RADIOACTIVITY MEASUREMENTS IN SOILS SURROUNDING FOUR COAL-FIRED POWER PLANTS IN SERBIA BY GAMMA-RAY SPECTROMETRY AND ESTIMATED DOSE

by

Ivana Ž. VUKAŠINOVIĆ [1*], ***Dragana J. TODOROVIĆ*** [2], ***Nataša S. NIKOLIĆ*** [1], ***Ana S. MIHAJLOVIĆ-RADOSAVLJEVIĆ*** [3], ***Snežana S. NENADOVIĆ*** [3], ***and Maja M. EREMIĆ SAVKOVIĆ*** [4]

[1]Faculty of Agriculture, University of Belgrade, Belgrade, Serbia
[2] Department of Radiation and Environmental Protection, Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia
[3] Department of Materials Science, Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia
[4] Institute of Occupational Health of Serbia "Dr. Dragomir Karajović", Belgrade, Serbia

Scientific paper
DOI: 10.2298/NTRP1404296V

The study of spatial distribution of activity concentration of ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th, ^{40}K, and ^{137}Cs radionuclides in the surface soil samples (n = 42) collected in the vicinity of four coal-fired power plants in Serbia is presented. Radioactivity measurements in soils performed by gamma-ray spectrometry showed values [Bqkg^{-1}] in the range: 15-117 for ^{238}U, 21-115 for ^{226}Ra, 33-65 for ^{210}Pb, 20-69 for ^{232}Th, 324-736 for ^{40}K, and 2-59 for ^{137}Cs. Surface soil radioactivity that could have resulted from deposition of radionuclides from airborne discharges or resuspension of ash from disposal sites showed no enhanced levels. It was found that variation of soil textural properties, pH values, and carbonate content influenced activity levels of natural radionuclides while radiocesium activities were associated with soil organic matter content. Modification of some soil properties was observed in the immediate vicinity (< 1 km) of power plants where the soil was more alkaline with coarser particles (0.2-0.05 mm) and carbonates accumulated. Calculated average values of the absorbed gamma dose rate and annual external effective dose originating from the terrestrial radionuclides were 69.4 nGy/h and 0.085 mSv, respectively.

Key words: natural radionuclide, soil property, gamma-ray spectrometry, coal-fired power plant

INTRODUCTION

Coal used as a fuel in the coal-fired power plants is still an important source of energy production. Natural radionuclides of the uranium and thorium series and ^{40}K contained in coal are of terrestrial origin and the levels of their activity concentrations are of the same order of magnitude as those found in soil [1]. Coals vary in natural radionuclide content depending on geological characteristics of deposits from which they were mined. In the process of coal combustion natural radionuclides may behave differently depending on several factors such as coal type and characteristics, percentage of ash in coal, coal calorific value, combustion temperature, chemical and physical forms of radionuclides in coal. After burning the coal, natural radionuclides become part of solid or gaseous combustion by-products, most of them being accumulated in the ash while radon gas emanated from coal is completely transferred to the flue gases [2]. Generally, the heavy fraction of ash, called bottom ash or slag, is placed and kept in the coal ash dumps. The other part, the light fraction, called fly-ash is retained from the stack gas using electrostatic precipitators or discharged through the stacks in small amounts. Consequently, natural background gamma radiation can be modified by natural radionuclide re-distribution in the vicinity of coal combustion facilities and coal ash disposal sites in the surrounding air, water, and soil environment. According to the IAEA, if radionuclide concentrations in the environment are elevated as a result of the coal-fired power plants (CFPP) activity, it is considered a NORM type of activity [3]. Levels of natural radionuclide concentrations for soil samples collected within a radius of 1 km and in the upper soil layers were elevated compared to the deeper layers around the CFPP in Spain [4], China [5, 6], Brazil [7], and Hungary [8]. The highest increment of radioactivity is detected in the topsoil around plants burning uraniferous coals (lignites or brown coals) [9]. Oppo-

* Corresponding author; e-mail: ivanavu@agrif.bg.ac.rs

sitely, some other studies revealed that activity releases near CFPP had no significant impact on the surrounding environment [10-12].

Soils are formed as a result of the interactions between the geological parent material, climate, native vegetation and topography over time. Natural and artificial radionuclide behaviour in soil depends on properties like soil granulometry, organic matter content, pH values, drainage status and is governed by the processes of weathering, precipitation, leaching, and sorption [13]. In the natural soil of the central Spanish Pyrenees, the strongest predictor of low mobility of ^{226}Ra, ^{232}Th, and ^{40}K radionuclides was the carbonate content [14]. Dowdall and O'Dea [15] found that the main soil parameter that influenced ^{226}Ra and ^{238}U activities in organic soil was the moisture content where the better drained soil levels exhibited greater depletion of ^{238}U relative to ^{226}Ra, and the depletion was less severe for samples taken from waterlogged areas. In the soils close to the CFPP (<1 km) in Spain [7], a significant increase of the natural radionuclide concentrations was recorded because strong acidity of the surface soil reduced their migration, preventing infiltration to the lower layers.

Radionuclides released into the atmosphere during the period of operation of a CFPP, in particulate or gaseous form, or re-suspended by the wind from the ash wastes can be removed further into the environment by dry deposition (to the ground and vegetation) and wet deposition (by rainout or washout). Content and spatial distribution of radionuclides potentially accumulated in the soils around the plants is important in assessing the soil contamination risk by radionuclides to human health. The main objectives of this study are: (1) to determine activity concentrations of naturally occurring radionuclides in surface soils in the vicinity of CFPP in central Serbia, (2) to investigate relationships between the radionuclide activities and the main soil physical and chemical properties that have an effect on their distribution in soil, and (3) to evaluate the associated absorbed gamma dose rate and annual effective dose rate originating from the terrestrial radionuclides.

MATERIALS AND METHODS

Study area

The four CFPP from Serbia studied are part of CE "Thermal Power Plants Nikola Tesla" that includes: "Nikola Tesla A" (Tent A), "Nikola Tesla B" (Tent B), "Kolubara" (TEK), and "Morava" (TEM) power plants. The region to which they belong is the central part of Serbia (fig. 1). Plants Tent A and Tent B are situated on the Sava river, 30-50 km away from

