Radionuclide and major element analysis of thermal and mineral waters in Croatia with a related dose assessment

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Abstract

Major elements concentrations (Na, K, Ca, Mg) and the activity concentrations of ^{226,228}Ra, ^{234,238}U, ^{210}Po, ^{210}Pb, ^{40}K and ^{137}Cs in northern and eastern Croatian thermal and mineral waters, collected directly from springs (or wells), are presented herein with total effective doses assessed for those waters that are considered as drinking "cures" and are available for consumption. The methods used for radionuclide determination included alpha-particle spectrometry, gas-proportional counting and gamma-ray spectrometry, while the major element composition was determined by ICP-MS. The activity concentrations of all of the radionuclides were found to be below the guidance levels set by the WHO and EC Directive, with the exception of one water sample that measured 0.26 Bq L^{-1} of ^{228}Ra. The effective ingestion dose assessment for the consumption of the so-called water "cures" during one, two or four weeks' time period throughout one year was well below the recommended 0.1 mSv for drinking water.

Key words: thermal waters; radionuclides; alpha-particle spectrometry; gamma-ray spectrometry; ICP-MS; dose assessment

INTRODUCTION

The northern and eastern parts of Croatia are very rich in geothermal water springs, with the majority located in the north, along the tectonic fault that extends from the Varaždin Spa to Čatež Spa in the neighbouring Republic of Slovenia. These parts of the country lie mostly in the Pannonian basin, and are dominated by sedimentary rocks of Quaternary and Tertiary age that overly the crystalline bedrock and, occasionally, Mesozoic sedimentary rocks. The gradient of this area is moderate to high and ranges from 0.03 °C m^{-1} to 0.07 °C m^{-1} (more than the world mean value), having considerable geothermal energy potential. The terrestrial heat-flow density is also high, ranging from 60 mW m^{-2} to 100 mW m^{-2} and occasionally up to 120 mW m^{-2}. The present-day high heat flow in the Pannonian basin can be explained by the depth-dependent extension of the lithosphere, which occurred during the Early to Middle Miocene time[1–5].

Thermal water occurrences are related to certain lithostratigraphic and tectonic conditions that must be fulfilled to enable underground waters to accumulate in the underground and spout out at the surface. The most important factors are the existence of deep folds that contain water-bearing strata, the existence of the link of water-carriers with the areas of atmospheric water collection and the link with the zones where aquifers reach near-surface areas[6].

Due to their specific properties, thermal waters are considered natural as well as national treasures. They are mainly used for medical purposes – treatment of various disorders and diseases, recreation and tourism, spas, etc., but are also being exploited for their geothermal potential – energy and heating. Many Croatian facilities have a long tradition of rehabilitation and tourism, like the Varaždin and Krapina Spas in the north, and the Daruvar and Bizovac Spas in the east. However, as much as these waters are considered cures, they could pose a health hazard for both the staff and patients/visitors due to higher exposure to natural radioactivity, as many are rich in radium isotopes[7–10].

The occurrence of natural radionuclides in thermal springs and groundwater is strongly influenced by the geological setting and bedrock of the surrounding area. Thermal waters are known to have elevated concentrations of naturally occurring radioisotopes, especially radium isotopes from uranium and thorium decay chains[11–13]. These activity concentrations strongly depend on the physico-chemical conditions and bedrock of the surrounding environment. Once radium has been ingested into the organism, it is easily incorporated into bones due to its chemical and biological similarity to other alkaline earth metals like calcium, strontium and barium. Short-lived radioactive progeny (such as ^{222}Rn, ^{218}Po, ^{214}Pb, ^{210}Pb, ^{210}Po), equally radiotoxic, are then generated within a short period of time which leads to their accumulation in the bones as well. Therefore, the national and international regulatory bodies, with the aim of assuring protection of the population, are being more focused on the quality of drinking water, food and the environment. For this reason, an accurate radioactivity measurement of specific radionuclides is required (with a related dose assessment), since these waters are abundantly used for human consumption (bathing, swimming, inhaling, and even drinking).

The currently available literature on radioactivity in Croatian thermal waters includes studies of radium activity concentrations[11], exposure to radioactivity (^{226}Ra and ^{228}Ra)[14] with associated health risks[15], and studies on radon activity concentrations[16]. This work presents the activity concentrations for a broader range of radionuclides: ^{226}Ra, ^{228}Ra, ^{238}U, ^{234}U, ^{210}Po, ^{210}Pb, ^{40}K and ^{137}Cs, along with major elements concentrations (Na, K, Ca, Mg) for Croatian thermal and mineral waters (as an extension of a previous work[17]), collected from the springs (or wells) as follows: i) Geothermal area of Hrvatsko Zagorje (T = 32–58 °C)

– Krapina Spa, Tuhelj Spa and Stubica Spa; ii) Geothermal area of Podravina-Međimurje (T = 58 °C) – Varaždin Spa; iii) Geothermal area of western Slavonija (T = 25–60 °C) – Lipik; iv) Geothermal area of eastern Slavonija (T = 74–125 °C) – Bizovac Spa (springs: Bizovka and Slavonka).

