QUANTIFICATION OF RADIOISOTOPIC POLLUTION OF SOIL FROM COAL FIRED POWER PLANT SURROUNDING

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Received September 6, 2019

Abstract. This paper is focused on determination of activity concentration of gamma emitters in surface layer of soil, in surrounding of the coal-fired power plant complex. Also, the impact of coal-fired power plant emissions on certain of physical and chemical properties of the soil was studied. The results of this study indicated that the operation of the power plant has no significant negative impact on the environment in terms of the content of radionuclides. The effect of the coal-fired power plant emissions on soil is a function of the pollutant gradient existing in the area. The increased soil acidity can adversely affect the microbiological and pedogenetic processes in soil which cause cation-anion imbalance and microbe population reduction to affect soil fertility.

Key words: Radioactivity; Power plant; Soil pollution.

1. INTRODUCTION

The contamination of environment by radionuclides and heavy metals presents one of the serious and global problems of humanity. The greatest contribution is the contamination of soil originating from radionuclides and heavy metals naturally found in the soil and originating from the parent substrate of the surface layer of the Earth's crust. *Naturally occurring radioactive materials* (NORM) form part of natural background radiation and in the environment the most frequently exist as members of the ^{238}U, ^{235}U, and ^{232}Th series, and the isotope ^{40}K. In the ecosystem, NORM mainly distributed by natural geological and geochemical processes [1].

Taking into account the limited amount of soil and the very slow process of its formation, irrational use and continuous contamination, soil should be considered conditionally renewable natural resource. It is necessary to reduce soil contamination, since soil contamination leads to imbalance in the quality and content of minerals in the soil, whereby this is a disturbing factor in the biological balance of organisms in the soil, that is, the living world of the loosened soil layer, which breaks down the biological flows.

Due to a kind of technological development and industrial processes, a large amount of by-products emits to the atmosphere, which can contain different concentrations of toxic and harmful substances. Human activities that degrade the soil most, primarily relate to the spread of cities, the construction of industrial complexes and roads, as well as the deposit of waste materials, where huge soil surfaces are exposed to an intense process of erosion. In addition to the above-mentioned NORM, the concept of technologically enhanced naturally occurring radioactive materials (TENORM) was introduced in the mid-seventies of the last century, due to the progression of contamination with radioactive substances far above the level in the natural environment, as well as the potential exposure of the population due to human activities [2].

Increasing the level of concentration of natural radionuclides in the environment can be due to technological procedures, such as: exploitation and processing of ore, coal combustion in power plants, exploitation and processing of oil and gas, use of phosphate in the production of mineral fertilizers, metal recycling [3–5].

Under contamination conditions, potential polluters should be identified in order to take protective measures, which include decontamination and soil remediation. Coal-fired power plants are definitely one of the mentioned sources of contamination. During the process of the operation of the coal-fired power plant, coal combustion can increase the level of environmental pollution in its surroundings due to ash emitted as solid combustion waste or due to inadequately secured landfills when wind is transmitted to large distances [6]. This process generates a number of pollutants, such as: sulfur oxides, carbon and nitrogen, toxic and heavy metals, and organic particles. This increases the concentration of pollutants at different distances from the source of contamination. Therefore, permanent monitoring of pollutants in the environment of the coal-fired power plant is necessary in order to enable the determination of the origin of contamination and the spatial distribution of all potential sources of pollution.

2. MATERIALS AND METHODS

2.1. STUDY AREA

The study area is surrounding of coal-fired power plant comlex “Kostolac A and B”, which is located in Kostolac municipality in eastern of Serbia (N: 44° 42’, E: 21° 10’). The complex of coal-fired power plants “Kostolac A” and “Kostolac B” have a total installation power of 1007 MW and use lignite for the production of electricity. As a by-product in the process of coal combustion, a large amount of ash is deposited in the surrounding of landfills. The position of “Kostolac” complex is shown in Figure 1.

