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DETERMINATION OF URANIUM CONTENTS IN THE SOILS

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Abstract: The usage of depleted uranium munitions was only indirectly forbidden (by General convention which is against environmental pollution) up to its mass application in the last decade of XX century (Iraq, Bosnia, Yugoslavia). The United Nations are on the good way of putting the depleted uranium to the list of forbidden weapons. Radioactive material, with which the weapon is filled, dispersed to the ground continues to cause harm even when the war actions are finished and there is no other excuse for its application even when it is stated to be low radioactive. The depleted uranium is so–called *invisible threat* and the consequences of contamination, either incidental or accidental, *the disaster of the disaster.* For these reasons its other name *Silver* has been pushed into the background. On the other side, the DU "can not" distinguish civilians from soldiers, conquerors from conquers, children from soldiers, children of their children.... and for that its name has been changed to *Deadly Bullet. Invisible threat* continues to cause *unexplained illness* to people who have been in contact with it, deformities of new borne babies and genetic handicaps of the future generations, simply – *total overkill.*

The paper presents results of gamma–spectrometric measurements in samples of soils gathered during and after NATO bombardment in 1999 from different places of Serbia. The aim of investigation was to establish a possible soil contamination by depleted uranium. Results have shown that in all soil samples,

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content of radionuclides was within the allowed limits and usual level of both natural and artificial radionuclides has been found. Measurements so far do show that presence of natural radionuclides in the sample of soil and sediment (ratio $^{238}U/^{235}U$) was normal. Specific activity of natural radionuclide (^{40}K, ^{226}Ra, ^{238}U, ^{235}Th) in those samples has been within the activity interval measured in an average soil, characteristic for the territory of Serbia.

Key words: depleted uranium, environment, biological chain of nutrition, uranyl ion, radionuclide, NATO bombing, soil.

Introduction

Soil is an important link in the chain of matter and energy cycling in the nature. Besides water and air, it has been increasingly exposed lately to various kinds of contamination, especially after air-strikes against Yugoslavia by NATO–forces during 78 days (Rajković, 2000). Considering that during the bombing various missiles were utilized and according to the evidence that ammunition with depleted uranium (DU) was used, an investigation on the consequences of depleted uranium ammunition use started immediately after the termination of war actions and even during them.

For these reasons, the aim of this work was to investigate whether there occurred a contamination of soils with DU at various sites in Serbia, as a result of NATO air–strikes, by comparing obtained results with natural background, and also to record all the aspects of DU ammunition application: from military, over environmental contamination and adverse effects on population, to the aspect of ecological right – right of living.

Depleted Uranium

Depleted Uranium (DU) is a waste product of the process employed to enrich natural uranium to be used in nuclear reactors and in nuclear weapons. Depleted Uranium is a low cost material readily available. By its definition, DU is a mixture of isotopes uranium: ^{238}U (99.8 %), ^{235}U (0.2%), ^{234}U (0.001 %) and ^{234}Th, ^{234}Pa, ^{231}Th and (probably) plutonium in traces. DU's high density (19.05 g/cm^3, 1.7 x more than 11.35 g/cm^3 for lead) and its high atomic number (Z=92) provide useful solution for γ–radiation shielding. DU is low α–radiation emitter (total specific activity of DU is 39.42 Bq/mg) and it contributes significantly to the radiation dose in the case of internal contamination (Rajković, 2001a).

DU's high density and low cost makes it a material of choice for application in the tips of bullets (caliber from 20 to 155 mm) with the intention of piercing armour plating. It may also be used in cruies missile nose cones and is used in the armoury of tanks, and for aircraft counterweights. In the case of weapons, this makes them extremely hard and able to pierce armour plating. (Balkans Task Force (BTF), 1999).

Schematic view of a DU bullet caliber 120 mm (M829A1) is shown in Figure 1. and DU's way across environment in Figure 2.