The aim of the present study was to characterize thermal waters from different parts of Croatia with regard to their major element content and assess the activity concentrations of naturally occurring (^{226}Ra, ^{228}Ra, ^{238}U, ^{234}U, ^{210}Po, ^{210}Pb, ^{40}K) and anthropogenic (^{137}Cs) radionuclides in order to obtain a wider picture of the radioactivity levels in Croatia's most visited thermal spas. Since some of these waters are also intended for human consumption, total effective doses due to ^{226}Ra, ^{228}Ra, ^{238}U, ^{234}U, ^{210}Po, ^{210}Pb, ^{40}K and ^{137}Cs intake were also assessed for consumption during one, two and four-week rehabilitation periods.

MATERIALS AND METHODS

Sample preparation

Samples of thermal and mineral waters were collected directly from springs or wells from northern and eastern Croatia (Figure 1), and transported to the laboratory immediately after collection. Samples of 50 L were used for ^{228}Ra, ^{40}K and ^{137}Cs determination by gamma-ray spectrometry (evaporation method), while another 50 L were acidified with 3 mL of concentrated HNO_3 per liter of the sample and used for major element (Na, K, Ca, Mg) analysis (by inductively coupled plasma mass-spectrometry) and for ^{226}Ra, ^{238}U, ^{234}U, ^{210}Po and ^{210}Pb determination (by alpha-particle spectrometry or gas-proportional counting).

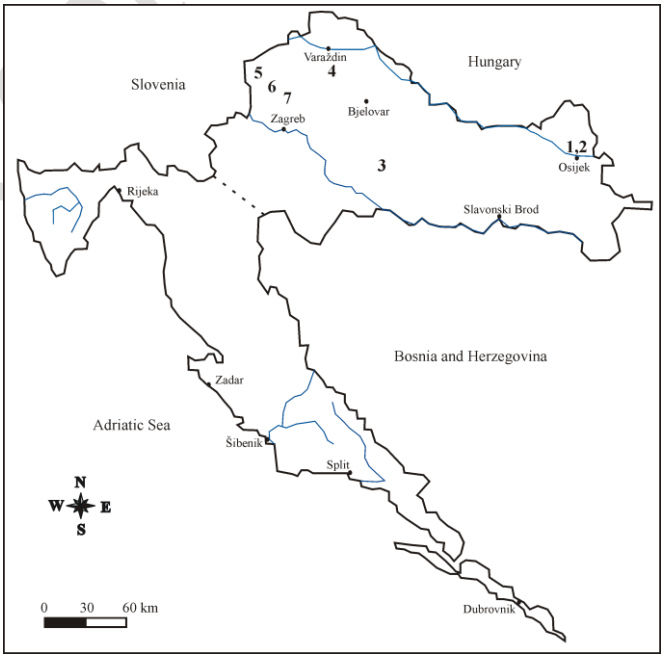

Fig. 1 Geographical locations of the thermal and mineral water samples

The samples were prepared and measured at four laboratories: Laboratory for Radioecology and Laboratory for Inorganic Environmental Geochemistry and Chemodynamics of Nanoparticles of the Ruđer Bošković Institute (Zagreb, Croatia), Radiation Protection Unit of the Institute for Medical and Occupational Health (Zagreb, Croatia) and the Group for Radioecology of the Jožef Stefan Institute (Ljubljana, Slovenia).

Chemicals and reagents

Multi-elemental reference standard (Fluka, Germany), containing Na, K, Ca and Mg, was used for major elements determination. Radioactive ^{133}Ba, ^{232}U and ^{209}Po tracer solutions were used for the evaluation of radiochemical yields in the determination of ^{226}Ra, ^{238}U, ^{234}U and ^{210}Po. Working solutions were prepared from standard solutions purchased from Analytics, Inc. (Atlanta, Georgia, USA). A standard of stable lead was prepared by dissolution of $Pb(NO_3)_2$ (Merck, Germany) and used for gravimetrical determination of radiochemical yield for ^{210}Pb determination. All other chemicals and reagents used were of analytical grade.

Instrumentation

Analysis of major elements (Na, K, Ca, Mg) in water samples was performed by High Resolution Inductively Coupled Plasma Mass Spectrometry (HR ICPMS) using an Element 2 instrument (Thermo, Bremen, Germany). More details on the analytical method used are described in the previous work[18].

