Assessing the Initial Radiological State of the Proposed Location for Croatia's Radioactive Waste Management Centre

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ABSTRACT

Before starting the construction of the Central storage of institutional radioactive waste and Long-term storage of the Krško NPP LILW, it is important to assess the initial radiological state of the proposed location. The assessment serves as a zero state against which future measurements can be compared, demonstrating that radionuclides are not leaching into the environment. The assessment also serves as a proof to the local community that we are capable of monitoring all the relevant radionuclides in the very low quantities and in all the media (soil, air, water).

The assessment was all-encompassing. During a full year, to ensure that there can be no seasonal influence on the final result, air and rainwater were continuously sampled, and ambient dose equivalent rate H*(10)/t was continuously measured.

The soil sampling sites were selected to cover the whole area as equally as possible, with greater density closer to the proposed site. Sediments were sampled from the rivers, creeks, and gullies in the vicinity of the proposed site. Apart from river, creek and gully water, the samples were also collected from the water supply and wells in the vicinity of the proposed site.

A large selection of bioindicators was selected for sampling, as equally as possible through the seasons, taking into account that some of them can only be found in certain seasons, divided

into several groups: fish, game animals (wild boar, roe deer, European hare,…), forest ecosystem samples (mushrooms, acorns, chestnuts, wild berries,…), bee products (honey, propolis,…), and products from local farms (cheese, eggs, fruits, salad,…).

All the samples were measured using the gamma ray spectrometry method. In addition, ^{3}H and total β count was analysed in waters, and ^{90}Sr in animal products, waters, and sediments. As expected, the radionuclides found were ^{137}Cs, ^{3}H, ^{90}Sr, ^{40}K, and elements of ^{232}Th and ^{238}U decay chains. To demonstrate that other radionuclides, including the fission products possibly found in the waste from the NPP Krško, can be detected if present, in all the samples a list of fission radionuclides, including ^{241}Am, ^{60}Co, and ^{51}Cr were analysed. As expected, none was found.

The results defined the initial radiological state of the examined area and indicated that, radiologically speaking, the proposed area does not differ significantly from the average Croatian area.

Keywords: *radioactive waste storage facility, sampling, bioindicators, natural radioactivity, fission products*

1 INTRODUCTION

The Republic of Croatia is in the process of constructing a radioactive waste management centre (the Centre). The Centre will store the institutional waste, as well as the Croatian part of the waste from the NPP Krško (only LILW) until the final disposal.

The proposed site is the location of the former military base *Čerkezovac* (Figure 1). The suitability of the macrolocation was established in the 1990's and confirmed through a series of studies during the last 30 years.

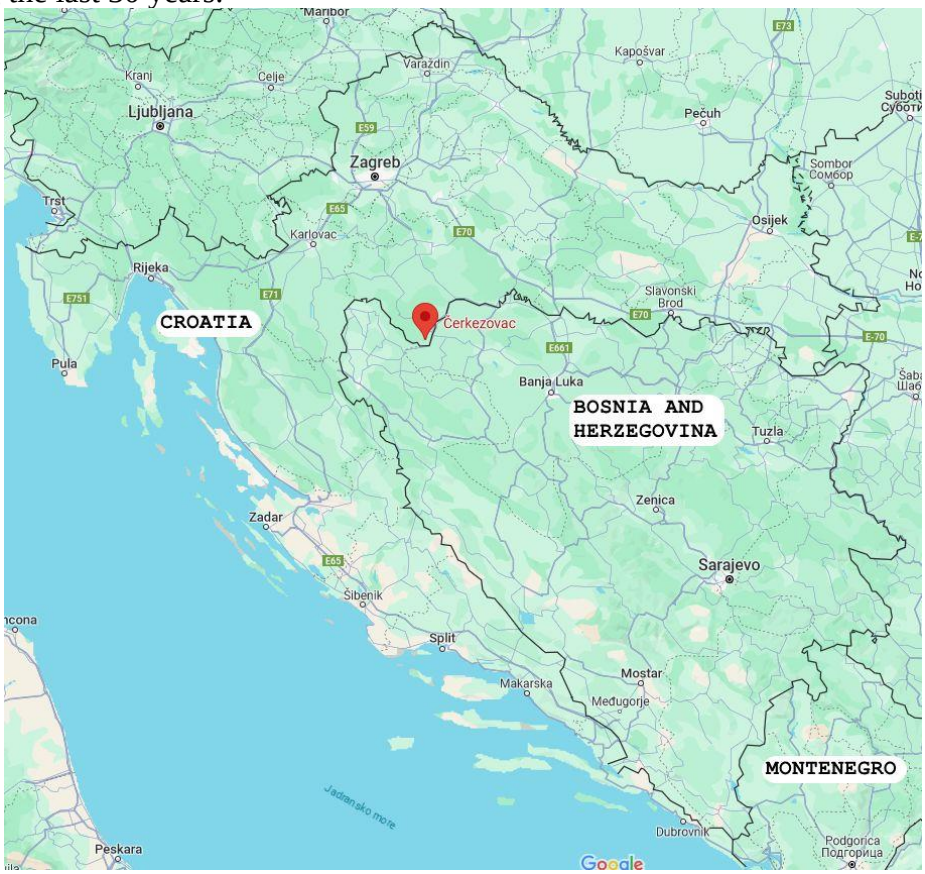

Figure 1: Čerkezovac location (source: Google Maps)

Before any work can begin at the proposed site, the initial radiological state has to be assessed. The initial radiological state serves as the basis for comparison of measurements made during the operation of the Centre, as well as those made after the Centre closes, to ensure that there is no radiological damage to the environment. The assessment of the initial radiological state may also indicate the areas around the Centre which have already been exposed to a higher level of radiological pollution (for example, from the Chernobyl accident) than expected. The assessment also serves as an example of the expected quality, sensitivity, and completeness of the measurements expected to be made during the operation of the Centre, demonstrating that even the negligible releases from the Centre will be detected.

2 MATHERIALS AND METHODS

2.1 Sampling

To ensure a comprehensive assessment of the initial radiological state, a sampling plan was created. The plan covered various sample types – air, surface water, wells, sediments, soil, fish, game, forest ecosystem samples, and farm products. The selection sites and frequencies were selected to ensure maximum coverage and effect depending on the sample type.

Sampling lasted one whole year, to avoid dependence on seasons.

Typically, the sampling locations were closer together closer to the proposed location of the Centre.

Sampling was performed by the University of Zagreb, Faculty of Agriculture (FoA) – game, forest ecosystem, and fish samples; Ruđer Bošković Institute (RBI) – water and sediment samples; Institute for Medical Research and Occupational Health (IMROH) – soil and air samples.

Table 1: Sample types

Surface water	40
Sediments	148
Biofouling	12
Drinking water	44
Air samples (air filters)	12
TLDs	50
Soil samples	61
Local produce	114
(animal-sourced)	30
Honey	39
Forest ecosystem samples	107
Fish	16
Game	16

2.2 Measurements

2.2.1 Ambient dose equivalent H*(10)

Ambient dose equivalent H*(10) was measured using thermoluminescent dosimeters (TLDs) at IMROH. Activity concentration of radionuclide ^{90}Sr was determined by beta counting at IMROH

and RBI, based on the sample. Activity concentrations of other radionuclides were determined using gamma ray spectrometry at IMROH and RBI, based on the sample.