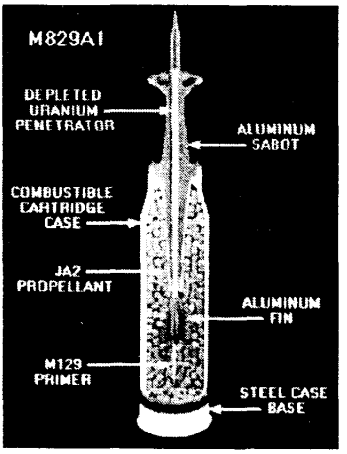

Fig. 1. – Schematic view of a DU bullet caliber 120 mm (M829A1)

The aluminium sabot of a DU bullet drops off within the first 100 m of the trajectory and the bare DU projectile then moves with velocity from 1.067 to 1.7 km/sec. Kinetic energy penetrators do not explode but they fragment into pieces and fine dust. Due to the pyrophoric nature of DU and the extreme flash temperatures 1200°C (thanks to relatively low melting point of DU 1.132°C) generated on impact (especially with steel) the dust in many cases catches fire and burns (so–called *Silver bullet*) forming particles of uranium oxides (diameter < 5 μm). (Figure 2.) (Rajković, 2001b).

Depleted Uranium Cycle and Contamination of Biological Chain of Nutrition

Because DU is thermochemically unstable relative to more oxidized forms of uranium U(IV) and U(VI), it will react to form oxides when in contact with the earth's atmosphere. The primary oxidation products are hyperstoichiometric U(IV)

oxides of the form UO_{2+x}, where $0<x<0.4$. Further oxidation to mixed U(IV) and U(VI) oxides may occur (Ebinger et al., 1990).

Uranium that is leached from fragments and dust particles of DU will be transported through the soil or bedrock as uranyl ions – UO_2^{2+} in ground (Figure 3.). Under oxidizing conditions, most of the dissolved uranium ions are in the form of soluble unary ions that can move through the environment and living organisms. Under reducing conditions, most uranium is solid or insoluble.

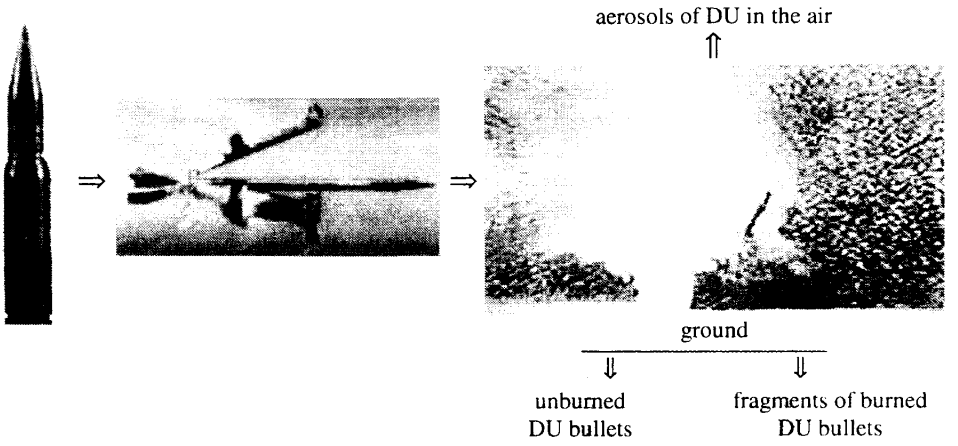

Fig. 2. – DU's way across the environment before and after striking in a target

The potential for the migration of uranium depends on the chemistry of local soils and pore waters as well as on oxidation products of DU. The mobility of dissolved uranium products will depend on the Eh, pH value and the presence of complexing ligands in local groundwaters. Uranium U(VI) is more mobile than U(IV) because of aqueous complexation reactions involving ligands commonly found in natural waters. Carbonate and phosphate are considered the most important of these. The transport of dissolved uranium can also be effected by attenuation reactions that reduce uranium concentration in groundwater and surface waters. These reactions of uranium with the soils include ion exchange and specific adsorption of uranium in organic matter, clay minerals, and ferric oxides and oxyhydroxides commonly present in soil.

Dissolved U(VI) exists in solution as the uranyl ion, and forms complexes with OH^-, CO_3^{2-}, F^-, PO_4^{3-}, SO_4^{2-} and organic ligands. The uranyl ion is

complexed primarily by fluorid between pH less than 4, and it is strongly complexed by phosphate between pH values of 4 and 7.5. At higher pH, dissolved uranium is present predominantly as uranyl carbonate complex.