For determination of ^{226}Ra, ^{238}U, ^{234}U and ^{210}Po, an alpha spectrometer (Alpha Analyst™, Canberra, USA) with a passivated implanted planar silicon (PIPS) semiconductor detector (active surface area of 450 mm^2 and 28% efficiency for a 25 mm diameter source disc) was used. The calibration of the detection system was performed by a standard radionuclide source containing ^{238}U, ^{234}U, ^{239}Pu and ^{241}Am (code: 67978-121), obtained from Analytics, Inc. Data acquisition and analysis was performed by Genie-2000 software. Counting time varied between 1 and 8 days, depending on the activity of a particular radionuclide.

A low background gas flow proportional counter (TENNELEC LB4100-W) was used for measurement of the ^{210}Pb daughter radionuclide ^{210}Bi, which was calibrated to account for correction due to the in-growth of ^{210}Bi and different self-absorption for samples with different radiochemical yields[19].

For determination of ^{226}Ra radiochemical yield (via ^{133}Ba), a high-resolution germanium detector (HPGe, Canberra, USA), with a relative efficiency of 25.4% and a resolution of 1.76 keV (FWHM) for the 1332.5 keV peak of ^{60}Co, connected to an 8192 channel analyser

(Meriden, USA) was used. Counting time was set to 3600 s for all of the samples. For energy calibration standard radionuclide point sources of ^{241}Am, ^{60}Co and ^{137}Cs (Area CERCA LEA, France) were used.

For gamma-ray spectrometric analyses of ^{228}Ra, ^{40}K and ^{137}Cs, a HPGe Coaxial Photon Detector System (ORTEC, USA), with relative efficiency of 74.2% and resolution (FWHM) 2.24 keV at 1332.5 keV ^{60}Co, was used. The detector was calibrated using standard sources supplied by the Czech Metrological Institute covering an energy range between 40 keV and 2000 keV.

Major elements analysis

Prior to the analysis, samples were diluted 10-fold, acidified with 2% (w/w) HNO_3 s.p. and In (1 μg L^{-1}) was added as an internal standard. The quality control of the analytical procedure used for multi-elemental analysis was performed by simultaneous analysis of the blank and certified reference material for water (SLRS-4, NRC, Canada). Good agreement between the analysed and certified concentrations within their analytical uncertainties for all elements was obtained (± 10%).

Radiochemical procedures for alpha-particle spectrometry and gas-proportional counting

The determination of ^{226}Ra by alpha-particle spectrometry was based on Ra(Ba)(Pb)SO_4 co-precipitation method[20], while determination of uranium isotopes was based on a separation method using UTEVA resin (Eichrom)[21] with source preparation by NdF_3 micro co-precipitation method [22,23]. For ^{210}Po and ^{210}Pb determination, a separation method using Sr resin (Eichrom)[24] was used. The polonium source was prepared by self-deposition on a silver disc from HCl solution and determined by alpha-particle spectrometry, while ^{210}Pb source was prepared by $PbSO_4$ precipitation and determined via its daughter radionuclide ^{210}Bi on a low background gas-flow proportional counter. All the used procedures are described in detail in the previous work[25]. The quality control of the radiochemical procedures is done regularly through participation in intercomparison and proficiency test programs.

^{228}Ra, ^{40}K and ^{137}Cs determination by gamma-ray spectrometry

The samples were evaporated to 1 L volume, packed into Marinelli beakers and stored for at least 30 days to reach secular equilibrium conditions between ^{226}Ra and its short-lived decay products. ^{228}Ra was determined from 209.40, 338.40, 911.07, 964.60, 968.90 and 1587.90 keV emissions from ^{228}Ac. ^{40}K and ^{137}Cs were calculated directly from 1460.75 and

661.62 keV lines, respectively. The quality assurance was implemented through participation in proficiency test programs organized by the IAEA and Joint Research Centre. The applied method is accredited according to the ISO/IEC 17025 international standard.

Total effective dose assessment by consumption of some Croatian thermal and mineral waters during rehabilitation period

For the total effective dose calculation (due to ^{226}Ra, ^{228}Ra, ^{238}U, ^{234}U, ^{210}Po, ^{210}Pb, ^{40}K and ^{137}Cs intake), Eqs. (1) and (2) and data from Tables 1 and 4 were used.

$$E_d = A_c \cdot q \cdot C_f \quad (1)$$

$$D = \Sigma A_c \cdot q \cdot C_f \quad (2)$$

where: E_d is the effective ingestion dose due to relevant radionuclide expressed in μSv; A_c is the radionuclide activity concentration in the water sample expressed in Bq L^{-1}; q is the water consumption rate expressed in L; C_f is the dose coefficient of the relevant radionuclide given in the European Commission Council Directive[26], and presented in Table 1; and D is the total effective ingestion dose received during rehabilitation period due to all determined radionuclides, expressed in μSv.