2.2.2 Activity concentration of ^{90}Sr

Activity concentration of ^{90}Sr was measured at IMROH and RBI.

At IMROH, ^{90}Sr activity concentration was determined in all the samples of animal origin (meat, milk, fish, cheese). The samples were dried at 105˚C and ashed at 650˚C. The activity concentrations of ^{90}Sr were determined after radiochemical separation with tri-n-butyl phosphate (TBP), by counting the beta emission of ^{90}Y (decay product of ^{90}Sr) using low-background, anti-coincidence gas proportional counter. The details of the method have been published previously [1], [2].

At RBI, the determination of ^{90}Sr was conducted in sediments and in water (drinking water (wells and springs), precipitation (rainwater) and surface water (water from rivers and streams).

Samples of water were filtered through 30 μm pore filter. Filtered water was then evaporized to dryness. ^{90}Sr in water was determined in the evaporated residue. The residue was dissolved in nitric acid and filtered through B-4 sinter funnel. Filtrate was evaporated almost to dryness and mixed with methanol. Sr isolation was performed on anion exchanger column (Amberlit CG-400 or Serdolit CG-400). Strontium was separated from remaining elements by elution of nitric acid in methanol. Sr was then stripped from the column with deionized water and separated from remaining alpha and beta emitters by precipitation of iron hydroxide and barium sulphate. Sr was then precipitated as $SrCO_3$ and left for 14 days until the equilibrium between ^{90}Sr - ^{90}Y was reached. Quantitative analysis was performed using beta counter with semiconductor detector i-Matic by Canberra, or by liquid scintillation counters Tri-Carb 3180TR/SL or Quantulus GCT 6220 (Perkin Elmer).

In case of determination of ^{90}Sr in sediments, a sample was mixed with the cation exchanger IR Amberlite 120 in H+ form (particles larger than 250 μm). After 3-4 hours of contact, the exchanger was separated from sediments on 250 μm sieve by washing out with deionised water. Sr and other bound cations were eluted from the exchanger with nitric acid. The eluate was evaporated and a mixture of nitric acid and methanol was added. The further separation of strontium and quantitative analyses was conducted in the same way as described earlier for filtered water samples.

2.2.3 Activity concentration of ^{3}H

Tritium (^{3}H) was measured in samples of all types of water. The determination of tritium was carried out on an aliquot of electrolytically enriched filtered water. Deionization by distillation of the water sample was done before and after electrolysis. A 7 mL aliquot of the sample, obtained after electrolysis and distillation, was pipetted into 20 mL volume counting vials and mixed with 13 mL of liquid scintillator (ULTIMA GOLD LLT Packard). The activity concentration was determined by measurement on a liquid scintillation counter Tri-Carb 3180TR/SL or Quantulus GCT 6220 (Perkin Elmer) using a quench correction efficiency curve.

2.2.4 Gross beta activity

Gross beta was measured at RBI. Total (gross) beta activity was determined in samples of all types of water, separately in filtered water and suspended matter. Determination of total beta activity in filtered water was conducted in accordance with HRN EN ISO 10704:2019. The filtered water sample was evaporated to dryness on the planchet, where the thickness of the deposit was not to exceed 5 mg/cm^2. For suspended matter, the sample was transferred to the planchet, taking into account that the thickness of the deposit did not exceed 50 mg/cm^2. The samples prepared in this way were measured using i-Matic semiconductor detector by Canberra.

2.2.5 Activity concentration of other radionuclides

Activity concentration of other relevant and requested radionuclides (gamma emitters) was measured at IMROH and RBI using gamma ray spectrometry.

At IMROH, Gamma-spectrometric measurements were conducted in samples of feed, food, soil and air. Samples were transferred into standard cylindrical polyethylene vials and measured on high purity germanium detectors (HPGe) by Ortec and Canberra. Gammavision software was used for spectrum collection and analysis. Efficiency calibrations were obtained empirically using standard materials of similar matrix.

At RBI, Gamma-spectrometric measurements were conducted in samples of sediments, algae, honey and all types of water (evaporated filtered water and suspended matter). Samples were transferred into standard cylindrical polyethylene vials and measured on high purity germanium detectors (HPGe) by Canberra. Genie2000 software was used for spectrum collection and analysis. Efficiency calibrations were obtained empirically using standard materials of similar matrix, or by mathematical calibrations using Canberra's LabSOCS (Laboratory Sourceless Calibration Software) tool.

2.3 Water samples

In total, 88 water samples were taken and measured, 48 from open waterways and 40 from springs and wells. All the sampling, preparation of the samples and measuring was done by RBI. The surface water samples were first filtered ($\phi \leq 30$ μm). Otherwise, surface and drinking water was prepared and measured in the same way. 60 to 65 l of water was collected for each sample. Water from each sample was evaporated, and the residual was transferred to the container in a well-defined geometry for gamma ray spectrometry. After the gamma ray spectrometry measurement, total beta count, ^{3}H and ^{90}Sr were measured.

148 samples of sediment and 12 samples of biofouling were also taken. 3 to 5 sediment samples were taken from each location where open water samples were taken, along with biofouling, where available.

Biofouling was dried (at 105°C, until mass was constant), homogenized and powdered. A representative part of each sample was packed into a polyethylene container for gamma ray spectrometry. Sediments were prepared in the same way, and after gamma ray spectrometry, ^{90}Sr was measured. ^{90}Sr was measured using combined sample from three sediment samples collected from the same general location.

Water from open waterways (rivers, creeks, and gullies) was sampled based on determined hydrogeological units. Five such units were determined: “Entrance”, “Javornik”, “Čemernica”, “Žirovnica”, and “Svinjca”. “Entrance” includes all the surface and underground waters near the proposed entrance to the facility and represents one of the most likely pathways for radionuclide contamination in case of the release. “Javornik”, “Čemernica”, “Žirovnica”, and “Svinjca” hydrogeological units represent parts of related rivers and creeks basins near the proposed location of the Centre and together represent all the possible liquid radionuclide release pathways. The sampling locations were selected at points where it was expected that any radioactive release would already mix into the waterway, except for control sampling locations, selected at the locations where radioactive contamination from the Centre would be almost impossible.

Local springs and wells were also sampled according to the same hydrological units as open waters.

At the proposed location of the Centre, rainfall was continuously collected and sampled. An effort to sample underground water was also made, but no water was found up to the depth of 193 meters.

2.4 Air samples

At the proposed location of the Centre, air was continuously sampled and analysed once a month. Air samples were collected using filters and high-volume air sampler set at the proposed location of the Centre. Each filter was exposed for a week, and composite samples of 4 or 5 filters (28- or 35-day samples) were packed into a polyethylene container in a well-defined geometry for gamma ray spectrometry. A total of 12 composite samples were collected and measured by the IMROH.

