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Radioactivity of soil in Croatia II: ^{137}Cs, ^{40}K, and absorbed dose rate

Marko Šoštarić[1], Branko Petrinec[1], Mak Avdić[1], Ljerka Petroci[1], Milica Kovačić[1], Željka Zgorelec[2], Božena Skoko[1], Tomislav Bituh[1], Jasminka Senčar[1], Gina Branica[1], Zdenko Franić[1], Iva Franulović[1], Davor Rašeta[1], Ivan Bešlić[1], and Dinko Babić[1]

[1] *Institute for Medical Research and Occupational Health, Zagreb, Croatia*
[2] *University of Zagreb Faculty of Agriculture, Department of General Agronomy, Zagreb, Croatia*

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We took samples of uncultivated soil from the surface layer (0–10 cm) at 138 sites from all over Croatia and measured their radionuclide activity concentrations with high-resolution gamma-ray spectrometry. This second part of our report brings the results on ^{40}K and ^{137}Cs to complement those on the ^{232}Th and ^{238}U decay chains addressed in the first part. Together they give the most complete picture of radioactivity of Croatian soil so far. Activity concentrations of ^{40}K were the highest in the Pannonian region, and there was an opposite trend for ^{137}Cs. We found that the concentrations of ^{137}Cs tended to increase with altitude, annual precipitation, and vegetation density. The concentration ratio of ^{137}Cs and K in soil, which indicates the potential for ^{137}Cs entering food chains via uptake by plants, was the lowest in agriculturally important areas in the east of the Pannonian region. In addition, we used the obtained results on activity concentrations to calculate the related absorbed dose rate as a measure of external exposure to ionising radiation from soil. The sum of the absorbed dose rates for naturally occurring radionuclides and ^{137}Cs showed that external exposure was generally the highest in the Dinaric region and Istrian Peninsula.

KEY WORDS: gamma radiation; high-resolution gamma-ray spectrometry; radioecology; representative radionuclides

Exposure to ionising radiation in the environment stems from both naturally occurring and anthropogenic radionuclides. Since life on Earth has evolved in the absence of anthropogenic radionuclides, their presence in any quantity is threatening. Nuclear fission is the main source of anthropogenic radionuclides, of which ^{137}Cs is considered particularly harmful to living organisms due to its long half-life $T_{1/2}$ of 30.1 years, large production rate, and chemical properties similar to those of other alkali metals. In fact, activity concentrations of ^{137}Cs in the environment are – together with those of ^{222}Rn – in the focus of radioecology (1). The ecological impact of ^{137}Cs is determined not only by its radioactivity (it emits both beta and gamma radiation) but also by the physical and chemical properties that govern its propagation through the environment and biota. The Cs^+ ionic state facilitates potassium and sodium (biogenic elements) substitution with ^{137}Cs in living organisms, which implies that ^{137}Cs concentrations in a given medium should be compared with the concentrations of K at least, which is possible by measuring radioactive ^{40}K.

Under non-accidental conditions, most of external exposure to ionising radiation originates from soil. In spite of a vast amount of related studies, radioactive properties of soil continue to attract attention and are investigated with regard to agronomy (2, 3), human activities (4–9), and the ecology of intact nature (10, 11). In the first part of the report (12) on the radioactivity of uncultivated soil in Croatia, we presented the activity concentrations (A) of the most significant members of the ^{238}U and ^{232}Th naturally occurring radioactive chains. Here we complement these results with those for ^{137}Cs and ^{40}K in the same samples and also present calculated absorbed dose rate for external exposure to ionising radiation from soil. Overall, our results for naturally occurring radionuclides and ^{137}Cs give the most complete picture of soil radioactivity in Croatia so far. As in (12), we use maps to present our results. Detailed numerical data can be found elsewhere (13) and are also available from the authors upon request.