RESULTS AND DISCUSSION

Major elements concentrations

The results of major elements analysis (Na, K, Ca, Mg) in thermal and mineral water samples are presented in Table 2.

Potassium, calcium and magnesium were found at their highest levels in sample 1 from eastern Slavonija. The potassium concentration in the thermal water from the Bizovka spring (sample 1) was twice as high compared to the one obtained for thermal water from western Slavonija (sample 3), and up to two orders of magnitude higher compared to thermal and mineral waters from Hrvatsko Zagorje (samples 5–7). Similarly, magnesium and calcium were found in concentrations of up to five and ten times, respectively, higher in sample 1 compared to those measured in the thermal and mineral waters from western Slavonija (sample 3) and Hrvatsko Zagorje (samples 5–7). Interestingly, all of these elements were found at significantly lower levels in the thermal water from the nearby Slavonka spring (sample 2).

The broadest range of concentrations in the analysed waters was observed for sodium, for which the highest concentrations were measured in the thermal waters from eastern (samples 1 and 2) and western Slavonija (sample 3), being up to two orders of magnitude higher compared to those measured in thermal and mineral waters from Hrvatsko Zagorje (samples 5–7).

It is interesting to note that the distribution of major elements significantly differed between thermal waters from locations 1 and 2, despite the fact that they originated from the same area. Thermal water from the Slavonka spring (sample 2) resembled other analysed waters regarding the levels of major elements (and the radionuclide content as well), with the exception of sodium. The similarity in the observed concentrations of Na in thermal waters 1 and 2 from the Bizovac Spa stems from the fact that these thermal waters were brine, while the thermal and mineral waters from Hrvatsko Zagorje (samples 5–7) were partially or completely of vadose origin. Although the thermal water of Lipik (sample 3) originates from a geothermal aquifer comprised of fractured middle and upper Triassic limestones and dolomites, the high Na concentrations in it, almost the same as in the thermal waters from the Bizovac Spa (samples 1 and 2), can be attributed to differences in local geology.

The obtained results point to significant variability in the chemical characteristics of the studied thermal and mineral waters, reflecting the differences in types and depths of reservoirs and local geology. The distribution of radionuclides in these waters is discussed below.

Activity concentrations of investigated radionuclides

The physico-chemical characteristics of the analysed Croatian thermal and mineral waters, including pH and temperature, are presented in Table 3. The pH values varied from neutral (6.8–7.2) to mildly alkaline (7.6–8.1), while water temperatures ranged from 30.1 °C to 92 °C. The differences in water temperatures are the result of a combined effect of local geology and depth of reservoirs. The thermal and mineral waters of Hrvatsko Zagorje and thermal water from Lipik belong to geothermal springs with water temperatures below 65 °C, originating from Triassic limestones and dolomites, while only the Bizovac area belongs to low-temperature (65–100 °C) geothermal reservoirs with thermal waters originating from deep aquifers (with depths up to 5000 m) situated in sediments of Neogene age.

The activity concentrations of naturally occurring radionuclides ^{226}Ra, ^{228}Ra, ^{238}U, ^{234}U, ^{210}Po, ^{210}Pb (from ^{238}U and ^{232}Th decay chains), primordial ^{40}K, and anthropogenic ^{137}Cs are presented in Table 4.

Activity concentrations of ^{226}Ra in thermal and mineral water samples ranged from (68.8 ± 4.8) mBq L^{-1} to (3624 ± 332) mBq L^{-1}, exceeding activity concentrations of ^{228}Ra in most cases (^{226}Ra/^{228}Ra activity ratios, as presented in Table 5, are found to be in range from 0.3 to 10.6). Activity concentrations of ^{228}Ra were measured in the similar range, from (36.8 ± 2.5) mBq L^{-1} to (3194 ± 21) mBq L^{-1}. The highest activity concentrations of both radium isotopes were measured in eastern Slavonija in sample 1, which can be attributed to its natural hypothermal salt composition rich in minerals (see also Table 3). Similar observations were

reported by Chau and co-workers[27] for Carpathian mineral waters in Poland characterized by high radium and total dissolved solids content. Lower ^{226}Ra content was found in sample 2 and in Hrvatsko Zagorje (samples 5 and 7), where lower ^{228}Ra contents were also found. These results are comparable to ^{226}Ra and ^{228}Ra content in thermal waters from neighbouring (Hungary, Bosnia and Herzegovina and Italy) as well as other countries, like France, Poland, Spain, etc., presented in Table 6.