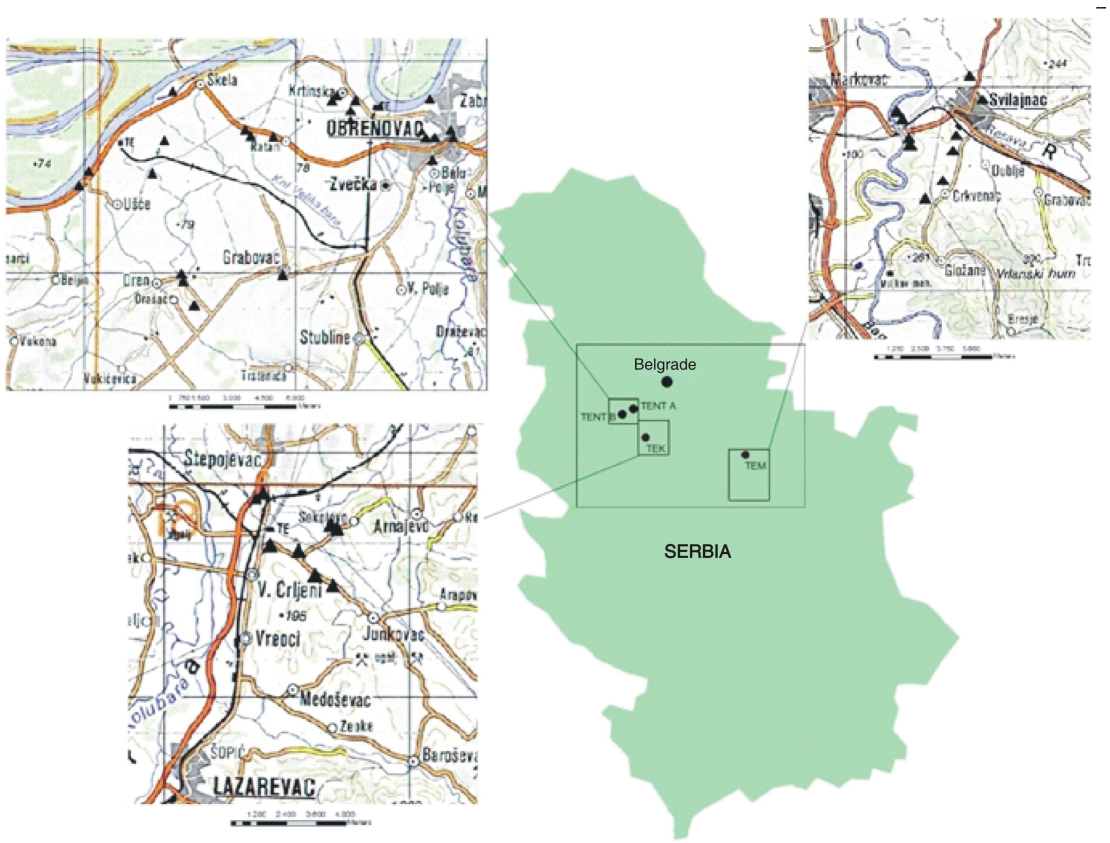

Figure 1. Locations of the four power plants studied in the Central part of Serbia. The position of the sampling points in the vicinity of: "Nikola Tesla" A and B (Tent A and Tent B), "Kolubara" (TEK), and "Morava" (TEM)

Belgrade, the capital of Serbia. CFPP "Kolubara" is situated on the Kolubara river and CFPP "Morava" on the right bank of the Great Morava river. Older plants (built before 1970) are TEM and TEK with a total installed power of 270 10^6 W and 125 10^6 W, respectively. Newer plants, Tent A with power of 1.65 10^9 W and Tent B with 1.24 10^9 W, were put into operation during the 1980.

All four CFPP use for combustion soft brown coals (lignites) from the Kolubara basin with caloric power of 6700 10% kJ/kg, 50% moisture content and 14-20% ash content. The maximum daily consumption of coal is up to 9 10^7 kg in plants Tent A and B that produce 1.7 10^7 kg per day of ash [16]. Those lignites used as feed coals are generally of low natural radionuclide concentration [17]. In newer plants flue gases are emitted into the atmosphere through stacks higher than 200 m, compared to older plants with 105 or 130 m stack height. The fly-ash and bottom ash disposal sites are located in the vicinity of CFPP within a 1 km distance, except for TENT B which is located 4 km from the plant. In Obrenovac, two ash dumps cover a surface area of 400 ha and 600 ha while ash deposits areas near TEM and TEK are smaller, 30 ha and 77 ha, respectively.

Soil samples were taken from the surface horizon of alluvial soils classified as Molic Fluvisols [18] that were developed in alluvial deposits distributed along the river valleys where the CFPP are situated. Alluvial sedimentary deposits are gravels and sands covered with silty loam or clays which represent the parent materials for the development of Fluvisols on the young alluvial flats. The area falls into the European moderate continental climate zone, with hot summers and cold winters and well distributed precipitation throughout the year. In this area, the average annual temperature is around 11°C with 74% humidity. The annual precipitation maximum occurs in the spring months (May-June).

Sample collection

In 2011, forty-two sites were chosen for soil sampling in the vicinity of four CFPP. The sampling points were chosen to be located within a radius of 6 km around each CFPP with more sampling sites in the direction towards the settlements (fig. 1). The sampling sites were denoted by their GPS co-ordinates (tab. 1) which were used to calculate their distance from the corresponding CFPP at each site. Surface soil samples were collected from a 0-5 cm depth. At each location about 1 kg of soil was stored in a plastic bag.

Sample treatment and measurement

Samples were air-dried at room temperature, crushed and sieved through a 2 mm mesh sieve. Soil reaction in water (1:2.5) and in 1M KCl (1:2.5) was measured potentiometrically [19]. The carbonate content was determined volumetrically according to the Scheibler calcimeter method [20]. Organic matter content was determined by the Tjurin method, modified by Simakov [21]. Particle size distribution analysis was conducted by the pipette method. The determined soil fractions were sand (particle sizes 0.2-2 mm and 0.05-0.2 mm), silt (0.01-0.05 mm and 0.002-0.01 mm) and clay (<0.002 mm).

Within the radius of 0-2 km, 2-4 km, and 4-6 km around each plant, a single soil sample was chosen to be ground further in order to obtain soil particles smaller than 10 μm in diameter. The mineralogical composition of the twelve soil samples was determined by X-ray powder diffraction (XRPD) using a Siemens D500 X-ray diffractometer and CuK 1 radiation. The XRPD patterns were recorded in the 2θ range of 4-70° with a step size of 0.02° and counting time of 1 s per step. The minerals were identified by using JCPDS data files and quantified by using the Powder Cell 2.4 software.

For determining natural radionuclide activity concentration, soil samples were packed in 500 ml Marinelli beakers, sealed and covered with beeswax film. Prepared like that, they were left for 4 weeks in order for ^{226}Ra and ^{232}Th to attain secular equilibrium with their decay products. Applying the gamma spectrometry method, measurements were performed with the HPGe detector (Canberra Industries, Inc., Meriden, Conn., USA) with 20% relative efficiency and energy resolution of 1.8 keV at the 1332 keV gamma ray energy of ^{60}Co. The detector was calibrated using standard reference material (silicone resin with homogeneously dispersed radionuclides ^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{137}Cs, ^{113}Sn, ^{85}Sr, ^{88}Y, and ^{203}Hg; total activity 40.624 kBq at April 15, 2008; Czech Metrological Institute Praha, 9031-OL-208/08) in the same geometry as the measured samples (Marinelli beaker, 500 ml).