Corresponding author: Dinko Babić, Institute for Medical Research and Occupational Health, Ksaverska cesta 2, 10000 Zagreb, Croatia,
E-mail: *dbabic@imi.hr*

GEOMORPHOLOGICAL, BIOGEOGRAPHICAL, AND CLIMATOLOGICAL CHARACTERISTICS OF CROATIA

Figure 1 shows a widely used division of Croatia with respect to geomorphological, biogeographical, and climatological characteristics. A more detailed description of the main regions and subregions has been given in the

Figure 1 Main geomorphological, biogeographical, and climatological regions of Croatia. Region I belongs to the Pannonian Plain, with subregion Ia comprising hilly areas and subregion Ib being a flat lowland. Region II belongs to the Dinaric Alps. In subregion IIa, the climate is cold continental and vegetation is subalpine, whereas in subregion IIb, karst prevails, and the climate is Mediterranean. Region III is Mediterranean in both climate and vegetation. In subregion IIIa the influence of regions I and II is stronger than in subregion IIIb. Sizeable areas of dense forests are indicated by letter F

first part of this report (12), and here we repeat the main points only.

Region I is part of the Pannonian Plain. Its western subregion (Ia) comprises hilly and flat terrains, whereas subregion Ib in the east is a flat lowland. The vegetation, soil types, and climate are typical of Central Europe, and the annual precipitation decreases from the west (~1200 mm) to the east (~500 mm) of the region. Region II is part of the Dinaric Alps, underlain by limestone and dolomite bedrock. In subregion IIa the vegetation is subalpine and the climate is cold continental, with annual precipitation mostly exceeding 1500 mm and being as high as 3500 mm in densely forested mountains. Subregion IIb is transitional and influenced by the vicinity of the Mediterranean. Annual precipitation is 1000–1500 mm. Region III comprises the eastern Adriatic coast, accompanying islands, and parts of the hinterland. The bedrock is again limestone and dolomite, whereas the climate and vegetation are Mediterranean. The annual precipitation ranges from ~700 mm in the southeast to ~1500 mm in the highest northeast of the Istrian Peninsula. Subregion IIIa is affected by the vicinity of subregion IIa, whereas subregion IIIb is barely influenced by the continental climate.

Regions I and II contain sizeable areas of dense forests, and these are indicated by letter F in Figure 1.

MATERIALS AND METHODS

Our experimental procedure has been explained in more detail in the first part of the report (12). Briefly, we sampled the surface layer of soil (0–10 cm) at 138 locations throughout Croatia in 2015 and 2016 following a recommended procedure for sampling and preparations for measurements (14). Radionuclide activity concentrations were determined by means of high-resolution gamma-ray spectrometry using a setup based on a high-purity germanium coaxial detector. We also applied corrections for self-attenuation (15) and coincidence summing effects (16). Detection limits were typically 2 Bq/kg for ^{40}K and 0.3 Bq/kg for ^{137}Cs.

RESULTS AND DISCUSSION

^{40}K

Figure 2 shows the distribution of the measured A of ^{40}K ($T_{1/2}$ =1.3 billion years) in the surface layer of soil in Croatia. The range was 62–769 Bq/kg, and the average was $\bar{A}$=423 Bq/kg. Globally, the reported median is 400 Bq/kg and the range 140–850 Bq/kg, and our results do not depart from those obtained elsewhere (including the rest of Europe) (17). Apart from some local deviations, there was a trend of A being above average in region I and below average in regions II and III. The A of ^{40}K was generally lower in the regions underlain by karst, where limestone and dolomite bedrock dominate (18). This behaviour was opposite to that found for the ^{238}U and ^{232}Th decay chains (12).

^{40}K accounts for 0.012 % of the total K found in nature, and its distribution is actually the same as that of K. Since K is a biogenic element, its concentration in soil depends not only on underlying geology but also on the exchange of matter between soil and living organisms. While the A of ^{40}K in the environment is comparatively large, which applies to our soil as well, this is usually not considered to be a threat, because ^{40}K is a primordial, naturally occurring radionuclide that has been present throughout the evolution of life on Earth. Generally, ^{40}K contributes significantly to absorbed dose rate for external exposure to ionising radiation from soil, but in our case, no health hazard can be associated with measured activity concentrations.