According to the World Health Organization Guidelines for Drinking Water Quality[28], the guidance levels for ^{226}Ra and ^{228}Ra activity concentrations in drinking waters are set to 1 Bq L^{-1}, and 0.1 Bq L^{-1}, respectively, for the general public, assuming a 2 L daily intake of water (Table 1). However, according to the new European Council Directive 2013/51/EURATOM, drinking water guidelines are set to 0.5 and 0.2 Bq L^{-1} for ^{226}Ra and ^{228}Ra, respectively[29], which was adopted by Croatian legislation in 2013[30] after it became an EU Member State. Although the Directive excludes mineral and thermal waters, in some Croatian spas these waters are available for oral consumption (waters from locations of Lipik, Varaždin, Krapina, Tuhelj, and Stubica Spas; samples 3–7, respectively). With respect to WHO and EC Directive guidelines, the mentioned waters are within the guidance limits for both of the radium isotope's activity concentrations, with the exception of ^{228}Ra in water from Lipik (sample 3), where a value of 0.26 Bq L^{-1} was measured. Despite this elevated ^{228}Ra level in the mentioned water sample it cannot be said that it does not comply to national regulation since the derived activity concentrations given in the Directive were calculated for an annual dose of 0.1 mSv, based on an annual intake of 730 litres (2 L per day), while thermal waters are consumed only seldom (for several weeks), and in smaller amounts (0.5–1 L per day).

The activity concentrations for ^{238}U and ^{234}U isotopes were considerably lower than the radium isotopes activities, and ranged from (1.8 ± 0.5) to (8.3 ± 1.5) mBq L^{-1} and (3.6 ± 2.3) to (19.2 ± 2.5) mBq L^{-1}, for ^{238}U and ^{234}U, respectively. Somewhat higher activity concentrations were measured in the regions of Podravina-Međimurje and Hrvatsko Zagorje (samples 4 and 5, respectively). All of the water samples unsurprisingly showed higher ^{238}U than ^{234}U activity concentrations as a consequence of the recoil effect[31], ranging from 1.5 to 4.0 ^{234}U/^{238}U activity ratios (Table 5). Both activity concentrations and activity ratios are comparable to uranium isotope content in thermal and mineral waters from similar reported studies in Bosnia and Herzegovina, Hungary, Egypt, Poland, Morocco and Tunisia (Table 6). It should also be emphasized that all of the water samples intended for human consumption (Lipik, Varaždin, Krapina, Tuhelj and Stubica Spas; samples 3–7, respectively) were below the WHO and EC Directive guidelines for uranium activity concentrations (Table 1).

^{210}Po and ^{210}Pb activity concentrations of the studied thermal and mineral waters were low and within the range (0.6 ± 0.1) – (9.3 ± 0.7) mBq L^{-1} and (1.8 ± 0.6) – (41.3 ± 1.7) mBq L^{-1} for ^{210}Po and ^{210}Pb, respectively, which is also within WHO guidelines and EC Directive requirements (Table 1) for waters intended for human consumption (Lipik, Varaždin, Krapina, Tuhelj and Stubica Spas; samples 3–7, respectively). The highest activities of these radionuclides were once again measured in eastern Slavonija (sample 1) and the lowest in the spas of Podravina-Međimurje and Hrvatsko Zagorje (samples 4 and 5–7, respectively).

Levels of primordial ^{40}K, which takes up 0.012 % of natural potassium, ranged between (64.4 ± 3.5) and (6540 ± 78) mBq L^{-1}. Higher ^{40}K activity concentrations were expected due to the high solubility of potassium in water, and due to high content of total dissolved solids in almost all of the water samples[15]. The highest activity concentrations were again found in eastern Slavonija (sample 1), and in western Slavonija (sample 3), which is in accordance with the elevated levels of pottasium in these waters (Table 2). The lowest ^{40}K content was found in waters from Hrvatsko Zagorje (samples 5 and 6), which is also in accordance with potassium determination by ICP MS (Table 2).

Anthropogenic ^{137}Cs was determined in all water samples with activity concentrations ranging from (0.04 ± 0.01) mBq L^{-1} in the Varaždin Spa (sample 4) to (7.8 ± 0.8) mBq L^{-1} in the Bizovac Spa spring Slavonka (sample 2). All of the samples, except for the water from the area of Podravina-Međimurje (sample 4), showed uniform ^{137}Cs levels, averaging to 5.8 mBq L^{-1}, which is below the recommended 10 Bq L^{-1} given by the WHO and 11 Bq L^{-1} by the EC Directive. Geochemical studies have shown that thermal and mineral waters in the northern part of Croatia originate from atmospheric precipitation and groundwater movement through tectonic areas[32]. The observed elevated activity concentrations of ^{137}Cs in thermal waters could originate from surface waters by leaching process.