2.5 Ambient dose rate equivalent

At 50 locations around the proposed location of the Centre, ambient dose equivalent H*(10) was measured. The measurements were done using thermoluminescent dosimeters (TLDs). TLDs were set at the location positioned 1 m above the ground and exposed continuously for the six months, after which they were measured in the laboratory. At each location the measurement lasted for 1 year. The locations were selected so that they cover possible release pathways for airborne release from the proposed site of the Centre, and to determine possible natural differences between the different geological formations comprising the bedrock of the wider area around the proposed location of the Centre.

2.6 Soil samples

The locations for sampling soil were selected so that soil developed over each of the lithostratigraphic units in the vicinity of the proposed site could be radiologically characterized. The number of the sampling locations was also adjusted so that a clear insight in the ^{137}Cs contamination form the Chernobyl accident and the atmospheric testing of the nuclear weapons in the area can be acquired. Furthermore, the results of the sampled soil together with the results of the biota were used to assess transfer factors.

IMROH collected 61 soil sample from selected locations around the proposed location of the Centre. At each location during the sampling ambient dose equivalent H*(10) was also measured, at 1 m above ground, using hand-held instrument Thermo FH40G-L-10 (proportional counter type). Uncultivated soil was sampled in a three-point (triangle) or five-point (X) pattern. 1,5 to 2 kg of soil was taken at each point and the sample was immediately cleared of rocks and foliage and homogenized. Up to 3 kg of the homogenized sample was taken to the laboratory. In the laboratory, the sample was dried at 105°C and sieved ($\phi \leq 2$ mm). The sample was packed in a container in a well-defined geometry for gamma ray spectrometry.

2.7 Bioindicators

2.7.1 Fish

16 samples of fish, 4 predators and 12 herbivores/omnivores, were sampled by FoA. The samples were taken from all the surface waters that surround the proposed location. Predators are rarely present in smaller surface waters around the proposed location of the Centre. The samples were prepared and measured at IMROH. Samples were first burned to ash, and the ash was packed into the appropriate containers and measured. All the samples were measured using the gamma ray spectrometry and, afterwards, ^{90}Sr was measured.

2.7.2 Local produce

FoA collected 114 samples from the local farms. Of those, 30 samples were of animal origin.

Local produce was collected from the following distinct areas [3]: the forest (ŠUMA in Figure 2), the area around the proposed site, the alluvial (Aluvij in Figure 2), the areas next to the rivers Una and Žirovnica, where there is a possibility that any released radionuclides may migrate to, and the control area (KONTROLA in Figure 2) (divided into two areas – control ("KONTROLA" in Figure 2) and connection ("VEZA" in Figure 2)) between the first two areas and to the north and the west, where there is no possibility for any released radionuclides to migrate to (**Error! Reference source not found.**).

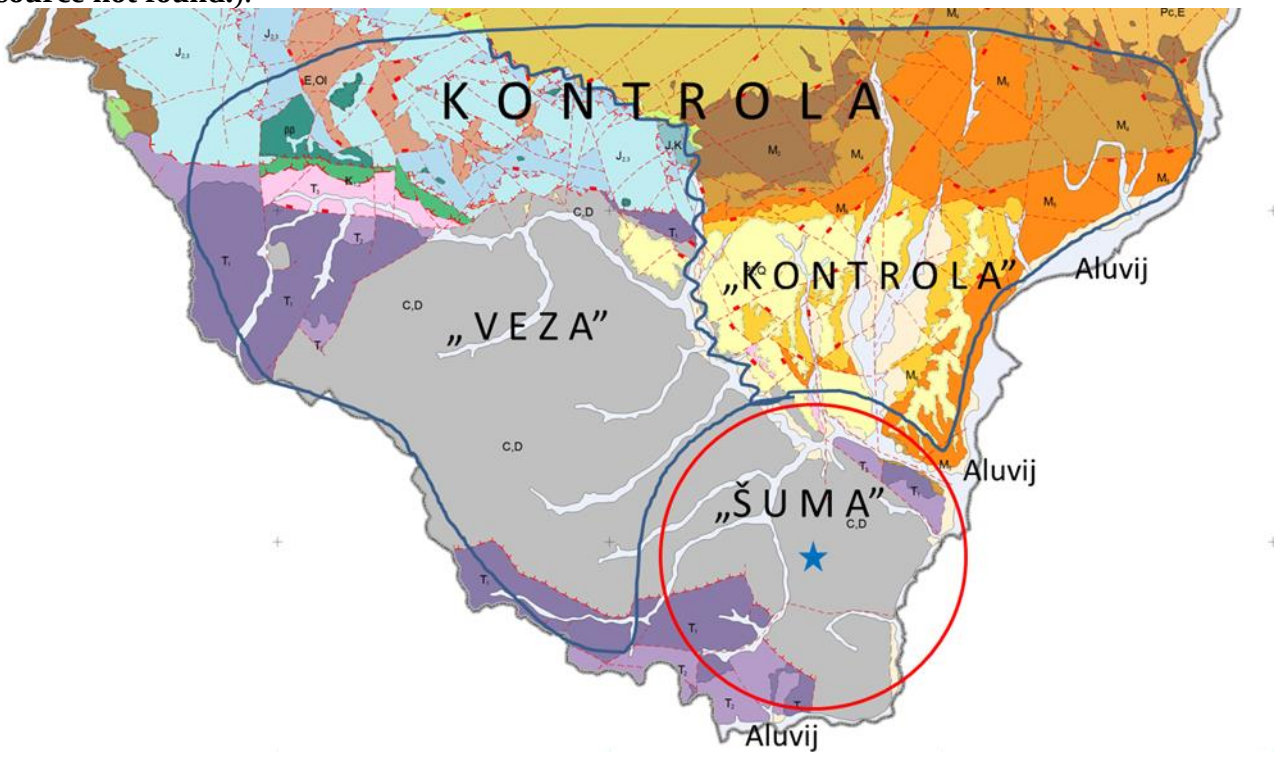

Figure 2: Sampling zones

Sampled animal products included eggs, cheese, meat, milk. Vegetables included salad, spinach, maise, wheat, potatoes, chard, beans, peas, oats. Fruits included apples, walnuts, pears, and plums.

All the samples were measured using the gamma ray spectrometry, while in animal products ^{90}Sr measurement was also performed. Sampled produce include corn, wheat, rye, oats, corn flour, potatoes, onions, celery, kale, cabbage, leek, Swiss chard, cucumbers, zucchini, carrots, beet, chicory, lettuce, beans, peas, eggplant, pepper, chilli peppers, cauliflower, quince, melons, watermelons, pears, apples, grapes, peaches, currants, walnuts, nuts, plums, turnips, flaxseeds, pumpkin seeds, hemp seeds, soy, cows' milk, cows' milk cheese, goats' milk cheese, chicken, eggs, pork, lamb, and rabbit. The samples were prepared and measured at IMROH. Smaller samples were packed into the appropriate containers and measured. Larger samples were first burned to ash, and the ash was packed into the appropriate containers and measured.

Since the wider area around the proposed location of the Centre is known for the production of honey, honey and other bee products (propolis, pollen) were sampled. Sampling of honey was done several times from spring to autumn, depending on the sort of the honey, pollen in late summer, and propolis in early autumn. The advantage of honey and other bee products is that they are randomized samples from a very wide area, bees collect nectar and pollen from the area with radius of up to 5 km. FoA collected 39 honey samples, including some from the beehives installed at the proposed location of the Centre specifically for the purpose of assessing the radioactive contaminants in honey. RBI performed gamma ray spectrometry on the samples.