Table 1. GPS co-ordinates of sampling sites with regard to distance from each CFPP

CFPP	Distance			
	Closest point		Farthest point	
	Latitude	Longitude	Latitude	Longitude
Tent A	N44°40'25.2"	E20°09'0.65"	N44°39'29.1"	E20°12'42"
Tent B	N44°38'05"	E20°02'19.5"	N44°36'01"	E20°06'41.5"
TEK	N44°28'30.1"	E20°18'16.8"	N44°27'22.1"	E20°20'32.1"
TEM	N44°13'15.3"	E21°09'51.1"	N44°14'17.5"	E21°12'34.3"

The ^{238}U activity was determined through its daughter product in equilibrium in soil samples ^{234}Th (63 keV). The activities of ^{226}Ra were determined by its decay products: ^{214}Bi (609 keV, 1120 keV, and 1764 keV) and ^{214}Pb (295 keV and 352 keV) and ^{232}Th activities by its decay product ^{228}Ac (338 keV and 911 keV). Using 46.5 keV γ-energy photons, ^{210}Pb activity concentrations were determined in 21 soil samples. Activities of ^{40}K and anthropogenic ^{137}Cs were obtained from their single gamma ray lines of 1460 keV and 661.66 keV γ-energy, respectively. The spectra were recorded and analysed using the Canberra Genie 2000 software. Counting time was about 70 000 s. Measurement uncertainty of the method is expressed as an expanded measurement uncertainty for the factor $k = 2$ that corresponds to a normal distribution with a confidence level of 95%.

Statistical analysis

To find relationships between radionuclide activities and the soil physical and chemical properties, Pearson's linear correlations were performed. Statistical analysis of data was performed by one-way analysis of variance (ANOVA), and the means were subjected to a least-significant difference test (F test) to specify the main differences in radionuclide activities and soil properties along the distance from each CFPP. Significant differences were considered at $p < 0.05$ level.

Calculation of the gamma dose rate

The terrestrial gamma radiation absorbed dose D in air at a height of 1 m above ground was calculated using the conversion factors in [nGyh^{-1}]/[Bqkg^{-1}]: 0.462 for ^{238}U, 0.604 for ^{232}Th and 0.0417 for ^{40}K [1]

$$D[\mathrm{nGyh^{-1}}] = 0.462C_{\mathrm{U}} + 0.604C_{\mathrm{Th}} + 0.042C_{\mathrm{K}}$$

where C_U, C_{Th}, and C_K denote the specific activities in [Bqkg^{-1}].

The annual external effective dose due to gamma radiation from soil, E, was calculated as [1]

$$E[\mathrm{mSv}]$$
$$D[\mathrm{nGyh}^{\ 1}]\ 8760\mathrm{h}\ \ 0.2\ \ 0.7[\mathrm{SvGy}^{\ 1}]\ 10^{\ 6}$$

using a conversion coefficient of 0.7 Sv/Gy to convert the adsorbed dose in air into the effective dose in the human body. The outdoor occupancy factor is 0.2 (taking into account that people spend about 20% of the time outdoors) and 8760 h is the annual exposure time.

RESULTS AND DISCUSSION

In tab. 2 a general description of natural radionuclides (^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th, ^{40}K) and ^{137}Cs activity concentrations in [Bqkg^{-1}] and physical and chemical properties of the soil samples collected around the four CFPP studied are presented.

The soil analysis results showed that almost all samples are Molic Fluvisols (soil organic matter, SOM), content ranged from 1.2% to 5.6%, and pH in water was >6) except for two samples that belong to Umbric Fluvisols (pH in water is less than 5.5 which indicates base saturation of less than 50%). Particle size analysis revealed uneven distribution of sand, silt, and clay particles. Sand fractions varied widely between sites (~90%). Silt and clay fractions varied notably less, 24% and 29%, respectively. Compared to the sand percentage whose average value was 11.2%, silt and clay fractions with an average 54.1 and 33.6%, respectively, prevailed in all soil samples. Among all sites, textural classes followed the sequence: silty clay loam > silty clay > clay loam. Regarding the calcium-carbonate content, approximately 30% of soil samples were carbonate free, and the rest were calcareous with carbonate content from 0.40% to 19.12%. Soil reaction in water of calcareous samples varied from neutral to slightly alkaline and in non-calcareous samples it was slightly acidic. At two locations, soil properties like SOM content (18.7%) and sand percentage (76%) exhibited unusually high values and were excluded from the analysed data set.

Within the radius of 0-2 km, 2-4 km, and 4-6 km around four plants, a single soil sample was chosen randomly in order to prove the uniformity of the mineral composition among the sites. The results of XRPD analysis showed that mineralogical constituents of twelve investigated bulk soil samples are quartz, feldspar, mica, montmorillonite/illite and carbonate minerals. The major minerals, quartz and feldspar are present in all soil samples and their contents ranged from 40.1-87.7% and 1-49.1%, respectively. Feldspar is more abundant at the TEM and TEK sites and even in the vicinity of Tent A and Tent B (<2 km) it could not be detected. Accessory minerals, naturally less abundant, ranged from 3.5-26.1% for mica, 0.8-34% for montmorillonite/illite, and 8.3-30.5% for carbonate minerals. Accessory minerals were not represented equally at all investigated locations which is why a significant relationship with radionuclide distribution could not be obtained. It was observed that montmorillonite/illite gradually increased in soil samples taken within the 2 km radius around the power plants. The mica mineral is present at TEK and rarely at the other investigated sites. Carbonate minerals were found to be more abundant at Tent A and Tent B compared to the TEM and TEK sites which is in accordance with carbonate distribution in soil determined by the Scheibler method. Soil with the main mineral

Table 2. General description of activity concentrations of ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th, ^{40}K, and ^{137}Cs, and physical and chemical properties determined in soil samples used in this study