The overall highest activities of ^{226}Ra, ^{228}Ra, ^{210}Po, ^{210}Pb, ^{40}K and ^{137}Cs measured in the thermal water from Bizovac Spa spring Bizovka (sample 1) are consistent with the results of major element analysis and geochemical data reported by Fiket and co-workers[17]. To be more precise, thermal water from the Bizovka spring was found enriched in major (this study) as well as trace[17] elements compared to thermal and mineral waters from Hrvatsko Zagorje (sample 5–7) and Lipik (sample 3), including thermal water from the nearby spring Slavonka (sample 2).

Effective dose assessment for consumption of some Croatian thermal and mineral waters during rehabilitation period

All of the analyzed waters are used for medical, bathing and recreational purposes, while waters from locations 3–7 (Lipik, Varaždin, Krapina, Tuhelj and Stubica Spas, respectively) are also recommended as drinking "cures". Although thermal and mineral water consumption is considered beneficial (e.g. for gastro-intestinal diseases, constipation, etc. (oral communication)), it could also result in possible higher exposure to natural radioactivity.

The assessment of the total effective doses due to ^{226}Ra, ^{228}Ra, ^{238}U, ^{234}U, ^{210}Po, ^{210}Pb, ^{40}K and ^{137}Cs intake by thermal and mineral water consumption from locations 3–7 is presented in Figure 2, assuming the recommended 1 L water intake (oral communication) per day for one, two and maximum four weeks (which is the most common time period for rehabilitation).

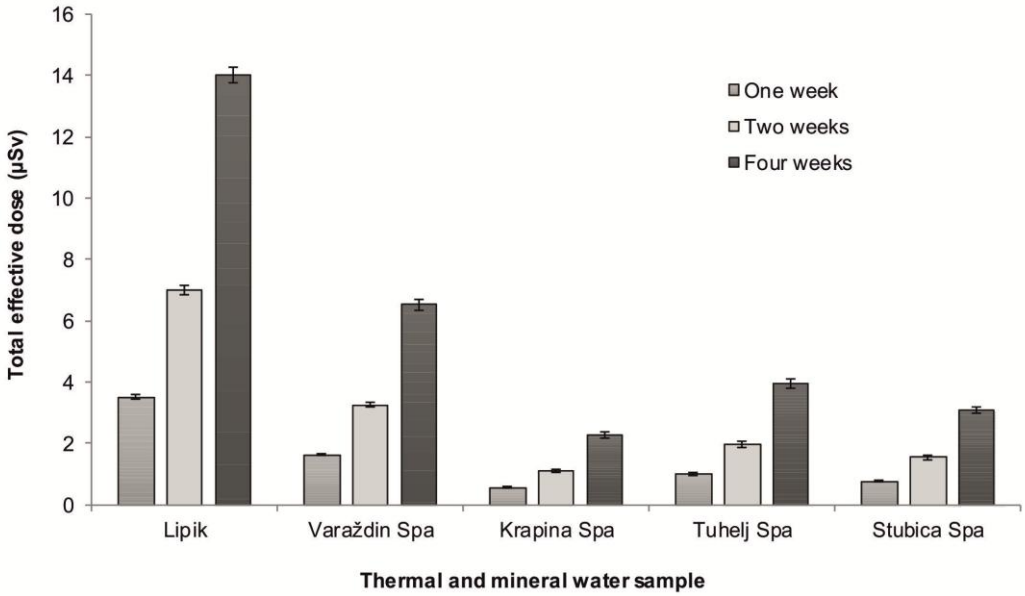

Fig. 2 Total effective doses (μSv) for adult population due to radionuclide intake by thermal and mineral water consumption for rehabilitation purposes at four Croatian Spas during one, two and four weeks' time periods, with combined standard uncertainties (k = 2)

The previously mentioned water from Lipik (sample 3), which exceeded WHO/EC Directive guidelines when it comes to the ^{228}Ra activity concentration, does not exceed the Croatian national regulation (0.1 mSv y^{-1} from drinking water) since the maximum received dose due to one, two and four weeks' time period of water consumption reached only 3.5 μSv, 7.0 μSv and 14.0 μSv, respectively. This makes up only 14% of the allowed annual dose for water intake. These waters are primarily set for medical purposes (bathing, hydro-massages, hydro-gymnastics, etc. (oral communication)) and are used only seldom as drinking, and

much more as bathing waters, in well-defined quantities and time periods. Doses for consumption of waters from locations of Krapina, Varaždin, Tuhelj and Stubica Spas (samples 4–7, respectively) for maximum of four weeks, ranged between 2.3 μSv and 6.5 μSv. So, it can be concluded that all of the analysed thermal and mineral waters are suitable for human consumption as drinking "cures" without significant hazard for human health due to periodically higher exposures to natural radioactivity.