2.7.3 Forest ecosystem samples

Forest ecosystem samples were collected depending on their growth period – mushrooms mainly in fall, strawberries in late spring, chestnuts in October, … Four main areas were designated: forest around the proposed location of the Centre, forests around alluvial areas, forests north of Žirovnica river, and forests south of Žirovnica river [3].

FoA collected 107 forest samples. Samples included apples, hawthorn, chestnuts, blackberries, strawberries, elder, mulberry, and mushrooms (*Ramaria*, *Leccium*, *Craterellus*, *Coprinus*, *Russula*, *Lactarius*, *Hydnum*, *Armallaria*, *Macrolepiota*, *Agaricus*, and *Boletus*). The samples were prepared and measured at IMROH. All the samples were measured using the gamma ray spectrometry. Smaller samples were packed into the appropriate containers and measured. Larger samples were first burned to ash, and the ash was packed into the appropriate containers and measured.

2.7.4 Game

Game animals are not a good indicator of a possible local contamination, since all the collected game (wild boar, roe deer, European hare) are highly mobile . However, game animals are of interest to the local population. Game was provided by the local hunters associations. Game was collected from five main designated areas – four areas largely overlapping the areas for sampling forest ecosystem, and the fifth one, a hunting area managed by the University of Zagreb, Faculty of Agriculture, which includes the upper part of the Žirovnica basin.

FoA collected 16 game samples (wild boar, roe deer, and European hare). The samples were prepared and measured at IMROH. Samples were first burned to ash, and the ash was packed into the appropriate containers and measured. All the samples were measured using the gamma ray spectrometry and, afterwards, ^{90}Sr was measured.

3 RESULTS

This paper presents results from the area around the proposed location of the Centre, with radius of around 4 km. This area mostly corresponds to the L1 designation for the samples (218 samples in total). The results are presented visually (graphs).

Lines connect the same radionuclides across the samples for easier reference, they do not imply any kind of connection between the values.

The results are grouped based on the type and the location. Within each type, samples from the close locations are close together.

No value means that the value measured was below the detection limit.

The measurements focused on the radionuclides expected to be found in the nature — ^{238}U decay chain, ^{232}Th decay chain, ^{40}K, ^{7}Be, ^{137}Cs, and ^{90}Sr. ^{238}U, ^{232}Th, and ^{40}K are primordial radionuclides, present since the formation of Earth. ^{7}Be is a cosmogenic radionuclide, constantly created in the atmosphere through the interaction with cosmic rays. ^{137}Cs and ^{90}Sr are fission products and are present in the environment as a result of the Chernobyl accident and of atmospheric testing of nuclear weapons. ^{40}K is also present in the living organisms, including humans, since 0.012% of natural potassium is ^{40}K.

The measurements also demonstrated that both previously mentioned institutes can detect and measure other gamma-emitting fission products expected to be present in the waste from an NPP, like ^{60}Co, ^{152}Eu, ^{154}Eu, ^{192}Ir, ^{241}Am, ^{94}Nb, ^{108m}Ag, ^{125}Sb, ^{134}Cs, ^{137}Cs, ^{54}Mn, ^{57}Co, ^{58}Co, ^{51}Cr, ^{59}Fe, ^{65}Zn, ^{95}Nb, ^{95}Zr, ^{103}Ru, ^{106}Ru, ^{110m}Ag, ^{113}Sn, ^{124}Sb, ^{131}I, ^{141}Ce, and ^{144}Ce, in concentrations of 0.5 Bq/kg [3].

Radionuclides with high activity concentration values (total beta, ^{40}K, and, in mushrooms, ^{137}Cs), are presented in a separate graph, to make variations in other radionuclides more presentable (otherwise, other radionuclides would look like a line just above zero).

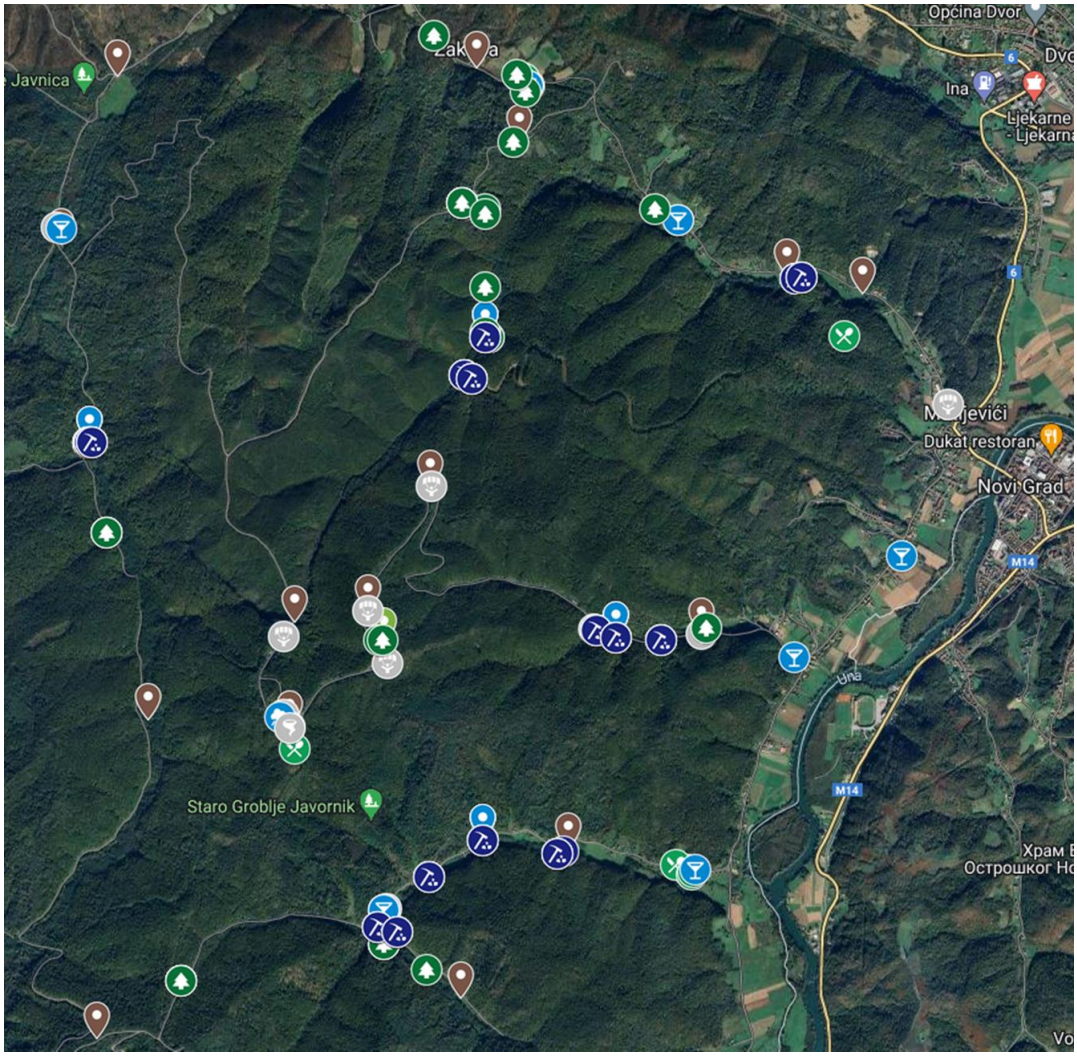

Figure 3: Sampling locations (source: Google Maps)