	^{238}U [Bqkg^{-1}]	^{226}Ra [Bqkg^{-1}]	^{210}Pb [Bqkg^{-1}]	^{232}Th [Bqkg^{-1}]	^{40}K [Bqkg^{-1}]	^{137}Cs [Bqkg^{-1}]	pH_{H_2O}	pH_{KCl}	SOM [%]	$CaCO_3$ [%]	Sand [%]	Silt [%]	Clay [%]
TEM (n = 10)													
Average	40	40	51	45	581	19	6.8	6.4	3	1.3	8.2	65.6	26.2
SD	7.6	2.7	3.3	5.2	62.8	4.7	0.6	0.6	1.6	1.2	5.2	80	9
CV [%]	19	6.8	6.5	12	10.8	25	8	9.7	23	94	63	12	34.6
Min	28	36	48	37	525	13	6.1	5.5	2.1	0.2	1.6	52.9	12.3
Max	57	44	57	51	736	28	7.6	7.2	4.1	3.9	15.6	73.4	41.9
TEK (n = 8)													
Average	59	62	49	60	544	38	6.4	5.7	3.5	0.4	51.3	58.4	33.8
SD	27.5	22	4.2	5	68.8	9.3	0.6	0.6	1	0.01	3.4	10	14
CV [%]	46.7	35.6	8.6	8.4	12.6	24	9	11	28	1.5	6.5	17.3	41
Min	27	44	46	54	419	21	5.6	5.1	2.5	0.39	48	38.6	13.0
Max	117	115	52	69	622	54	7.4	6.9	5.6	0.40	57	69.8	57.8
Tent A (n = 12)													
Average	30	37	46	37	516	23	7.5	6.9	4.8	2.4	26.8	41.6	31.6
SD	7.4	5.2	7.6	8	87.7	12	0.3	0.2	4.5	2.4	18.5	12.4	8.6
CV [%]	25	14	17	22.4	17	52.5	4	2.6	93	100	69	30	27
Min	16	25	33	20	389	6	7.1	6.6	1.8	0.4	10	12.6	11.3
Max	42	45	56	50	683	48	8.3	7.2	18.7	9.6	76	61.9	43.1
Tent B (n = 12)													
Average	42	43	51	48	597	13	7.0	6.3	3.1	6.0	10	52.9	36.9
SD	12	11	10.6	12	116	6	0.8	0.8	1	7.0	10	7.6	6
CV [%]	29	26	21	24.8	19.5	51	12	13	33	116	99.5	75.5	16.6
Min	15	21	34	24	324	2	5.4	4.7	1.2	0.6	3.8	39.9	28
Max	57	56	65	62	723	20	7.9	7.2	4.2	19.1	32.1	64.2	49

composition of quartz, feldspar, mica and montmorillonite is classified as a group with moderate activities [Bqkg^{-1}] estimated to be 500-900 for ^{40}K, 20-90 for ^{228}Ra and 20-90 for ^{226}Ra [22].

Radioactivity measurements

Summary statistics of activity concentrations of natural radionuclides and ^{137}Cs in soil are presented in tab. 3. It can be observed that the determined average activity values for natural radionuclides in the vicinity of CFPP in Serbia are slightly above the world average values for natural background gamma radiation for soil in the UNSCEAR 2000 report [1]: 33 for ^{238}U, 32 for ^{226}Ra, 45 for ^{232}Th, 420 for ^{40}K. Radioactivity measurements in soil showed values in the range: 15-117 for ^{238}U, 21-115 for ^{226}Ra, 33-65 for ^{210}Pb, 20-69 for ^{232}Th, 324-736 for ^{40}K, and 2-59 for ^{137}Cs. The obtained results are comparable with those given in literature (tab. 4) for radioactivity levels of soils in the vicinity of CFPP from different regions of the world.

If we compare radioactivity levels with respect to the sites, they appear in the following order:

TEK > TEM ~ Tent B > Tent A.

Average activity concentrations of ^{238}U, ^{226}Ra, and ^{232}Th in soils at TEK are nearly two times higher when compared to the Tent A site. Those higher levels are in good agreement with the levels reported in soils in the area located near the surface coalmine Kolubara (Rudovci tableland near the TEK site) and should be attributed to the levels of natural background radiation from soil [23]. The overwhelming majority of samples had ^{232}Th levels slightly enriched over ^{238}U and ^{226}Ra. The thorium concentration in the soil is considerably higher than uranium due to its low mobility and water insolubility. Mortvedt [24] reported that alluvial soils tend to have higher and more evenly distributed concentrations of ^{232}Th indicating their greater mobility

Table 3. Summary statistics for activity concentration of natural radionuclides ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th, ^{40}K, and fallout ^{137}Cs

	^{238}U [Bqkg^{-1}]	^{223}Ra [Bqkg^{-1}]	^{210}Pb [Bqkg^{-1}]	^{232}Th [Bqkg^{-1}]	^{40}K [Bqkg^{-1}]	^{137}Cs [Bqkg^{-1}]
Average	39	42	49	46	563	21.6
SD	12.5	9.3	7.2	10.9	90.5	12.7
CV [%]	32	22	15	24	16	59
Skewness	1.23	0.19	–0.79	–1.15	–0.76	1.75
Kurtosis	1.14	–1.16	–1.19	–0.62	0.40	0.14

Table 4. Comparative data for ^{238}U, ^{226}Ra, ^{232}Th, ^{40}K, and ^{137}Cs in soil in this work and other from different countries of the world in the vicinity of CFPP found in the literature and undisturbed soil from Serbia

Location	^{238}U [Bqkg^{-1}]	^{226}Ra [Bqkg^{-1}]	^{232}Th [Bqkg^{-1}]	^{40}K [Bqkg^{-1}]	^{137}Cs [Bqkg^{-1}]
Spain (soil near CFPP)[9]	19-55	24-79	30-76	200-940	0-85
India (soil near CFPP)[11]	–	32-121	19-45	195-505	–
China (soil near CFPP)[5]	–	28-49	44-61	640-992	–
Brazil (soil near CFPP)[7]	10-273	15-270	10-59	55-412	–
West and Central Serbia (undisturbed soil)[25]	9-117	11-55	7-60	162-586	6-197
Belgrade (undisturbed soil)[26]	–	23-68	28-76	450-760	8-160
Rudovci tableland (disturbed soil)[23]	28-44	–	59-71	335-517	–
This study	15-117	21-115	20-62	324-736	2-54

as organic complexes. Comparison was made as well with the values for background gamma radiation (tab. 4) from undisturbed soils of central and west Serbia [25] and those typical for the city of Belgrade [26] which do not differ from surface soil radioactivity levels recorded in the vicinity of coal-fired power plants.

Based on the kurtosis and skewness values (tab. 3), it can be noted that distributions of all radionuclides follow normal distribution. Variation coefficients for natural radionuclide activity concentrations were relatively small: the least 16% for ^{40}K, about 20% for ^{226}Ra and ^{232}Th, and about 30% for ^{238}U. Since terrestrial radiation is mainly determined by the geology of the site [1], small spatial variations of natural radionuclides indicate that the investigated area is homogeneous with respect to its lithological composition. This is also consistent with strong and significant correlations ($p < 0.001$) between ^{232}Th, ^{226}Ra, and ^{238}U radionuclides in investigated soil presented in tab. 5. Correlations found between ^{226}Ra and ^{232}Th (0.92), ^{238}U and ^{232}Th (0.73), and ^{238}U and ^{226}Ra (0.71) confirm that they predominantly belong to the parent soil materials [14]. In the surficial environment, ^{226}Ra and ^{232}Th are regarded as immobile while uranium is considered mobile under oxidizing conditions and could be removed relative to radium and thorium [15].

The relatively weak but significant correlations (p 0.001) of potassium isotope ^{40}K with ^{238}U (0.42) and stronger with ^{232}Th (0.52) were obtained because potassium and thorium are less mobile in contrast to uranium which was in mobile form during the soil formation [27]. Higher correlation coefficients between ^{40}K and ^{232}Th compared to ^{40}K and uranium series nuclides in soil are often recognized in the literature [28-30]. ^{40}K contained in the soil mineral components is usually uniformly distributed, but in the surface layer of soil that contains vegetation and roots, biological activities can affect ^{40}K removal from topsoil [31].