CONCLUSION

Activity concentrations for naturally occurring (^{226}Ra, ^{228}Ra, ^{238}U, ^{234}U, ^{210}Po, ^{210}Pb, ^{40}K) and anthropogenic (^{137}Cs) radionuclides were determined for Croatian thermal and mineral waters from Croatia's most visited spas for both recreation and rehabilitation purposes, with major element (Na, K, Ca, Mg) composition determined as well.

The highest activities were measured for ^{226}Ra, ^{228}Ra and ^{40}K, which was expected due to high total dissolved solids content of these waters. The overall highest activities, along with the highest major elements levels, were measured in the thermal water from Bizovac Spa spring Bizovka (sample 1) in eastern Slavonija, and the lowest generally in the spas of Hrvatsko Zagorje (samples 5–7).

The waters from Varaždin (sample 4), Krapina (sample 5), Tuhelj (sample 6) and Stubica (sample 7) Spas, intended for human consumption, were below the recommended activity concentrations for all of the determined radionuclides. Only in the water from Lipik Spa (sample 3) did the ^{228}Ra activity concentration (0.26 Bq L^{-1}) exceed both WHO and EC Directive guideline levels for drinking water (based on 730 L intake per year). Since thermal waters are rarely consumed, only for specific purposes and in pre-defined quantities, it cannot be said that the water from Lipik does not comply to national regulation (0.1 mSv y^{-1} for drinking waters). The maximum doses for four weeks' rehabilitation period due to consumption of the mentioned waters ranged between 2.3 μSv and 14.0 μSv, which is well below the allowed 0.1 mSv per year, indicating that a consumption more frequent than just four weeks per year would also be acceptable.

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460 **TABLES**

461

462 Table 1. Dose coefficients of the determined radionuclides (C_f) expressed in μSv Bq^{-1}, and
463 guidance levels (Bq L^{-1}) for members of the public.

Radionuclide	C_f (μSv Bq^{-1})[a]	Guidance level (Bq L^{-1})	
		WHO[b]	EC EURATOM[c]
^{226}Ra	0.28	1	0.5
^{228}Ra	0.69	0.1	0.2
^{238}U	0.045	10[d]	3.0[e]
^{234}U	0.049	1[d]	2.8[e]
^{210}Po	1.2	0.1	0.1
^{210}Pb	0.69	0.1	0.2
^{40}K	0.0062	–	–
^{137}Cs	0.013	10	11

464 [a] EC Directive 1996/29/EURATOM[(26)]
465 [b] WHO 2011[(28)]
466 [c] EC Directive 2013/51/EURATOM[(29)]
467 [d] Guidance level for individual uranium isotopes is given only in terms of radioactivity (Bq L^{-1}). Provisional
468 guideline for total content of uranium in drinking water is 30 μg L^{-1} based on its chemical toxicity, which is
469 predominant compared to its radiological toxicity.
470 [e] Taking into account only radiological characteristics of uranium, not its chemical toxicity.
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472

473 Table 2. Concentrations of major elements (mg L^{-1}) in analyzed Croatian thermal and mineral
474 water samples

Sample ID	Na	K	Ca	Mg
1	875	204	454	56.2
2	1127	13.8	10.0	1.65
3	754	83.9	42.3	12.1
4	81.6	11.6	114	20.4
5	8.15	2.62	50.5	27.5
6	6.43	2.04	64.2	32.4
7	23.8	6.88	65.9	22.9
Range	6.43 – 1127	2.04 – 204	10.0 – 454	1.65 – 56.2

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Table 3. Temperature, pH and other characteristics of analyzed Croatian thermal and mineral spring waters.

Sample ID	Water sample	Description*	*T* (°C)	pH
1	Bizovac Spa (spring: Bizovka)	Hypothermal salt water rich in minerals	92	7.9
2	Bizovac Spa (spring: Slavonka)	Thermal salt water rich in minerals	81	7.6
3	Lipik Spa	Thermo-mineral water rich in F^-, Na^+, Ca^{2+} and HCO_3^-	~ 60	7.2
4	Varaždin Spa	Thermal water abundant with sulfur	54.6	6.8
5	Krapina Spa	Thermal water rich in Ca^{2+}, Mg^{2+} and HCO_3^-	39.2	7.2
6	Tuhelj Spa	Mineral water	30.1	8.1
7	Stubica Spa	Thermal water with optimal mineral composition	51.8	6.9

* Marović et al. 1996[15]

Table 4. Activity concentrations (mBq L^{-1}) of selected radionuclides in analyzed Croatian thermal and mineral spring waters.

