГОИСТОЧНЕ ЕВРОПЕ

Циљ истраживања био је да се испита природна и вештачка радиоактивност у узорцима из заштићених подручја Копаоника, Власине и Риле. За предмет истраживања изабрани су земљиште (укључујући језерски седимент), пијаћа изворска вода и четинари на наведеним локацијама Југоисточне Европе, због њиховог значаја за људе и животну средину у глобалу. Методом гамаспектрометрије лабораторијски су одређене специфичне активности ^{226}Ra, ^{232}Th, ^{40}K, ^{238}U, ^{235}U, ^{137}Cs, ^{210}Pb и ^{7}Be које су упоређене са просечним вредностима у свету. Урађена је процена ризика и одређен је трансфер фактор земљиште – биљка за ^{226}Ra, ^{40}K, ^{137}Cs и ^{210}Pb. Ово је прво истраживање радиоактивности високопланинских подручја Власине и Копаоника у Србији и Риле у Бугарској и може се сматрати нултим стањем и основом за даља истраживања.

Кључне речи: гамаспектрометрија, процена ризика, смрча, Копаоник, Рила, Власина