Correlations with soil properties

Soil granulometry has an important influence on radionuclide distribution in soil because activity concentration decreases with particle-size increase [32]. A study of Blanco Rodriguez *et al*. [33] showed that activity concentration of the finer fractions is strongly correlated with the activity concentration of the bulk soil. High radionuclide activities in clays come from adsorption of radionuclides onto negatively charged clay mineral surfaces. In investigated Fluvisol, according to Pearson's correlation, ^{40}K and ^{232}Th radionuclides were associated with clay fractions. The highest activities detected were associated with the finest soil fraction that is related to the significant proportion of montmorillonite/illite (potassium bearing mineral) in the total clay content.

^{238}U, ^{226}Ra, and ^{232}Th activity concentrations are moderately dependent on silt size fractions of soil positively and on sand fractions negatively (tab. 5). Activities of the coarser soil particles are usually associated with the most resistant soil phases [33]. This was also evidenced by the strong correlation of quartz

Table 5. Pearson's correlation coefficients among the radionuclides themselves and between the radionuclides and the main soil properties of the Fluvisols in the vicinity of four CFPP studied

	^{238}U	^{226}Ra	^{210}Pb	^{232}Th	^{40}K	^{137}Cs	pH_{KCl}	$CaCO_3$	SOM	Clay	Silt	Sand
^{238}U	1	0.71^{a}	0.50	0.73^{a}	0.42^{a}	0.37	–0.63^{a}	–0.46^{b}	ns	ns	0.46^{b}	–0.41^{b}
^{226}Ra		1	0.68^{a}	0.92^{a}	0.36	0.44^{b}	–0.74^{a}	–0.62^{a}	ns	ns	0.38	–0.46^{b}
^{210}Pb			1	0.66b	ns	ns	–0.58^{b}	–0.52	ns	ns	ns	ns
^{232}Th				1	0.52^{a}	0.40	–0.73^{a}	–0.59^{a}	ns	0.37	0.42^{b}	–0.56^{a}
^{40}K					1	ns	ns	–0.37	ns	0.54^{a}	ns	ns
^{137}Cs						1	–0.38	–0.44^{b}	0.40^{b}	ns	ns	ns

Significance level: ns – not significant, p 0.05, ^{b}p 0.01, ^{a}p 0.001

percentages in soil with fractions of coarse sand (0.02-2 mm) positively ($p < 0.02$) and the negative one with the ^{232}Th and ^{226}Ra content ($p < 0.05$). Fluvisol permanent or seasonal water saturation affects radionuclide mobility in surface soil through the processes of leaching, dissolution and precipitation [13]. Sand particles with small specific surface area are chemically inert and because of their large sizes water travels through them easily while silt particles, smaller in size, with larger surface areas are usually transported with water flow [34].

^{137}Cs had higher spatial variation (~60%) revealing its uneven distribution and accumulation in soil that is characteristic of radiocesium derived from the radioactive fallout from the Chernobyl accident and may not be the result of CFPP activities. Its activity concentration values found in soils were within the range expressed by regional levels (tab. 4). Radiocesium is essentially considered non-exchangeable and most of it is irreversibly sorbed onto the clay or soil organic matter particles [35]. According to simple linear regression analysis (tab. 5), variance of SOM percentages in Fluvisol samples affected ^{137}Cs spatial distribution ($p < 0.01$). This connection is also found by Dragović *et al*. [26], who studied depth distribution of ^{137}Cs in Fluvisol profiles that were collected in the alluvial plain of the Sava river which is flooded periodically. They observed that the trend of soil properties and ^{137}Cs activities depends on characteristics of the layers and length of periods of soil formation after or between flood events.

Moderate correlation was established between ^{137}Cs and natural ^{238}U (0.37), ^{226}Ra (0.44), and ^{232}Th (0.40). It can be assumed that this correlation presents a not explicitly obtained relation of those natural radionuclides with soil organic matter that varied more (40%) than activities of natural radionuclides (20-30%). Radionuclides are known to complex with organic matter in soil. Uranium could be retained by organic matter complexation or mobilized if complexes are soluble [36]. A study of radium sorption by soil particles showed that it is affected by SOM rather than soil granulometry [37]; tetravalent thorium is strongly complexed with SOM which increases its mobility [24]. Very similar results were obtained for soils in the vicinity of CFPP in the Megalopolis basin (Greece) [12] where total organic carbon (stored in the soil organic matter) partially influenced the distribution of ^{238}U, ^{226}Ra, and ^{137}Cs while the clay content influenced the distribution of ^{232}Th and ^{40}K.

Activity concentration of ^{210}Pb ranged from 33-65 Bq/kg with spatial variation of 15%. A correlation between ^{210}Pb and SOM contents, usually established in literature, was not observed in Fluvisol. Significant and high correlations (tab. 5) of ^{210}Pb with ^{226}Ra (0.68), ^{232}Th (0.66), and ^{238}U (0.50) indicated that ^{210}Pb is rather connected with soil mineral fractions similar to findings of the investigation of natural catchment soils where the distribution of the accumulated ^{210}Pb demonstrated its preferential adsorption by finer soil particles [38].

The main correlation, moderate to strong and a negative one, for all natural radionuclides in Fluvisol soil samples were found with carbonates and soil pH (except with ^{40}K). Radioactivity decreased with the increase of soil pH and carbonate content. Carbonates explained approximately 40% of ^{226}Ra and ^{232}Th variations and less (15-20%) of ^{238}U, ^{40}K, and ^{137}Cs variations. In the study of Navas *et al*. [14], the highest activities of natural ^{226}Ra, ^{232}Th, and ^{40}K were found in soils (Calcaric Fluvisols) where carbonates have been leached and opposite, lower radioactivity was in the soils with the highest carbonate contents which explains the negative relationship. Negative correlations between pH and radionuclides of the uranium and thorium series were recorded by Tsai *et al*. [29], who concluded that radionuclides extracted from soil leached into the water in neutral and alkaline media could decrease the fixation of nuclides in the soil.

Correlations with the distance

The one-way analysis of variance (ANOVA) test was performed to indicate the main differences in radionuclide activities and soil properties along the distance from each CFPP. Firstly, implied by the test results, there were statistically significant differences ($p < 0.01$) between means of contents of fine sand and silt + clay fractions in the area within the 1 km radius compared to the 1-2 km and 2-6 km zones around the CFPP. In the <1 km zone, a lack of silt + clay (<0.01 mm) and accumulation of fine sand (0.05-0.2 mm) particles was observed which resulted from the reaction of soil with ash particles. Continuous input of ash into the topsoil around the ash pond results in the coarsening of the soil due to excessive silt and fine sand-sized particles (constituents of ash) leading to a decrease in the net clay content [39]. Secondly, mean activity concentrations of natural radionuclides, carbonate content and pH values in the <1 km zone differed significantly ($p < 0.05$) from those in the 1-2 km zone, but not compared to the 2-6 km zone (fig. 2). Pearson's linear correlations were also performed to find relationships of the natural radionuclides with the distance and positive and significant correlations were established within the 2 km radius for ^{238}U ($r = 0.63, p < 0.01$), ^{226}Ra ($r = 0.54, p < 0.05$), ^{232}Th ($r = 0.67, p << 0.01$), ^{40}K ($r = 0.55, p < 0.05$), and ^{210}Pb ($r = 0.45, p << 0.05$). It could be noticed that this increase of activity concentrations of the detected natural radionuclides are with the differences not exceeding 30% along the 0-2 km distance.