^{137}Cs

^{137}Cs, in contrast, represents a serious radioecological threat. The origin of most of the present-day ^{137}Cs in Croatia is radionuclide release during the Chernobyl disaster in 1986. Much smaller contributions come from nuclear weapons tests and the Fukushima accident (9, 19). The distribution of the A of ^{137}Cs in Croatian soil (in 2015–16) is shown in Figure 3. The measured values ranged from 0 (below the detection limit) to 205 Bq/kg, with $\bar{A}$=25 Bq/kg.

Generally, the A of ^{137}Cs in our samples was lower than that of ^{232}Th, ^{238}U, ^{226}Ra, ^{210}Pb, and ^{40}K. It did not depend on the distance from Chernobyl, as the lowest values (~4 Bq/kg in average) were measured in subregion Ib, closest to Chernobyl.

In order to understand results in Figure 2, one has to address several factors which might have affected the deposition of (initially airborne) ^{137}Cs onto the ground and its fixation in soil. These factors are expected to be primarily related to atmospheric phenomena and geomorphological properties, including physical and chemical properties of soil (2). ^{137}Cs is still abundant in the upper atmosphere and is deposited on the ground mainly via precipitation. When we compare results in Figure 2 with altitude and annual precipitation (20) at sampling locations, we notice that higher altitudes and more precipitation have $A > \bar{A}$. The effect of altitude might be a consequence of the pinning of clouds by high mountains, so that ^{137}Cs could be deposited onto the ground directly from the moist air, without actual precipitation. However, there are other variables involved, such as specific soil properties that favour ^{137}Cs fixation on the surface layer, as discussed for chernozem in subregion Ib (2).

Due to similar electronic structures K and Cs have similar chemical properties, and at insufficient concentrations of K in soil, plants tend to take up chemically similar elements, including ^{137}Cs (21). This is, in fact, why fertilisers rich in K have been used to reduce ^{137}Cs uptake in heavily polluted areas (22). For the same reason the ratio R of atomic concentrations of ^{137}Cs and total K is used as a measure of ^{137}Cs potential to enter food chains through plant uptake. This ratio can be calculated as

$$R = 2.82 \times 10^{-12} \frac{A_{Cs}}{A_K} \qquad (2)$$

where A_{Cs} and A_K are activity concentrations of ^{137}Cs and ^{40}K, respectively. Figure 4 shows that R is lower in region I than regions II and III, which is a consequence of a relatively high A_K and low A_{Cs}. It is of particular importance that R is the lowest in subregion Ib, where the majority of intense agricultural production is taking place in Croatia.

Absorbed dose rate

Internal exposure to ionising radiation due to soil radioactivity depends on numerous factors and has to be estimated on the basis of specific conditions. On the other hand, there is a well-established method of assessing external exposure from measured activity concentrations of radionuclides in soil and their gamma emissions. For naturally occurring radionuclides, the absorbed dose rate D_N at 1 m above the ground can be calculated using the following equation;

$$D_N = 0.0417A_K + 0.463A_U + 0.604A_{Th} \text{ (23)},$$

where D_N is expressed in nGy/h, and activity concentrations A_K, A_U, and A_{Th} of ^{40}K, ^{238}U, and ^{232}Th, respectively, are expressed in Bq/kg. Therefore, our results are sufficient for calculating the distribution of D_N for Croatia, as shown in Figure 5. D_N ranged from 23 to 131 nGy/h. Its average $\bar{D}_N$ was 63 nGy/h, which moderately exceeds the global median value of 51 nGy/h (17).