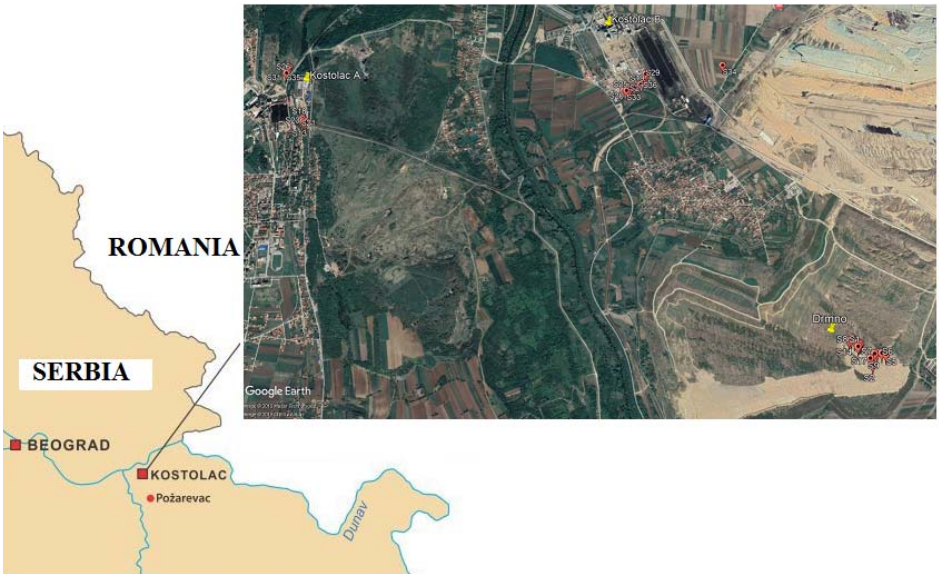

Fig. 1 – The position of "Kostolac" complex.

2.2. SAMPLING AND SAMPLE PREPARATION

Sampling of non-cultivated soil, which is presumed not being treated, in the investigated area of "Kostolac" complex (A and B), as well as soil-mullock samples from the coal mine of Drmno was performed in December 2015. Soil samples were collected in the surface layer in triplicate, depth up to 15 cm, after removal of vegetation. About 2 kg wet weight of soil were collected in polyethylene bags and transported to laboratory. The sampling was performed in accordance with the recommendations given in [7].

In order to prepare 22 soil samples and 14 soil-mullock samples for determination of soil properties, the samples was air-dried to constant mass, samples were homogenized and passed through a 2 mm sieve. For determination of radioisotopic content, samples were dried at temperature of 105°C for 24 hours, after then each sample was crushed, grinded to powder in laboratory mortar, homogenized and sieved through a stainless steel sieve (screen size 250 μm). Dry-weight samples were packed in geometry of plastic box of 200 mL, sealed with beeswax and stored for a period of four weeks before counting, so that secular equilibrium can be attained between ^{226}Ra and its short lived decay products.

2.3. METHODS OF ANALYSIS

Basic physical and chemical soil properties were analyzed by standard analytical techniques: granulometric composition (particle size distribution) was conducted

by pipette method [8], potentiometric method (in water and 1M KCl) for soil pH, volumetric method by Scheibler's calcimeter for $CaCO_3$ content [9], Tjurin's method for total organic carbon (TOC) which is modified by Simakov for the content of humus [10,11], cation exchange capacity (CEC) as the sum of adsorbed base cations and the extractable acidity [12].

Radioactivity measurements have been done on high-resolution gamma-ray Canberra detector, *p*-type with relative efficiency of 50%. The system is provided with Genie 2000 Canberra software for spectrum acquisition, evaluation and analysis. The measurement time of samples activity or background was 60000 s. The detection array was energy calibrated using ^{60}Co and ^{133}Ba standard calibration sources. The efficiency calibration curve was made using secondary reference material, soil matrix in geometry of 200 mL volume plastic box, spiked with the certified reference liquid radioactive mixture solution which contained of following radionuclides (^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{88}Y, ^{113}Sn, ^{85}Sr, ^{137}Cs, ^{210}Pb).