Legend:

- TLD measurement location
- Forest ecosystem sampling location
- Locally sourced food sampling location
- Drinking water sampling location
- Game sampling location
- Atmospheric precipitation sampling location
- Air sampling location
- Sediment sampling location
- Soil sampling location
- Surface water sampling location
- Proposed location of the Centre

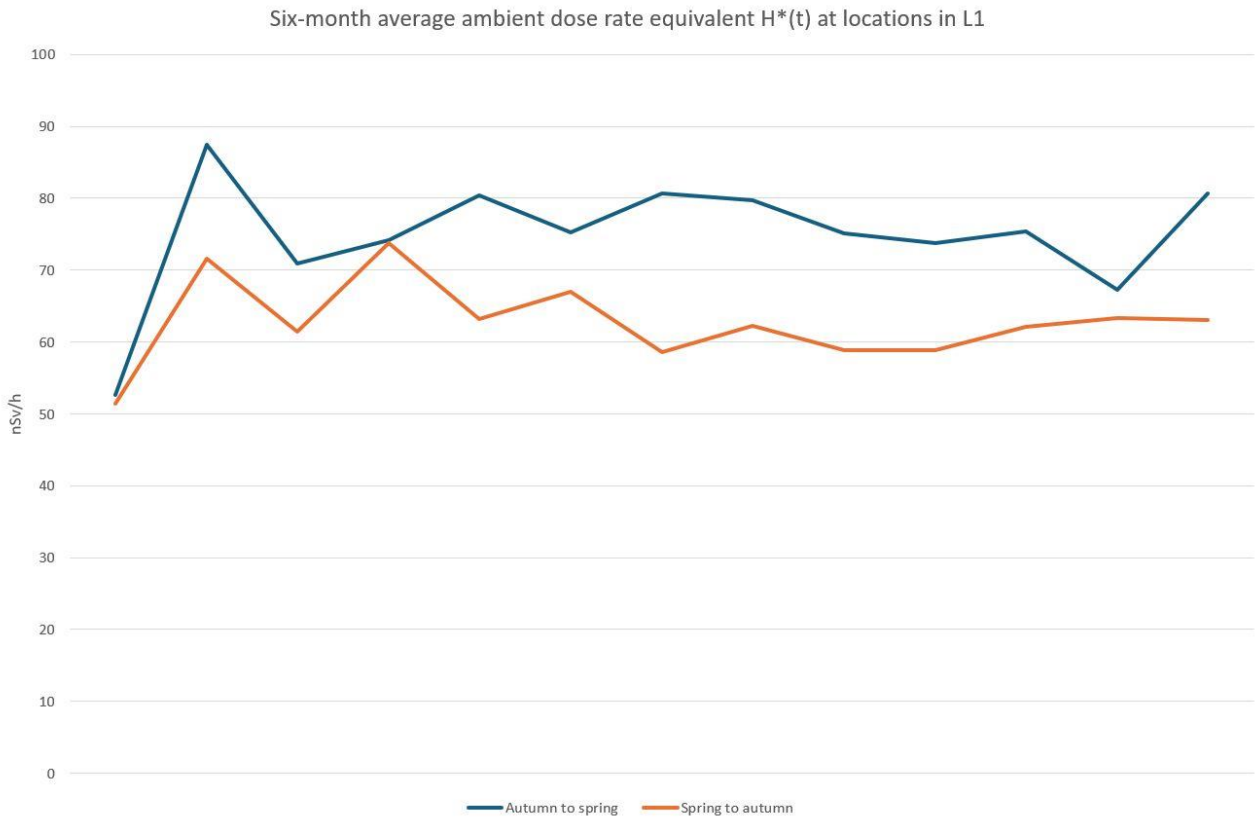

Figure 4: Ambient dose rate equivalent at the locations in L1

Monthly average ambient dose rate measurements (Figure 4) are somewhat lower than the Croatian average (99 nSv/h, **Error! Reference source not found.**), but within monthly averages (between 52 and 134 nSv/h). The results do not differ in a meaningful way from an average location in Croatia.