In the case of ^{137}Cs, there is no universal equation for calculating the related absorbed dose rate D_{Cs} from A_{Cs}. Hence, we have to rely on estimates based on other results and models. There are arguments that 1 Bq/m^2 due to ^{137}Cs in soil results in about 0.001 nGy/h at 1 m above the ground (24, 25). Other studies indicate that only the topmost ~10 cm layer of soil contributes to D_{Cs}, since A_{Cs} significantly decreases with depth (26, 27) and self-attenuation effects (15). Total ^{137}Cs activity in the upper 10 cm of a 1 m^2 surface layer of soil therefore equals $0.1\rho A_{Cs}$ numerically, where ρ is soil mass density in kg/m^3. This implies that

$$D_{Cs} \approx 10^{-4}\rho A_{Cs}$$

expressed in nGy/h. By taking into account measured A_{Cs} and ρ, we obtained results shown in Figure 6. D_{Cs} ranged from 0 to 24 nGy/h, and the average $\bar{D}_{Cs}$ was 2.7 nGy/h, which is considerably lower than D_N. Therefore, while ^{137}Cs in Croatia may still pose a certain threat regarding internal exposure due to its competition with K in food chains, its contribution to external exposure is comparatively small.

Figure 7 shows the distribution of the total absorbed dose rate ($D_{tot} = D_N + D_{Cs}$) due to soil radioactivity in Croatia. It ranged from 24 to 136 nGy/h, and its average $\bar{D}_{tot}$ was 66 nGy/h. In most of region II, D_{tot} was above average, which was not surprising, because only activity concentrations of ^{40}K were not elevated there. D_{tot} in the northwest of subregion IIIa, i.e., on the Istrian Peninsula, were also above average at most of the sampling spots (along the western coast in particular).

CONCLUSIONS

In this second part of our report on uncultivated soil radioactivity in Croatia we focus on ^{137}Cs, ^{40}K, and absorbed dose rate. Since ^{137}Cs and K have similar chemical properties, they compete in uptake by plants, which implies that their relative concentrations in soil are of interest for the propagation of ^{137}Cs through food chains. Measured activity concentrations of ^{40}K were the highest in the Pannonian part of Croatia, and ^{137}Cs showed the opposite trend. Their ratio was the smallest in the Pannonian region, especially in its eastern part, where the majority of Croatian intense agricultural production has been taking place. Activity concentrations of ^{137}Cs tended to be above average at high altitudes, in areas with dense vegetation and annual precipitation above average. By combining these results with those for the ^{232}Th and ^{238}U decay chains presented in the first part, we determined that the highest dose rates were