The activity concentration of ^{210}Pb and ^{40}K were determined from the energy lines of 46 and 1460 keV, respectively. The activity concentration of ^{235}U was calculated from the 186 keV peak after subtraction of the overlapping ^{226}Ra peak, while the activity of ^{238}U was determined *via* ^{234}Th (63 keV) or by ^{234}Pa (1000 keV). The ^{226}Ra radionuclide was estimated by its decay products: ^{214}Bi (609 keV, 1120 keV and 1764 keV) and ^{214}Pb (295 keV and 352 keV), while the activity of ^{232}Th was determined *via* ^{228}Ac (338 keV and 911 keV) [5, 13, 14].

2.4. QUANTIFICATION OF RADIATION HAZARD INDICES

In order to assess the level of contamination and the possible radiation hazard indices of analyzed radioisotopes in the soil samples, *radium equivalent activity* (Raeq), absorbed gamma dose rate (*D*), gamma radiation hazard index ($I\gamma$), external hazard index (H_{ex}), *annual effective dose* (AED), *excess lifetime cancer risk* (ELCR) were calculated. The concept and calculation methods for above mentioned parameters are described complete in study by El-Taher *et al*. [5, 15].

3. RESULTS AND DISCUSSION

3.1. RADIOISOTOPES IN SOIL AND SOIL CHARACTERISTICS IN INVESTIGATED SAMPLES

The descriptive statistics of analyzed radioisotopes for investigated samples from coal-fired power plant complex "Kostolac" is summarized in Table 1. The soil-mullock samples were selected with different levels of influence from the installation, in such a way that they had different levels of radioactive contamination. The range of measured activities in investigated soil samples differed widely and expressed

variability was noticed, which depends of physical, chemical and geo-chemical properties of investigated radionuclides and the pertinent environment. The average concentrations of analyzed radioisotopes expressed as Bq kg^{-1} are the following: 86.22 for ^{210}Pb, 60.64 for ^{238}U, 3.32 for ^{235}U, 34.97 for ^{226}Ra, 53.75 for ^{232}Th and 601.39 for ^{40}K. The radionuclide concentrations in soil obtained in this study were similar to equivalent data reported around in the worldwide literature [16–19]. Also, the obtained values are in good agreement with the recommended values for background gamma radiation reported for worldwide soils given in UNSCEAR [20]. It should be mentioned that naturally occuring radionuclides are inclined to accumulate in the upper soil layer (0–20 cm) or lower.

Table 1

Descriptive statistics of radioisotopes concentration (Bq kg^{-1}) around complex "Kostolac"

Parameter	^{210}Pb	^{238}U	^{235}U	^{226}Ra	^{232}Th	^{40}K
Average	86.22	60.64	3.32	34.97	53.75	601.39
St. deviation	48.61	30.14	1.68	13.40	15.81	162.08
Median	80	56	3	38	57	560
Minimum	12	10	1.2	6	6	300
Maximum	210	170	9.8	63	80	1010
Range	198	160	8.6	57	74	710
Skewness	0.9195	0.9409	0.1071	–0.7093	–1.9929	0.2377
Kurtosis	–0.0093	4.4517	6.7034	–0.3908	1.9545	0.5198

The descriptive statistics of soil properties for investigated samples is summarized in Table 2. In investigated soil samples basic physical and chemical properties of the soil were determined, such as particle size distribution, pH, *organic matter* (OM), *carbonate content* (CC), *total organic carbon* (TOC) and *cationic exchange capacity* (CEC). The particle size distribution according to the USDA diagram [21] shows that the soil texture spread from clay loam to sand clay loam. Soil pH in water varied from slightly alkaline to strongly alkaline (range 7.21−8.89), while soil pH in KCl varied from slightly acid to moderately alkaline (range 6.10−8.30), but must soils were found to be neutral (6.6−7.3). Organic matter varied from 0.02 to 13.14% (mean 4.64% is characteristic of medium humus soil), while carbonate content varied from 0.33 to 16.89% (mean 9.26%), but these properties have shown significant variations between sampling locations. Total organic carbon and cationic exchange capacity, also have shown significant variations in related to sampling sites, ranging from 0.01 to 7.64% (TOC) and from 1.52 to 43.75% (CEC). In order to investigate any relations between the soil profile and radionuclide concentrations, the basic physical and chemical properties of the soil were studied. The investigated soil properties may influence migration and adsorption of radionuclides [22].