Interractions between local soils and groundwater may affect the concentration of DU transpoted through a soil profile. These interractions include precipitation of secondary uranium minerals, ion exchange of DU in clay minerals, and specific–ion adsorption of DU on mineral surfaces. All these types of mass–transfer interractions could decrease the concentration of DU in groundwater migrating through a soil profile.

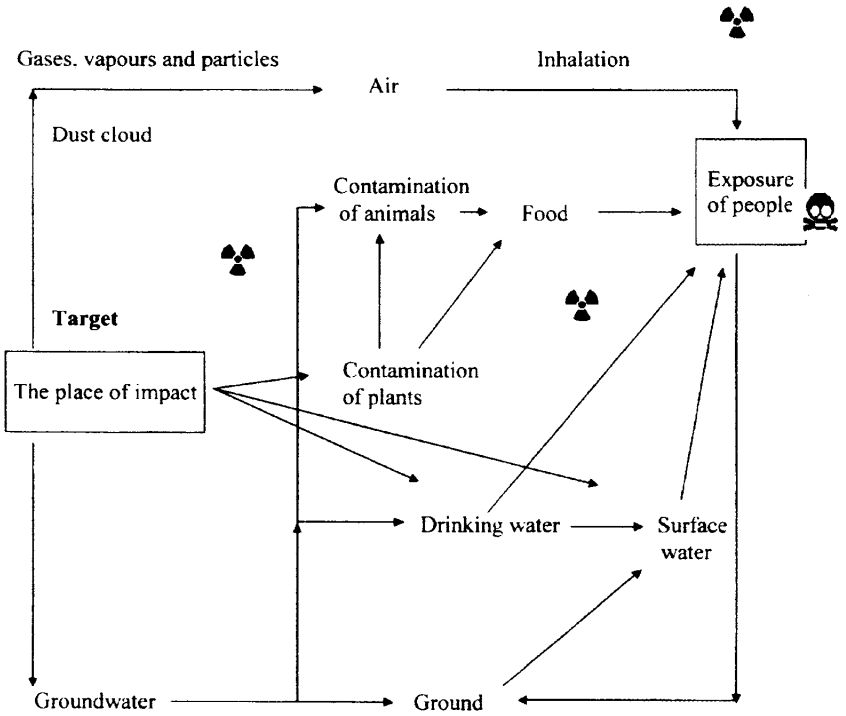

Fig. 3. – The depleted uranium cycle and contamination of Biological chain of nutrition (Rajković and Vucelić–Radović, 2001)

Erikson et al. (1990) found that DU penetrators principally corrode into hydrated U(VI) oxides that were very soluble in water. Erikson further found that when native soils were acidic, they could attenuate uranium species, probably through adsorption reactions. They also found that soils with high carbonate had the lowest capacity, probably due to the formation of very soluble uranyl carbonate

such as UO_2CO_3, $UO_2(CO_3)^{2-}$ and $UO_2(CO_3)_3^{4-}$. Under aerobic conditions, iron can play a key role in controlling the movement through soil. Uranium will bind to many iron materials. Humic matter adsorps uranium too in the soil. Uptake (complexation) by organic compounds will slow the migration of uranium through soil by several orders of magnitude, so that it becomes essentially immobile.

For aqueous conditions, such as those in surface water, corrosion rates tend to be higher than at atmospheric oxidation rates. The reaction of DU with water is complex. Initially, it reacts to form uranium dioxide and hydrogen:

$$U + 2H_2O \rightarrow UO_2 + 2H_2.$$

The transport of uranium from DU on the ground surface to the groundwater will continue for many years ($4.5 \cdot 10^9$ years). However, in an affected area no effects on the environment are likely due to contaminated groundwater.

Material and Methods

Soil samples were collected during 2000 from various sites in Serbia, from the existing bomb craters or 10 and 100 m distant spots, from soil layers 0–5 or 0–30 cm deep. Samples of sediments in the Danube were collected from the river bed. After the sampling, the soil was air dried by spreading it in a thin layer in a clean and well ventilated room. After that, the samples of soil and sediment were dried at 105°C till achieving a constant mass, ground and homogenized and sieved through a sieve. A fraction of particle size < 250 μm was used for measurements.

Gammaspectrometric analysis of soil samples was performed as follows: soil samples were homogenized, dried at 105°C (for 6 hours) and put into a container (marinelli) of appropriate geometric shape and kept closed airtight (30 days) in order to achieve radioactive equilibrium (Book of regulations, 1999).