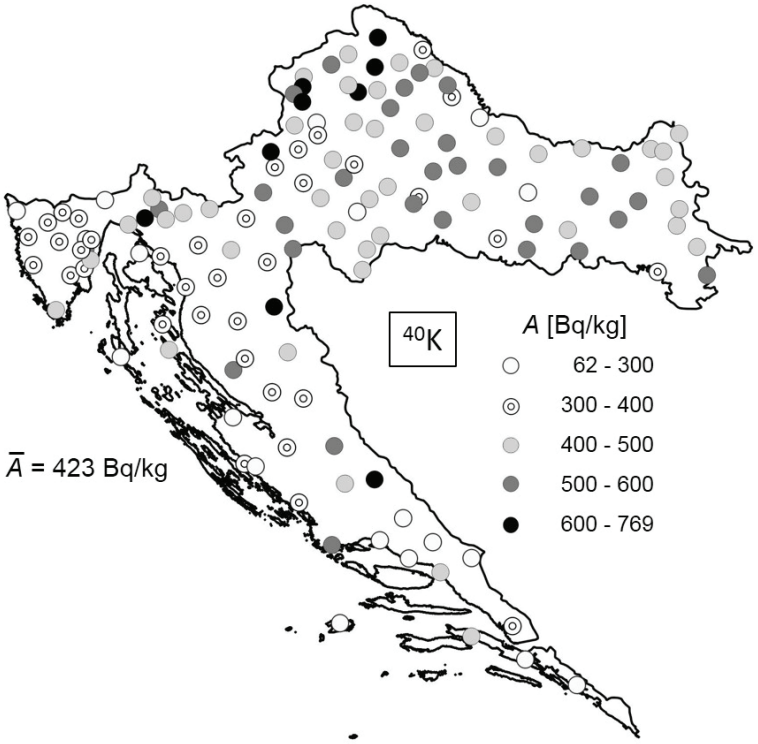

Figure 2 Distribution of the *A* of ^{40}K in Croatian soil

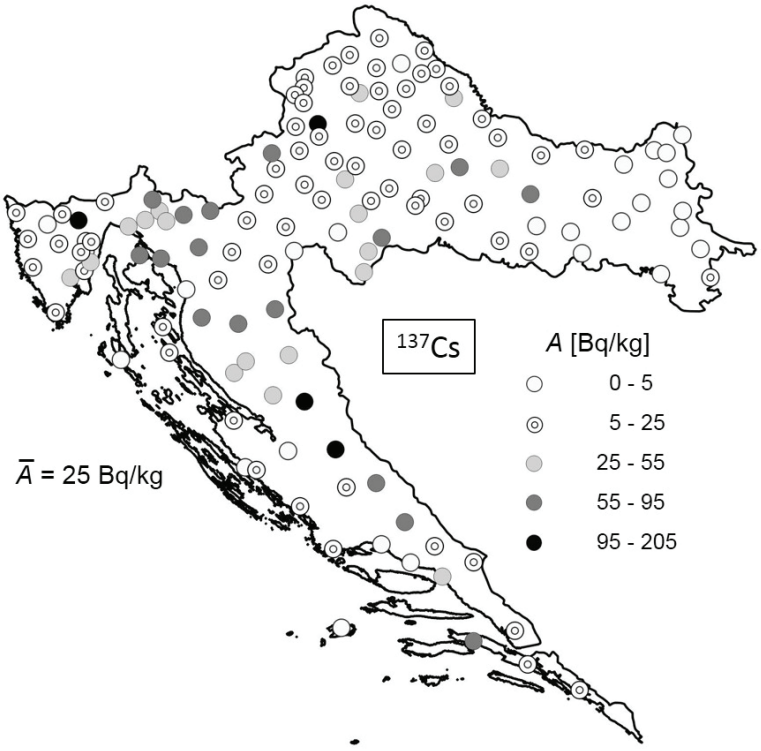

Figure 3 Distribution of the *A* of ^{137}Cs in Croatian soil