Table 2

Descriptive statistics of soil properties around complex "Kostolac"

Parameter	Sand (%)	Silt (%)	Clay (%)	pH in H_2O	pH in KCl	OM (%)	CC (%)	TOC (%)	CEC (%)
Average	53.06	20.55	26.39	8.05	7.33	4.64	9.26	2.70	22.06
St. deviation	12.73	4.94	9.27	0.49	0.46	3.70	4.73	2.15	12.06
Median	52.2	21.85	25.35	7.90	7.13	4.42	8.65	2.57	24.69
Minimum	21.6	0.2	2.40	7.21	6.10	0.02	0.33	0.01	1.52
Maximum	97.4	26.0	52.40	8.89	8.30	13.14	16.89	7.64	43.75
Range	75.8	25.80	50.0	1.68	2.20	13.12	16.56	7.63	42.23
Skewness	2.812	–3.312	–1.692	0.919	1.649	0.011	–0.658	0.002	–2.178
Kurtosis	3.869	8.082	1.208	–1.185	–0.120	–0.728	–0.965	–0.728	–1.499

3.2. QUANTIFICATION OF RADIOISOTOPIC POLLUTION

Based on the measured values of activities of ^{226}Ra, ^{232}Th, ^{40}K and certain conversion factors, it can be calculated the radiation hazard indices, that represent significant values in the estimation of the radiation risk for the population. Descriptive statistics of calculated factors of radioisotopic pollution quantification is summarized in Table 3. It can be observed from Table 3 that the values of radium equivalent activity in soil samples fluctuated from 61.6 Bq kg^{-1} to 253.7 Bq kg^{-1}. The calculated values of Ra_{eq} in this tudy are lower than the allowed maximum value that amounts 370 Bq kg^{-1} [23]. The values of absorbed dose rates due to gamma radiations in air at 1 m above the ground surface were calculated assuming that all decay progenies are in radioactive equilibrium with their precursors and that another radionuclides, such as ^{137}Cs, ^{90}Sr insignificantly contribute to the total dose due to the external exposure. The average absorbed dose rate of 73.7 nGy h^{-1} is insignificantly higher than the allowed maximum value of 59 nGy h^{-1} given in UNSCEAR [20]. The values of another radiation hazard indices called the representative level index (I_γ) and external hazard index (H_{ex}) were lower than unity. Radiation risk due to external exposure is not considered significant if the parameter value is less than unit.

Table 3

Descriptive statistics of calculated factors of radioisotopic pollution quantification

Parameter	Ra_{eq} (Bq/kg)	D (nGy/h)	I_γ	H_{ex}	AED (μSv)	ELCR (10^{-4})
Average	158.1	73.7	1.17	0.43	90.4	3.48
St. deviation	42.0	19.4	0.31	0.11	23.8	0.92
Median	158.5	73.4	1.16	0.43	90.1	3.47
Minimum	61.6	31.8	0.51	0.17	39.1	1.50
Maximum	253.7	118.9	1.89	0.69	145.9	5.62
Range	192.2	87.1	1.38	0.52	106.8	4.12
Skewness	–0.0324	0.0976	0.0789	–0.0323	0.0976	975.5
Kurtosis	0.2072	0.1182	0.1303	0.2072	0.1182	1182.1

The estimated annual effective dose was calculated assuming that is outdoor occupancy time amounts 20% and obtained average value is 90.4 μSv, but this value is higher than the world average value at 70 μSv [24]. One of the parameters of quantification of radioisotopic pollution is excess lifetime cancer risk due to terrestrial exposure, which is calculated based on average duration of life (70 year) and fatal cancer risk for stochastic effects. The values of lifetime cancer risk due to terrestrial exposure varied from 1.5×10^{-4} to 5.6×10^{-4} with average value of 3.4×10^{-4} that is similar with world average value of 2.9×10^{-4} [20].