Gammaspectrometric measurements were performed by three pure germanium detectors manufactured by EG&G "ORTEC", Germany, with the efficiency of 25-30% and energy resolution 1.75-1.95 keV. The detectors were connected to a multichannel analyser by the same manufacturer and to corresponding computer equipment. Energy calibration, as well as calibration of detector efficiency was performed by radioactive standard supplied by Amersham. The measurement time for one sample was 60,000 to 100,000 sec, and the basic radiation was measured after 250,000 sec.

Measurements of total activity were performed by α–β anticoincidental proportional gass counter ("COUNTERMASTER") with basic radiation of 1 imp/min. Planchet radius was 2.3 cm. Counter efficiency amounted to 24% and was determined by a standard of ^{90}Sr.

Results and Discussion

On the basis of found ammunition remnants with DU (Figure 4), depleted uranium reached Yugoslav territory in two ways:

– by airplanes A–10 that use ammunition of 30 mm caliber which was fired from multibarrel airplane guns GAU-8/A (*Avenger*) and PGU-14A/8 (API – *Armor Piercing Incendiary*). According to the available data, only the ammunition of 30 mm caliber was used, which contains 298 g of depleted uranium. According to the evidence of Pentagon, in 100 flights with airplanes A-10 "Thunderbolt", about 31,000 of these projectiles were fired only in Kosovo and Metohia, and 3,000 – 5,000 in the territory of central Serbia (eight spots and one in Montenegro – the peninsula Luštica, cape Arza near Herceg Novi), which amounts to a total of 10 t DU thrown over Yugoslavia by NATO official reports. According to the estimations of Yugoslav Army, about 50,000 projectiles were fired, i.e. 15-20 t of DU was deposited in Yugoslavia.

– by cruising missiles which were fired at all sites in Serbia. It is estimated that one average cruising missile carries about 20 kg of depleted uranium. Over Yugoslavia (mainly Serbia) there were fired approximately 400 cruising missiles that can be supposed to have carried DU (but it cannot be confirmed with certainty). It can be calculated, on the basis of these data, that 8 t of DU has been deposited in the environment of Serbia.

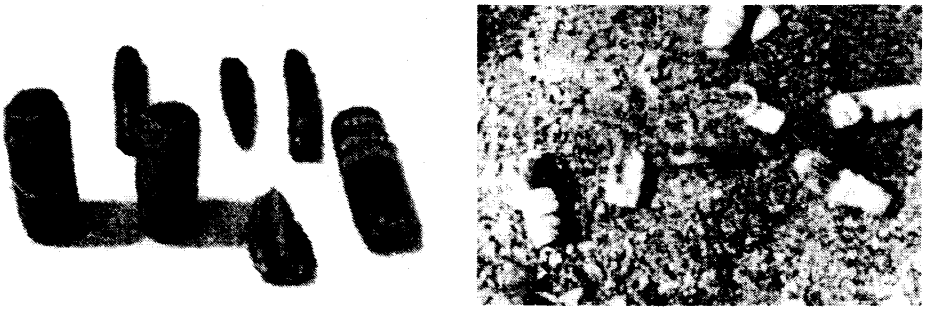

Fig. 4. – Remnants of burned missile of 30 mm caliber with DU collected at the site of the action

Cruising missiles, utilized during NATO air strikes, were nevertheless charged with conventional explosive (320–455 kg of conventional explosive in a warhead or with 166 pieces of cassette bombs BLU–97/B), because investigations have been performed of all the sites that had been targets, but the presence of depleted uranium has not been proved in any case (R. Pavlović and S. Pavlović, 2001).

Uranium is a natural radioactive element occurring in the earth crust and it contributes to the varying values of natural background for every site (the ratio $^{238}U/^{235}U$ in natural uranium amounts to 21.4). For that reason, soil activity has been determined for each location and compared to the natural background (Radovanović et al., 1992).

As the airport in Batajnica was a "legitimate target" and was on innumerable occasions aimed at by missiles with great variety of loads and sizes (Rajković and al., 2000; Antić and al., 2000), investigations were carried out to show whether there occurred a contamination of humous–accumulative Ah–horizon of the carbonate chernozem in the area of Batajnica and in the immediate vicinity of the airport and of aluvial deposits in the Danube. The results of gammaspectrometric analyses of radioactivity in soil samples from Batajnica and in aluvial deposits and clay from the Danube are represented in Table 1.