In the <1 km area, more alkaline pH levels (7.1-7.9) occurred due to larger carbonate amounts in soil which is why more negatively charged binding sites were available on soil mineral surfaces. The mo-

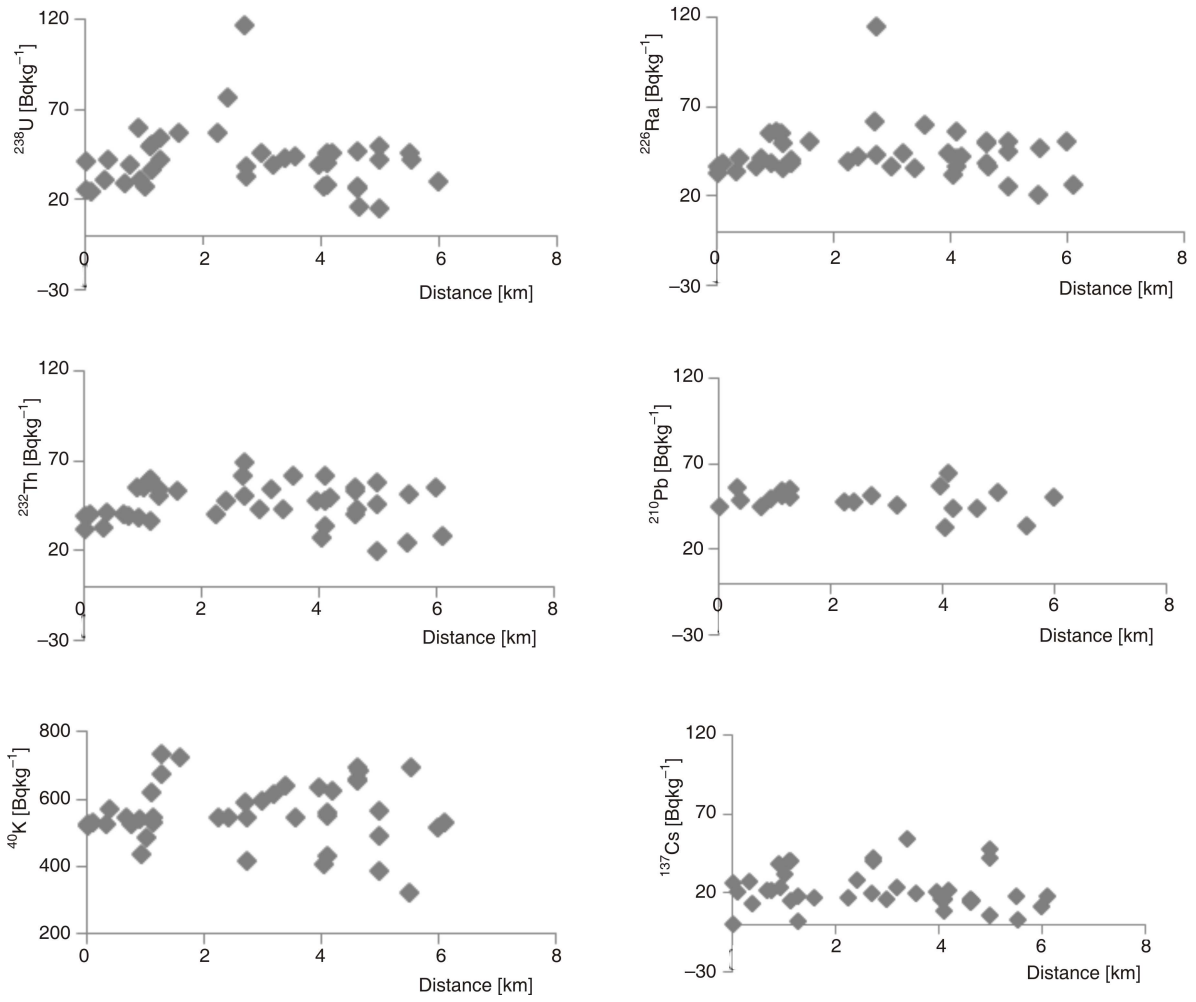

Figure 2. Activity concentration of ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th, ^{40}K, and ^{137}Cs in surface soil within a radius of 6 km surrounding CFPP

bility of ^{238}U was rather enhanced due to the formation of uranium-carbonate complexes, the main inorganic form of transport in the soils at values of pH >6.5 [36]. Carbonate leaching and precipitation, influenced by soil pH, are the main factors controlling the solubility of natural radionuclides, especially ^{232}Th and ^{238}U, which become mobilized, can migrate, and become fixed by the organic matter [30]. Enhanced removal of natural radionuclides is also connected with the presence of drainage water in the <1 km area and with more intense water circulation in general through less dense soils caused by the collapsing of finer soil fractions. At greater distances (1-2 km area), natural radionuclide activities tend to increase (fig. 2) due to gradual soil pH level reduction and carbonate mineral weathering and removal. In that area, carbonate leaching from the topsoil is connected with the relative accumulation of feldspars (which explains the sharp ^{40}K increase) and montmorillonite/illite clays that may adsorb natural radionuclides on the clay surfaces or fix them within the lattice structure [14]. This slight gradual increase of natural radionuclide concentrations could also occur during the period of CFPP operation as it is known that radioactivity "escapes" from the power plant in the form of fine particles. It was evaluated that the maximal deposition of particulate dispersion from a 120 m high stack could take place 400 m downwind from the stack and as the wind speed increases, this maximum is correspondingly removed [2].

The absorbed gamma dose rate in this study ranged from 35.0 nGy/h to 97.9 nGy/h. A similar range of values was reported in the region, in Romania (20-125 nGy/h) and Montenegro (28-50 nGy/h) [40]. The estimated average value of 69.4 nGy/h was higher than 57 nGy/h, the population weighted average dose in the region with 3/5 of the world population [1]. It was also slightly higher than the average value of 62.8 nGy/h for Serbia [41], but less than the dose of 91.3 nGy/h reported for the area affected by uranium mining [42].

The results obtained for the annual effective dose in this study ranged from 0.043 mSv to 0.120 mSv which is comparable with the range from 0.3 mSv to 1.0 mSv adopted in the UNSCEAR, 2010 report [40]. The mean value in our investigation is 0.085 mSv which is greater than 0.07 mSv, the world average

value of the outdoor annual effective dose from terrestrial radiation [40], but similar to the median value of the annual effective dose in Serbia estimated to be 0.081 mSv [41]. It could be concluded that there is no important consequence with regard to natural radionuclide activity concentrations in soils in the vicinity of CFPP in Serbia.