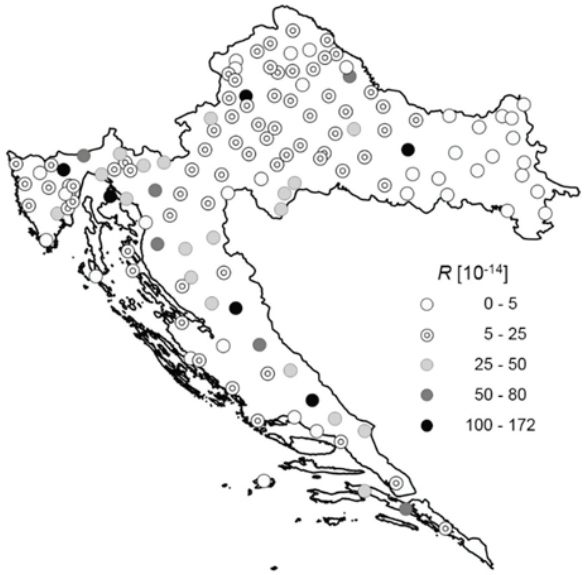

Figure 4 Ratio of the concentrations of ^{137}Cs and K in Croatian soil

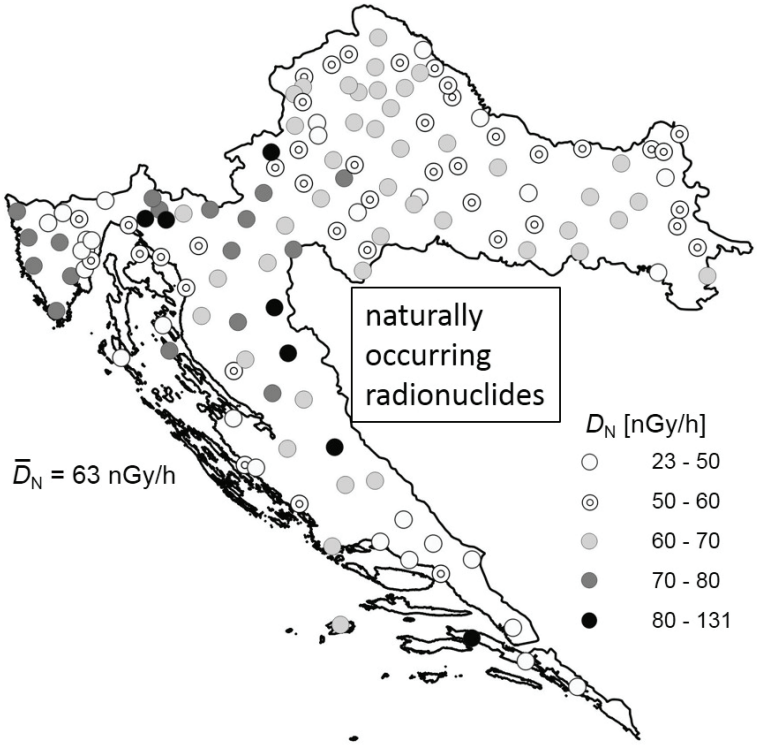

Figure 5 Absorbed dose rate due to naturally occurring radionuclides in Croatian soil