Tab. 1. – Results of gammaspectrometric analysis of radioactivity in soil samples from sites near Batajnica and from the Danube (in Bq/kg)

Radionuclide	Soil samples from Batajnica	Aluvial deposits and clay from Danube
^{40}K	540–548 ±20	278±12
^{134}Cs	<0.3	<0.3
^{137}Cs	11.0–11.3 ± 0.5	8.3±0.5
^{232}Th	48.8–51.4 ± 2.3	25.2 ±1.9
^{226}Ra	48.5–51.3 ± 4.1	28.6±4.9
^{238}U	56.2–65.3 ± 9.1	24.3±9.9
^{235}U	2.4–2.8 ± 0.2	1.1±0.3
$^{238}U/^{235}U$	23.3	22.1

From Table 1 it may be seen that the analysed soil samples show usual levels of the activities of both natural and artificial radionuclides, which means that no increase of radioactivity occurred in comparison with the natural background. Activity ratio of natural isotopes ^{238}U and ^{235}U in analysed samples (23.3 and 22.1) is in accordance with their ratio in natural uranium, which indicated that the content of artificial radionuclides is not increased. Somewhat higher values are the result of the application of phosphate mineral fertilizers containing uranium.

The results of measurements of specific activities of individual radionuclides in various soil samples from the regions of Belgrade, Niš, Novi Sad, Subotica, Zaječar and Užice are represented in Tables 2 and 3. (Pantelić at al., 1999, 2000).

T a b. 2. – Specific activity of individual radionuclides in soil samples (in Bq/kg)

Radionuclide	Soil from crater	Uncultivated soil	Cultivated soil	Natural phone of soil
^{238}U	15–57	24–62	13–65	1–72
^{235}U	< 0.6–2.4	< 0.7–2.0	< 1.0–2.3	–
^{232}Th	13–49	38–56	30–55	1–10
^{226}Ra	13–53	32–66	25–50	2–105
^{40}K	89–918	511–765	399–768	150–980
^{137}Cs	0.5–3.4	3.2–28	5.4–26	–

On the basis of the determined values, compared with the natural soil background (Radovanović et al., 1992), that are represented in Table 2, it has been found that the activities of the isotopes ^{238}U, ^{226}Ra and ^{40}K in soil samples are within the limits of natural background. The ratio of ^{238}U and ^{235}U activities in the analysed samples correspond to their ratio in natural uranium (21.4), while the activities of artificial isotopes ^{235}U, ^{232}Th and ^{137}Cs are above the permitted value. The presence of ^{137}Cs isotope is expected as a consequence of the Chernobyll accident, while the activity of ^{232}Th isotope exceeds the natural background several times.

The results of the determinations of total β–activity and specific activities of individual radionuclides in the samples from national parks are presented in Table 3. In Tables 2 and 3, minimal and maximal activities are given of soil samples, soil from the crater, soils 10 and 100 m away from the crater (control samples). The results of the investigation of soil samples from Vojvodina and central Serbia (north from Niš, together with Niš region) are presented in Table 3. There has been no samples from Kosovo territory.

T a b. 3. – Specific activity of individual radionuclides in soil samples from national parks (in Bq/kg)

Radionuclide	Soil from crater	Soil out of crater
^{238}U	15–255	16–221
^{235}U	0.6–9.4	0.8–8.1
^{232}Th	16–200	23–126
^{226}Ra	17–225	18–118
^{40}K	276–1020	349–756
^{137}Cs	1.2–106	4.7–137

If the activity of isotopes in the soil of national parks, taken from the crater, is compared to the activity of control samples, it may be concluded that in almost all

the cases the activity is increased compared to the natural background. Soil from the crater shows an increased activity by 10 to 50 wt. %, depending on the isotope. All this indicates a basic fact that the contamination with DU in the territory of Serbia was of purely local character at individual microsites. The sites were contaminated only within the range of 100 m, making the total area of contamination 1000 m^2.