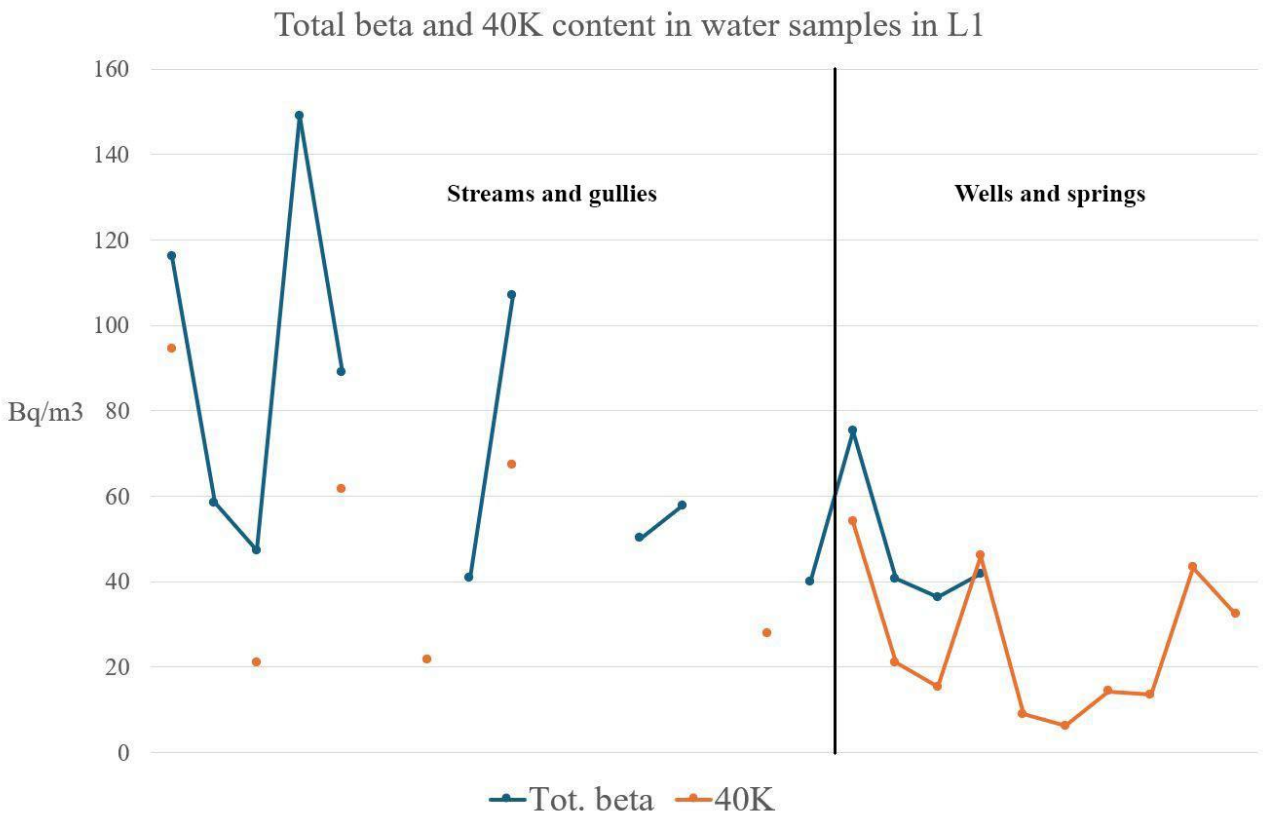

Figure 5: Total beta and ^{40}K content in water samples in L1

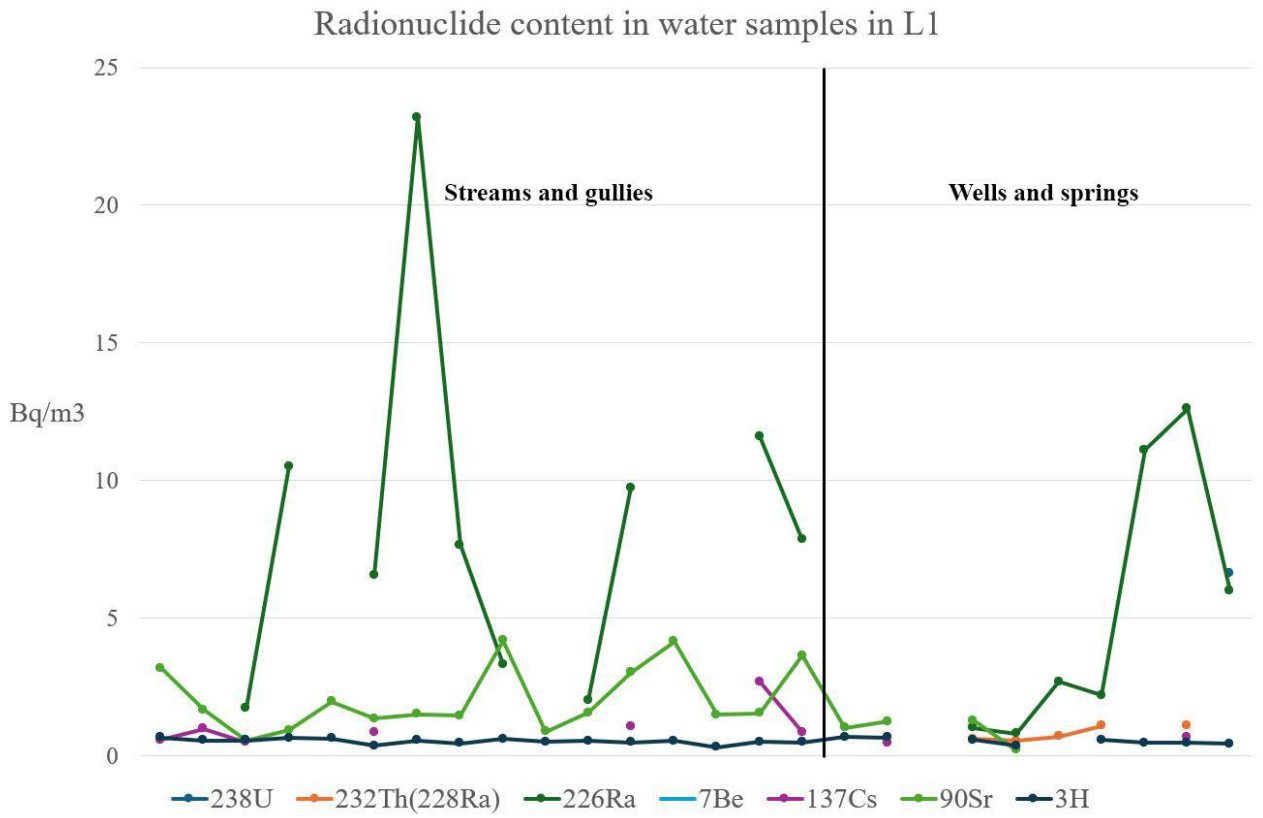

Figure 6: Radionuclide content in water samples in L1

Error! Reference source not found. and **Error! Reference source not found.** show radionuclide content in all the sampled waters. In general, drinking water (wells and springs) contains less radionuclides than non-drinking water (streams and gullies). The absence of ^{7}Be in open waterways can be explained by the sampling – sampling was done in fair weather, and when soil has had time to dry, to avoid mud.