The lowest values of parameters of quantification of radioisotopic pollution are calculated for soil-mullock from "Drmno" coal mine, marked as S1 on the map, while the highest values of the same parameters are obtained for soil from coal-fired power plant complex "Kostolac A", marked as S26 on the map. The average values of calculated parameters of radiation risk are in accordance with literature values and due to this fact, it can be observed that radiation risk is low.

3.3. CLUSTER ANALYSIS

The hierarchical grouping analysis was applied, based on the method between groups and Pearson's correlation as the rule of amalgamation, in order to examine the correlation between the concentration of activity of the investigated radionuclides and the properties of the soil. The results obtained are presented in a dendrogram together with the derived Pearson product moment correlation coefficient (Figure 2).

		1	2	3	4	5
1	^{210}Pb	1.00				
2	^{238}U	0.43	1.00			
3	^{235}U	0.32	0.84	1.00		
4	^{226}Ra	0.01	0.40	0.18	1.00	
5	^{232}Th	0.08	0.40	0.28	0.58	1.00
6	^{40}K	0.14	0.66	0.45	0.58	0.66
7	Sand	-0.29	-0.58	-0.49	-0.26	-0.76
8	Silt	0.36	0.40	0.33	0.07	0.56
9	Clay	0.21	0.59	0.50	0.33	0.74
10	pH	-0.14	-0.02	-0.07	-0.07	-0.27
11	OM	0.15	0.09	0.22	-0.24	0.05
12	CC	-0.10	0.01	0.01	-0.05	0.01
13	TOC	0.15	0.09	0.22	-0.24	0.05
14	CC	0.16	0.28	0.35	-0.06	0.37

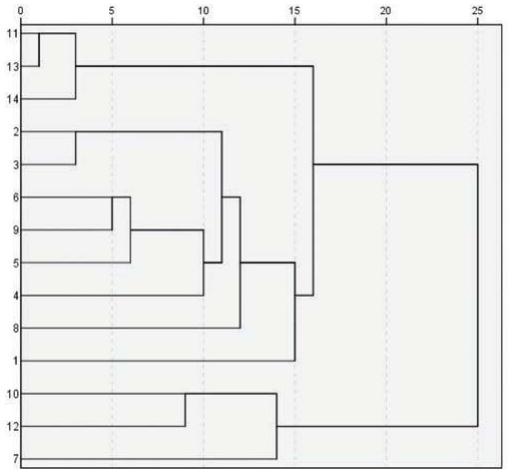

Fig. 2 – Dendrogram together with the derived Pearson product moment correlation coefficient.

Two main clusters can be observed: the first comprising, carbonate content (CC), pH, and sand and the second consisting of ^{210}Pb, ^{238}U, ^{235}U, ^{226}Ra,^{232}Th, ^{40}K, slit, clay, *organic matter* (OM), *total organic carbon* (TOC), *cationic exchange*

capacity (CEC). In this study, the correlation between all radionuclides is positive, and the largest degree of correlation exists between the ^{235}U and ^{238}U. All radionuclides were positively correlated with clay and silt fractions but showed negative correlations with sand. This correlation analysis showing that the fine-grained soil fraction has a higher tendency for radionuclide adsorption than coarse-grained soils because the soil particle surface area is larger [25–27]. There is a negative correlation between pH and radionuclide, except for ^{232}Th [27, 28]. There is no significant correlation between radionuclides and *organic matter* (OM), *carbonate content* (CC), *total organic carbon* (TOC) *and cationic exchange capacity* (CEC).

4. CONCLUSION

This paper presents the detailed study of the radioactivity level, apropos enrichment of analzyed gamma emmitters in soil and soil-mullock samples, and also these results provide information on the environmental impact of the one of the bigger coal-fired power plants in the Republic of Serbia. It is observed that the highest enrichment was obtained for ^{210}Pb. The parameters of quantification of radioisotopic pollution at some sampling sites were higher than the mean values for worldwide soils. In order to reduce the impact of the ash disposal site on soil quality, consequently on groundwater flows, some recovery measures must been implemented in this area. It has been confirmed by the results presented in this study.

Acknowledgement. The authors would like to thank to the Ministry of Education, Science and Technological Development of the Republic of Serbia for material support (Grant III 43009).

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