At the contaminated sites, the determined radioactivity was 1100 times higher than the allowed limit. Only those persons who happened to be at the site of an attack or came into an immediate contact with the DU loaded projectile or particles remained after hitting the target, could suffer acute consequences. If they survived the physical attack, the main danger threatening them lies in chemotoxicity of soluble inhaled aerosols. Within a 100-m radius, the main danger lies in radiotoxicity of insoluble aerosols. This danger is not acute.

Conclusion

The usage of depleted uranium munitions was only indirectly forbidden (by General convention which is against environmental pollution) up to its mass application in the last decade of XX century (Iraq, Bosnia, Yugoslavia). The United Nations are on a good way of putting the ammunition with depleted uranium to the list of forbidden weapons. Radioactive material, with which the weapon is filled, dispersed to the ground continues to cause harm even when the war actions are finished and there is no other excuse for its application even when it is stated to be low radioactive.

According to the results of soil sample analysis in Serbia, at various sites, it may be concluded that the activity of long-lived radionuclides of artificial origin (^{137}Cs) (Chernobyl accident) has significantly decreased.

Activity of natural radionuclides is within the limits of average values for soils from the investigated regions of Serbia. Detected increased activity of individual soil samples indicates that the contamination with depleted uranium has been of purely localized character and connected with certain microsites. Soils are contaminated up to a 100-m distance from the center of the impact, the total area being 1000 m^2. At the contaminated spots, the determined activity has been several times higher than the permitted value.

Only after a wider survey of all threatened territories and after collecting samples from the sites where the attacks of NATO alliance were harder (especially from the territory of Kosovo), the real risk for population health, living at these sites can be estimated.

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ODREĐIVANJE SADRŽAJA URANIJUMA U ZEMLJIŠTIMA

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Rezime

Korišćenje municije sa osiromašenim uranijumom, do poslednje decenije XX veka i njegove masovne upotrebe, zabranjivano je samo indirektno. Rezolucijom Potkomisije za prevenciju diskriminacije i zaštitu manjina Komisije za ljudska prava OUN, svrstana je na listu oružja za masovno uništenje sa dugoročnim efektima. Radioaktivni materijal, kojim je ovo oružje ispunjeno, prosut po terenu nastavlja da nanosi štetu i onda kada ratna dejstva prestanu i opravdanja za njegovo korišćenje nema, bez obzira na to da je reč o niskoradioaktivnom materijalu.

Iz tih razloga se osiromašeni uranijum naziva *invisible threat* ("nevidljivi neprijatelj"), a posledice izazvane kontaminacijom sa osiromašenim uranijumom, bilo incidencijalno ili akcidencijalno, nazvane *the disaster after disaster* ("nesreća nakon nesreće"), bacaju u drugi plan njegov popularni naziv *silver bullet* ("srebrni metak"). Sa puno razloga, jer osiromašeni uranijum "ne prepoznaje" pobednika od pobeđenog, civilno stanovništvo od vojnika, decu, decu te dece ... Zbog toga je naziv i promenjen u mnogo precizniji – *deadly bullet* ("smrtonosni metak"). *Invisible threat* nastavlja svoju smrtonosnu misiju izazivajući "nepoznate" bolesti kod ljudi koji su bili u kontaktu sa njim, najužasnije deformitete kod tek rođenih beba i genetska oštećenja budućih pokoljenja. Jednostavno – *total overkill*.

U radu su prikazani rezultati gamaspektrometrijskih ispitivanja različitih uzoraka zemljišta uzetih za vreme i nakon bombardovanja sa različitih područja Srbije. Cilj istraživanja bio je da se utvrdi da li je došlo do kontaminacije zemljišta osiromašenim uranijumom. Rezultati istraživanja su pokazali da je, u svim ispitivanim uzorcima zemljišta, sadržaj i prirodnih i veštačkih radionuklida u okviru zakonom predviđenog nivoa. Odnos aktivnosti izotopa ^{238}U i ^{235}U u mernim uzorcima odgovara njihovom odnosu u prirodnom uranijumu, što ukazuje da nije povećan sadržaj veštačkih radionuklida. Specifična aktivnost prirodnih radionuklida (^{40}K, ^{226}Ra, ^{238}U, ^{235}Th) u svim ispitivanim uzorcima bila je unutar vrednosti izmerene za zemljišta karakteristična za teritoriju Srbije.

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