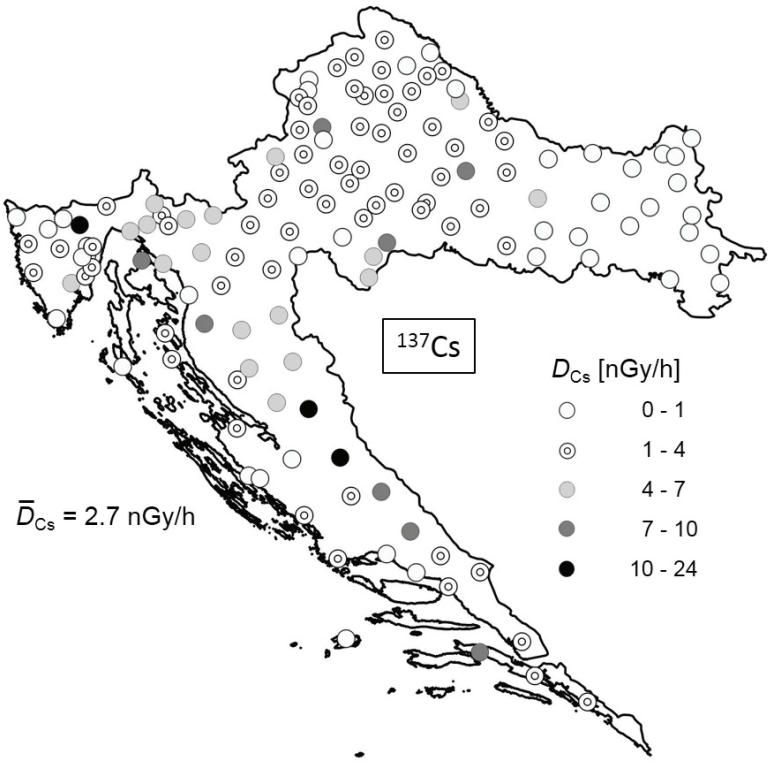

Figure 6 Absorbed dose rate due to ^{137}Cs in Croatian soil

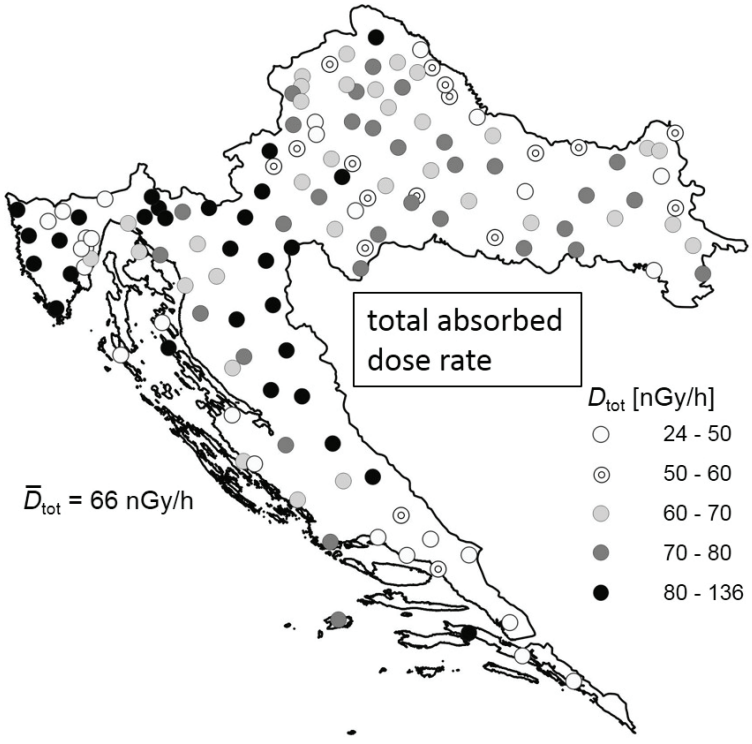

Figure 7 Total absorbed dose rate due to radionuclides in Croatian soil

in the Dinaric region and on the Istrian Peninsula. Since this study relied on long-lived radionuclides, our findings are likely to remain current for a prolonged period of time and may also serve for reference in case of accidental radioactivity bursts in the environment of Croatia.

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Radioaktivnost tla u Hrvatskoj II.: ^{137}Cs, ^{40}K i brzina apsorbirane doze

Uzorkovali smo površinski sloj (0–10 cm) nekultiviranog tla na 138 mjesta diljem Hrvatske i mjerili koncentracije aktivnosti radionuklida u prikupljenim uzorcima visokorezolucijskom gamaspektrometrijom. U ovom radu, koji je drugi dio naše dvodijelne prezentacije, fokus je na ^{40}K, ^{137}Cs i brzini apsorbirane doze zbog prisutnosti radionuklida u tlu. Ti rezultati dopunjuju one vezane uz ^{232}Th i ^{238}U lance raspada, što vodi do dosad najcjelovitije slike radioaktivnosti tla u Hrvatskoj. Koncentracije aktivnosti ^{40}K bile su najviše u hrvatskom panonskom području, a trend za ^{137}Cs bio je suprotan. Našli smo da su koncentracije ^{137}Cs pokazivale tendenciju porasta s nadmorskom visinom, količinom oborine i gustoćom vegetacije. Omjer koncentracija ^{137}Cs i K u tlu, a koji predstavlja potencijal za ulaz ^{137}Cs u hranidbene lance apsorpcijom putem biljaka, bio je najmanji na istoku panonskoga područja gdje se nalaze poljoprivredno važne površine. Rezultate za koncentracije aktivnosti iskoristili smo za izračun posljedične brzine apsorbirane doze kao mjere vanjske izloženosti ionizirajućem zračenju iz tla. Zbroj brzina apsorbirane doze za prirodnopojavne radionuklide i ^{137}Cs pokazao je da je vanjska izloženost općenito bila najveća u dinarskom području i na istarskom poluotoku.

KLJUČNE RIJEČI: gama-zračenje; reprezentativni radionuklidi; visokorezolucijska gamaspektrometrija