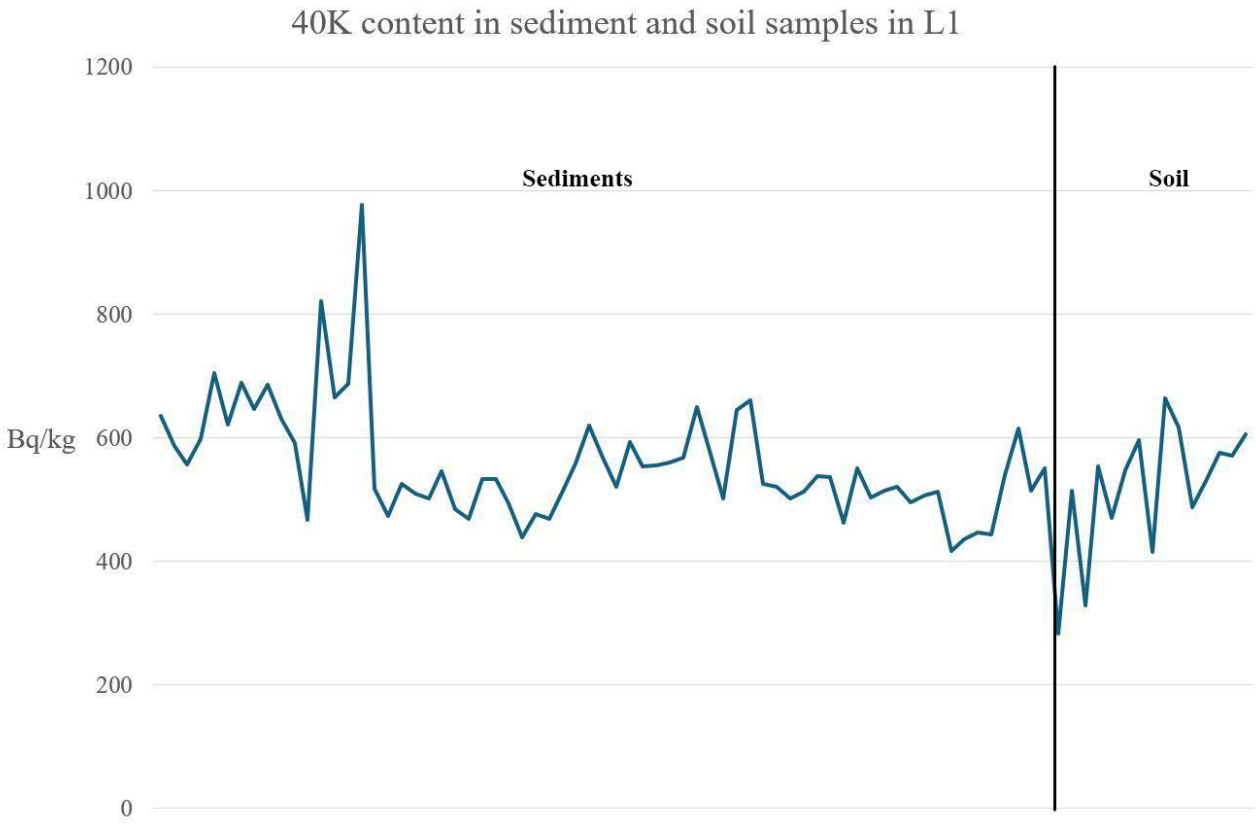

Figure 7: ^{40}K content in sediment soil samples in L1

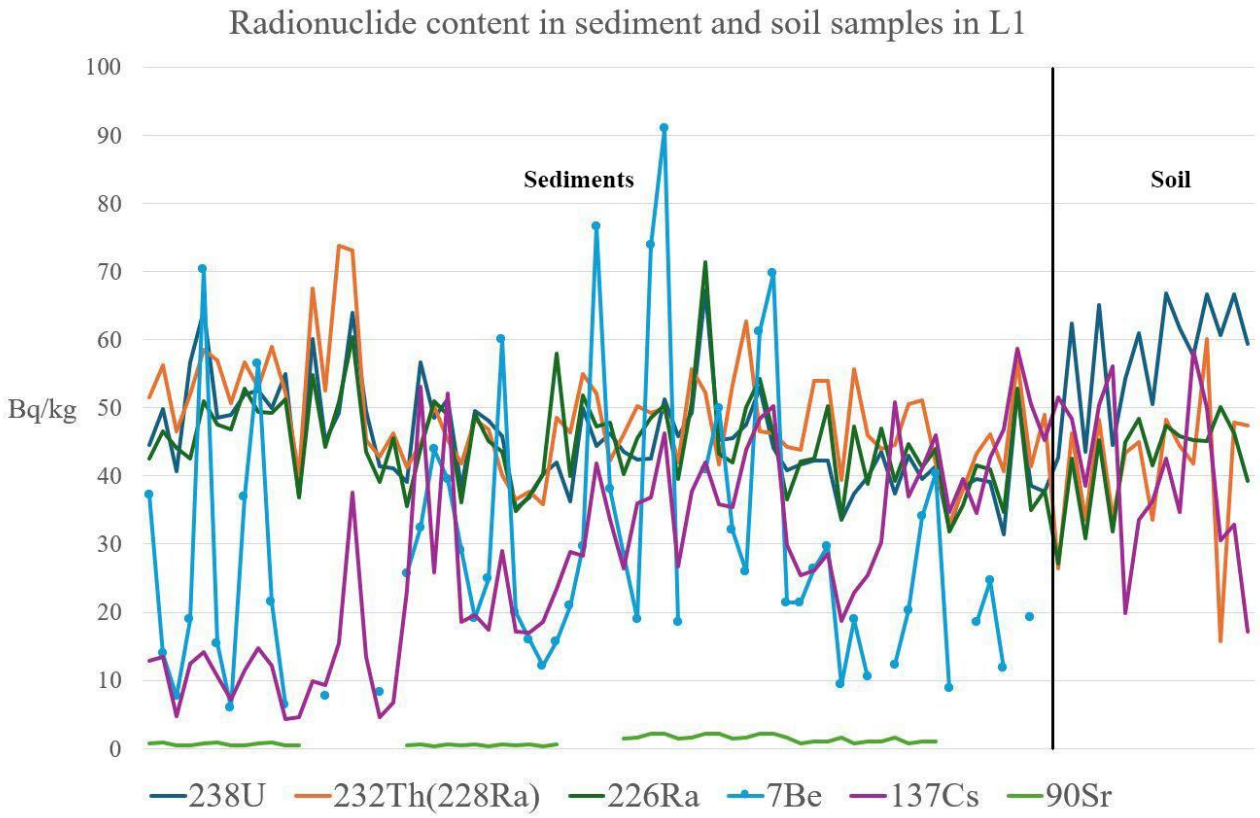

Figure 8: Radionuclide content in sediment soil samples in L1

Figure 7 and Figure 8 show radionuclide content in sediment samples (taken around the locations where water samples from open waterways were taken) and soil samples. Radioactive content of all the samples is similar and is similar to Croatian and world averages [4], [5]. Activity concentration of ^{226}Ra follows well activity concentration of ^{238}U, especially in sediment samples.