CONCLUSIONS

In the surface soils in the vicinity of four CFPP from Serbia, no enhancement of natural radionuclides ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th, and ^{40}K was found that could have resulted from airborne discharge or the presence of ash at disposal sites. Activity values of fallout ^{137}Cs in soil were within the range expressed by regional levels. Study of particle size distribution showed that clay fractions influenced ^{40}K and ^{232}Th while silt fractions moderately influenced ^{238}U and ^{226}Ra distribution demonstrating their association with the mineral composition of soil. In the <1 km area surrounding the CFPP, the lack of silt + clay (<0.01 mm) and accumulation of fine sand (0.05-0.2 mm) particles together with an increase of soil pH and carbonate content was observed, resulting from the reaction of soil with particles of ash. In that area, natural radionuclides were mobilized with enhanced water movement through less dense soils enriched with sand particles. In view of the fact that lignites from the Kolubara basin used as feed coals for combustion are low in uranium and thorium content, natural radionuclide activity concentrations in surface soil near the CFPP correspond to the background levels.

ACKNOWLEDGEMENTS

This paper was realized as a part of the project "Studying climate change and its influence on the environment: impacts, adaptation and mitigation" (no. 43007) financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia within the framework of integrated and interdisciplinary research for the period 2011-2014.

AUTHOR CONTRIBUTIONS

Theoretical analysis was carried out by I. Ž. Vukašinović, D. J. Todorović, and S. S. Nenadović, and experiments were carried out by D. J. Todorović, N. S. Nikolić, A. S. Mihajlović-Radosavljević, and M. M. Eremić- Savković. All authors analysed and discussed the results. The manuscript was written by I. Ž. Vukašinović and D. J. Todorović, and the figures were prepared by I. Ž. Vukašinović.

REFERENCES

[1] ***, Sources and Effects of Ionizing Radiation, United Nations Scientific Committee on the Effect of Atomic Radiation, Report to the General Assembly, New York, USA, 2000
[2] Papastefanou, C., Escaping Radioactivity from Coal--Fired Power Plants (CPP) Due to Coal Burning and the Associated Hazards: a Review, *J. Environ. Radioact., 101* (2010), 3, pp. 191-200
[3] ***, Naturally Occurring Radioactive Materials (NORM IV), *Proceedings*, International Conference Held in Szczyrk, Poland, May 17-21, 2004, IAEA-TECDOC-1472, Vienna, Austria, 2005
[4] Baeza, A., *et al*., Enhancement of Natural Radionuclides in the Surroundings of the Four Largest Coal-Fired Power Plants in Spain, *J. Environ. Monit., 14* (2012), 3, pp. 1064-1072
[5] Lu, X., *et al*., Measurement of Natural Radioactivity and Assessment of Associated Radiation Hazards in soil around Baoji Second Coal-Fired Thermal Power Plant, China, *Radiat. Prot. Dosim., 148* (2012), 2, pp. 219-226
[6] Dai, L., *et al*., Spatial Distribution and Risk Assessment of Radionuclides in Soils around a Coal-Fired Power Plant: A Case Study from the City of Baoji, China, *Environ. Res., 104* (2007), 2, pp. 201-208
[7] Flues, M., *et al*., The Influence of a Coal-Fired Power Plant Operation on Radionuclide Concentrations in Soil, *J. Environ. Radioact., 63* (2002), 3, pp. 285-294
[8] Papp, Z., *et al*., Significant Radioactive Contamination of Soil around a Coal-Fired Thermal Power Plant, *J. Environ. Radioact., 59* (2002), 2, pp. 191-205
[9] Charro, E., *et al.*, Chemometric Interpretation of Vertical Profiles of Radionuclides in Soils Near a Spanish Coal-Fired Power Plant, *Chemosphere, 90* (2012), 2, pp. 488-496
[10] Bem, E. M., *et al*., Studies of Radionuclide Concentrations in Surface Soil in and around Fly Ash Disposal Sites, *Sci. Total. Environ., 220* (1998), 2, pp. 215-222
[11] Mahur, A. K., *et al*., Radon Exhalation and Gamma Radioactivity Levels in Soil and Radiation Hazard Assessment in the Surrounding Area of National Thermal Power Corporation, Dadri (UP), India, *Radiat. Meas., 50* (2012), 1-6, pp. 130-135
[12] Papaefthymiou, H. V., *et al*., Spatial and Vertical Distribution and Risk Assessment of Natural Radionuclides in Soils Surrounding the Lignite-Fired Power Plants in Megalopolis Basin, Greece, *Radiat. Prot. Dosim., 156* (2013), 1, pp. 49-58
[13] ***, Applicability of Monitored Natural Attenuation at Radioactively Contaminated Sites, Technical Reports Series No. 445, International Atomic Energy Agency, Vienna, Austria, 2006
[14] Navas, A., *et al*., ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th, and ^{40}K Activities in Soil Profiles of the Flysch Sector (Central Spanish Pyrenees), *App. Radiat. Isot., 57* (2002), 4, pp. 579-589
[15] Dowdall, M., O'Dea, J., ^{226}Ra/^{238}U Disequilibrium in an Upland Organic Soil Exhibiting Elevated Natural Radioactivity, *J. Environ. Radioact., 59* (2002), 1, pp. 91-104
[16] Popović, A., *et al*., Speciation of Trace and Major Elements from Coal Combustion Products of Serbian Power Plants (II) – Obilic Power Plant, *Energy Sources – Part A: Recovery, Utilization and Environmental Effects, 33* (2011), 24, pp. 2309-2318
[17] Djurašević, M., *et al*., Natural Radioactivity in Lignite Samples from Open Pit Mines "Kolubara", Ser-