Sample ID	Radionuclide activity concentration (mBq L^{-1})							
	^{226}Ra	^{228}Ra	^{238}U	^{234}U	^{210}Po	^{210}Pb	^{40}K	^{137}Cs
1	3624 ± 332	3194 ± 21	5.1 ± 0.7	8.3 ± 1.0	9.3 ± 0.7	41.3 ± 1.7	6540 ± 78	5.4 ± 1.7
2	68.8 ± 4.8	209.7 ± 5.6	2.3 ± 1.8	3.6 ± 2.3	2.2 ± 0.2	2.8 ± 1.1	492.6 ± 13.8	7.8 ± 0.8
3	453.5 ± 25.6	261.0 ± 3.8	3.3 ± 0.9	7.8 ± 1.5	1.9 ± 0.2	4.8 ± 0.7	3020 ± 23	7.0 ± 0.5
4	201.8 ± 13.5	207.7 ± 2.8	4.9 ± 1.0	11.4 ± 1.7	0.6 ± 0.1	2.6 ± 0.9	483.3 ± 10.7	0.04 ± 0.01
5	156.6 ± 11.1	37.3 ± 1.8	8.3 ± 1.5	19.2 ± 2.5	1.5 ± 0.1	1.8 ± 0.6	103.7 ± 3.2	4.8 ± 0.4
6	389.6 ± 18.2	36.8 ± 2.5	1.8 ± 0.5	7.2 ± 1.1	0.6 ± 0.1	2.1 ± 0.5	64.4 ± 3.5	6.0 ± 0.5
7	177.9 ± 12.3	59.8 ± 2.0	4.3 ± 0.6	6.6 ± 0.8	0.6 ± 0.1	2.4 ± 0.7	264.5 ± 9.1	4.0 ± 0.3
Range	68.8 – 3624	36.8 – 3194	1.8 – 8.3	3.6 – 19.2	0.6 – 9.3	1.8 – 41.3	64.4 – 6540	0.04 – 7.8

485 Table 5. Activity ratios for $^{234}U/^{238}U$ and $^{226}Ra/^{228}Ra$ isotopes in the analyzed Croatian
486 thermal and mineral water samples.

Sample ID	$^{234}U/^{238}U$	$^{226}Ra/^{228}Ra$
1	1.6	1.1
2	1.6	0.3
3	2.4	1.7
4	2.3	1.0
5	2.3	4.2
6	4.0	10.6
7	1.5	3.0
Range	1.5 – 4.0	0.3 – 10.6
Median	2.3	1.7

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488

489 Table 6. Activity concentrations (A) of ^{226}Ra, ^{228}Ra, ^{238}U and ^{234}U (mBq L^{-1}) in thermal and
490 mineral waters in other countries.

Country	A (mBq L^{-1})				Reference
	^{226}Ra	^{228}Ra	^{238}U	^{234}U	
Algeria	271 – 2101	–	–	–	Amarouche-Yala et al. 2015[33]
Bosnia and Herzegovina	1.1 – 791	0.2 – 221	13 – 304	–	Kasić et al. 2015[34]
Egypt	< 280 – 3940	–	35.0 – 90.0	–	Khater 2003[35]
France	532 – 2243	102 – 639	–	–	Condomines et al. 2010[12]
Hungary	48 – 837	–	–	–	Baradacs et al. 2001[36]
	5 – 1985	–	6 – 113*		Erőss et al. 2015[37]
Italy	800 – 7300	–	–	–	Cantaluppi et al. 2012[38]
Jordan	3800 – 6810	1420 – 2370	–	–	Saqan et al. 2001[9]
Morocco	9.10 – 3696	2.40 – 620	0.59 – 8.51	2.40 – 54.46	Hakam et al. 2001[7]
Poland	29 – 2250	25 – 359	1.1 – 328	4.7 – 313	Nowak et al. 2012[8]
	≤ 2 – 758	≤ 10 – 877	–	–	Chau et al. 2012[27]
Romania	30 – 1820	–	–	–	Roba et al. 2012[39]
Spain	4 – 3660	–	–	–	Ródenas et al. 2008[40]
Tunisia	34 – 3900	–	1.5 – 42.7	1.1 – 82.2	Labidi et al. 2002[13]
Turkey	100 –1200	–	–	–	Tabar et al. 2013[41]

491 * $^{238}U + ^{234}U$ reported