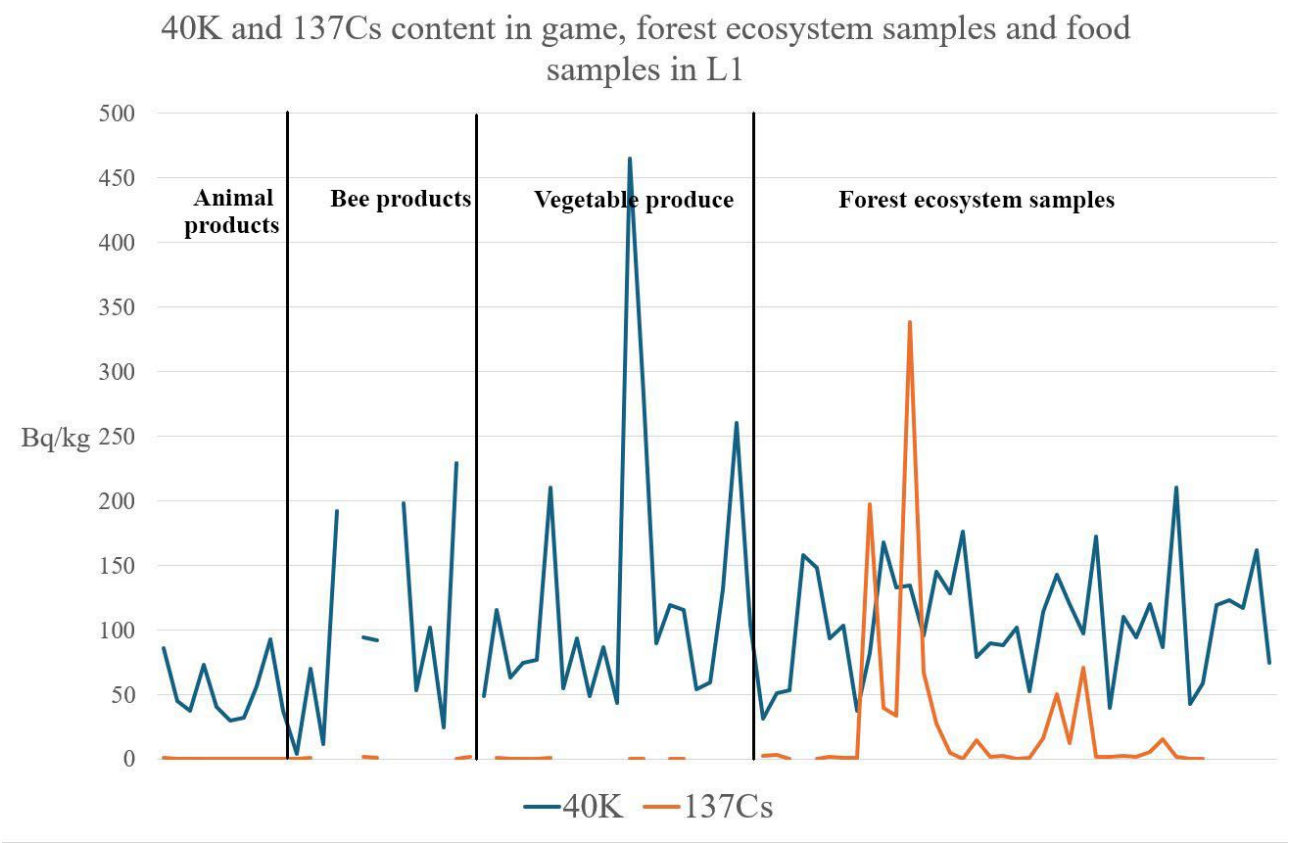

Figure 9: ^{40}K and ^{137}Cs content in game, forest ecosystem, and food samples in L1

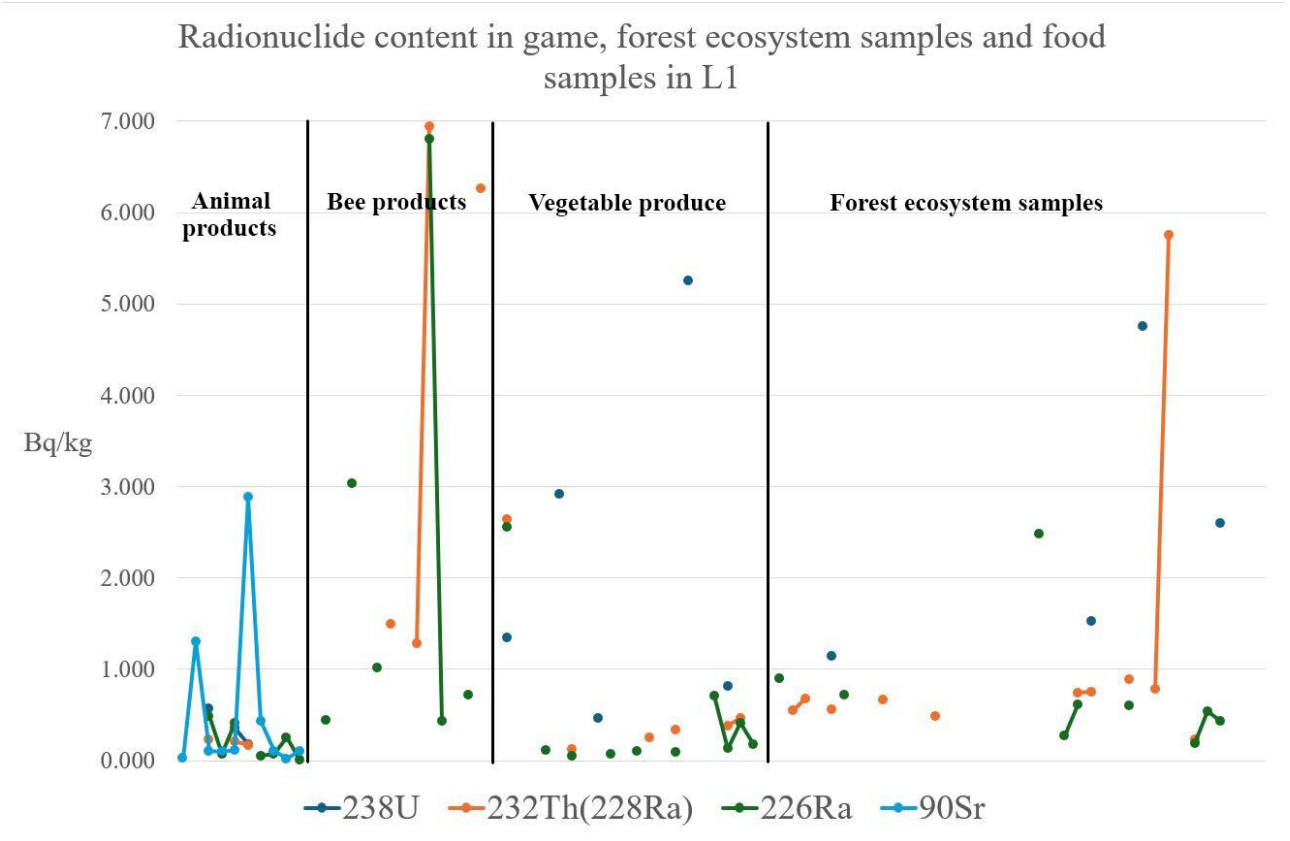

Figure 10: Radionuclide content in game, forest ecosystem, and food samples in L1

Figure 9 and Figure 10 show radionuclide content in game, forest ecosystem, and food samples, that is, in people's food – produce, honey and other bee products, game, mushrooms, chestnuts, and similar.

Next to ^{40}K, which is present in all the food that contains potassium, higher levels of ^{137}Cs were measured in mushroom samples. Otherwise, all the results are below 7 Bq/kg.

4 CONCLUSION

The extensive measurement program has shown that the radioactive content in nature around the proposed site location (soil, air, water, food) does not differ significantly from the Croatian averages. Only primordial radionuclides, and ^{137}Cs and ^{90}Sr, as anthropogenic radionuclides, were detected. Looking at radiological content, the area could be considered as roughly average for Europe. The activity concentrations of primordial radionuclides are neither particularly high, nor particularly low, and ^{137}Cs and ^{90}Sr are present, primarily from the Chernobyl accident. The area received roughly average contamination from the Chernobyl accident.

From radiological point of view, there is no reason not to site the Centre at the proposed location. The initial radiological state has been well analysed, and continuous radiological survey of the area will be able to detect any potential release.

REFERENCES

[1] Z. Franić,, N. Lokobauer, G. Marović, Radiostrontium activity concentrations in milk in the Republic of Croatia for 1961–2001 and dose assessment. *Health Physics*, Vol. 87, No. 2, pp 160–165 2004.

[2] HASL-300, EML procedures manual, 28th edition, 1997.

[3] Tehničke specifikacije za mjerenja radioaktivnosti za definiranje nultog (postojećeg) stanja na lokaciji Centra za zbrinjavanje radioaktivnog otpada in a području općine Dvor s procjenom godišnje efektivne doze za pojedinca, Fund for financing the decommissioning of the Krško Nuclear Power Plant and the disposal of Krško NPP radioactive waste and spent nuclear fuel, Zagreb, 2020. *(Croatian only)*

[4] Institut za medicinska istraživanja i medicinu rada, Praćenje stanja radioaktivnosti u okolišu u Republici Hrvatskoj, IMI-CRZ-103, Zagreb, 2022. https://civilna.zastita.gov.hr/UserDocsImages/CIVILNA ZAŠTITA/PDF_ZA WEB/Izvjestaj MUP 2022.pdf

[5] UNSCEAR 2008 Report Volume I, UN, New York, 2010.