bia-Risk Assessment, *Appl. Radiat. Isot., 87* (2013), pp. 73-76
[18] ***, World Reference Base for Soil Resources. Food and Agricultural Organization of United Nation, Rome, Italy, 2006
[19] Mineev, V. G., Laboratory Manual of Agricultural Chemistry (in Russian), MGU, Moscow, 2001
[20] ***, Soil Quality – Determination of Carbonate Content – Volumetric Method, International Organization for Standardization, Geneve, Switzerland, ISO 10693, 1995
[21] Burt, R., Soil Survey Laboratory Methods Manual, Soil Survey Investigations Report No. 42, USDA Natural Resources Conservation Service, 2004
[22] Megumi, K., *et al*., Relationships between the Concentrations of Natural Radionuclides and the Mineral Composition of the Surface Soil, *Radiat. Prot. Dosim., 24* (1988), 1-4, pp. 69-72
[23] Nenadović, S., *et al*., Vertical Distribution of Natural Radionuclides in Soil: Assessment of External Exposure of Population in Cultivated and Undisturbed Areas, *Sci. Total Environ., 429* (2012), pp. 309-316
[24] Mortvedt, J. J., Plant and Soil Relationships of Uranium and Thorium Decay Series Radionuclides – A Review, *J. Environ. Qual., 23* (1994), 4, pp. 643-650
[25] Pantelić, G., *et al*., Radionuclides Activity Concentration in Soil in Serbia, *Proceedings*, Third European IRPA Congress; June 14-18, 2010, Helsinki, Finland, 2010
[26] Dragović, S. D., *et al*., Edaphic Factors Affecting the Vertical Distribution of Radionuclides in the Different Soil Types of Belgrade, Serbia, *J. Environ. Monit., 14* (2012), 1, pp. 127-37
[27] Cowart, J. B., Burnett, W. C., The Distribution of Uranium and Thorium Decay-Series Radionuclides in the Environment – A Review, *J. Environ. Qual., 23* (1994), 4, pp. 651-662
[28] Montes, M. L., *et al*., Assessment of Natural Radioactivity Levels and Their Relationship with Soil Characteristics in Undisturbed Soils of the Northeast of Buenos Aires Province, Argentina, *J. Environ. Radioact*., *105* (2012), pp. 30-39
[29] Tsai, T. L., *et al*., The Effects of Physico-Chemical Properties on Natural Radioactivity Levels, Associated Dose Rate and Evaluation of Radiation Hazard in the Soil of Taiwan Using Statistical Analysis, *J. Radioanal. Nucl. Chem., 288* (2011), 3, pp. 927-936
[30] Navas, A., *et al*., Spatial Distribution of Natural and Artificial Radionuclides at the Catchment Scale (South Central Pyrenees), *Radiat. Meas., 46* (2011), 2, pp. 261-269
[31] Fujiyoshi, R., Sawamura, S., Mesoscale Variability of Vertical Profiles of Environmental Radionuclides (^{40}K, ^{226}Ra, ^{210}Pb, and ^{137}Cs) in Temperate Forest Soils in Germany, *Sci. Total Environ., 320* (2004), 2-3, pp. 177-88
[32] Belivermis, M., *et al*., The Effects of Physicochemical Properties on Gamma Emitting Natural Radionuclide Levels in the Soil Profile of Istanbul, *Environ. Monit. Assess., 163* (2010), 1-4, pp. 15-26
[33] Blanco Rodriguez, P., *et al.*, Influence of Soil Texture on the Distribution and Availability of ^{238}U, ^{230}Th, and ^{226}Ra in SOIL, *J. Environ. Radioact., 99* (2008), 8, pp. 1247-1254
[34] Golmakani, S., *et al*., Factors Affecting the Transfer of Radionuclides from the Environment to Plants, *Radiat. Prot. Dosim., 130* (2008), 3, pp. 368-375
[35] Tamponnet, C., *et al*., An Overview of BORIS: Bioavailability of Radionuclides in Soils, *J. Environ. Radioact., 58* (2008), 5, pp. 820-830
[36] Vandenhove, H., *et al*., Can We Predict Uranium Bioavailability Based on Soil Parameters? Part 1: Effect of Soil Parameters on Soil Solution Uranium Concentration, *Environ. Pollut., 145* (2007), 2, pp. 587-595
[37] Vandenhove, H., Van Hees, M., Predicting Radium Availability and Uptake from Soil Properties, *Chemosphere, 69* (2007), 4, pp. 664-674
[38] He, Q., Walling, D. E., Interpreting Particle Size Effects in the Adsorption of ^{137}Cs and Unsupported ^{210}Pb by Mineral Soils and Sediments, *J. Environ. Radioact., 30* (1996), 2, pp. 117-137
[39] Praharaj, T., *et al*., Geochemical Studies to Delineate Topsoil Contamination around an Ash Pond of a Coal-Based Thermal Power Plant in India, *Environ. Geol., 45* (2003), 1, pp. 86-97
[40] ***, Sources and Effects of Ionizing Radiation, United Nations Scientific Committee on the Effect of Atomic Radiation, UNSCEAR, 2008, Report to the General Assembly, New York, USA, 2010
[41] Dragović, S., *et al*., Population Doses from Terrestrial Gamma Exposure in Serbia, *Arch. Oncol., 15* (2007), 3-4, pp. 78-80
[42] Momčilović, M., *et al*., Distribution of Natural Radionuclides in Surface Soils in the Vicinity of Abandoned Uranium Mines in Serbia, *Environ. Monit. Assess., 185* (2013), 2, pp. 1319-1329

Received on July 21, 2014
Accepted on November 14, 2014

**Ивана Ж. ВУКАШИНОВИЋ, Драгана Ј. ТОДОРОВИЋ,
Наташа С. НИКОЛИЋ, Ана С. МИХАЈЛОВИЋ-РАДОСАВЉЕВИЋ,
Снежана С. НЕНАДОВИЋ, Маја М. ЕРЕМИЋ САВКОВИЋ**

МЕРЕЊЕ АКТИВНОСТИ РАДИОНУКЛИДА У ЗЕМЉИШТУ У БЛИЗИНИ ЧЕТИРИ ТЕРМОЕЛЕКТРАНЕ У СРБИЈИ МЕТОДОМ СПЕКТРОМЕТРИЈЕ ГАМА ЗРАЧЕЊА И ПРОЦЕНА ДОЗЕ

Испитивана је просторна расподела концентрације активности природних радионуклида ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th, ^{40}K и произведеног ^{137}Cs у узорцима површинског слоја земљишта (n = 42) сакупљених у близини четири термоелектране у Србији, ТЕ "Колубара", ТЕ "Морава", ТЕ "Никола Тесла" А и Б. Применом методе спектрометрије гама зрачења, измерене активности радионуклида у земљишту [Bqkg^{-1}] показале су вредности у интервалу 15-117 за ^{238}U, 21-115 за ^{226}Ra, 33-65 за ^{210}Pb, 20-69 за ^{232}Th, 324-736 за ^{40}K и 2-59 за ^{137}Cs. Активност радионуклида површинског слоја земљишта која би могла да потиче и од депозиције радионуклида при њиховом испуштању у атмосферу из димњака термоелектрана или путем ресуспензије материјала са депоније пепела није показала повишене нивое. Установљено је да је просторна промена механичких особина земљишта (гранулометријског састава), pH вредности и садржаја карбоната била у складу са променама нивоа активности природних радионуклида док су активности радиоцезијума биле повезане са варијацијама садржаја органске материје земљишта. У близини самих термоелектрана (<1 km) примећена је битна акумулација крупнијих честица (дијаметра 0.05-0.2 mm), карбоната и виша алкална реакција земљишта у односу на веће удаљености. Процењене средње вредности апсорбоване дозе и годишње екстерне ефективне дозе које потичу од терестијалног гама зрачења износиле су 69.4 nGy/h и 0.085 mSv, респективно.

Кључне речи: природни радионуклид, особина земљишта, спектрометрија гама-зрачења, термоелектрана