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ORIGINAL PAPER

Environmental risk assessment of radioactivity and heavy metals in soil of Toplica region, South Serbia

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Abstract Activity levels of natural and artificial radionuclides and content of ten heavy metals (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn and Hg) were investigated in 41 soil samples collected from Toplica region located in the south part of Serbia. Radioactivity was determined by gamma spectrometry using HPGe detector. The obtained mean activity concentrations ± standard deviations of radionuclides ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs were 29.9 ± 9.4, 36.6 ± 11.5, 492 ± 181 and 13.4 ± 18.7 Bq kg^{-1}, respectively. According to Shapiro–Wilk normality test, activity concentrations of ^{226}Ra and ^{232}Th were consistent with normal distribution. External exposure from radioactivity was estimated through dose and radiation risk assessments. Concentrations of heavy metals were measured by using ICP-OES, and their health risks were then determined. Enrichment by heavy metals and pollution level in soils were evaluated using the enrichment factor, the geoaccumulation index (I_{geo}), pollution index and pollution load index. Based on GIS approach, the spatial distribution maps of radionuclides and heavy metal contents were made. Spearman correlation coefficient was used for correlation analysis between radionuclide activity concentrations and heavy metal contents.

Keywords Radionuclides · Heavy metals · Spatial distribution · Environmental risk · GIS

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Introduction

Permanent background radiation arises from natural (terrestrial and cosmic) and anthropogenic sources (UNSCEAR 2008). Main contributors to natural radiation are terrestrial radionuclide ^{40}K and radionuclides of the ^{238}U and ^{232}Th series. The external exposure of population due to background radiation is mainly coming up from soil. Since they originated from various geological formations, knowledge about levels and spatial distribution of these radionuclides is substantially for possible risk assessment to gamma-ray exposure. Fission product ^{137}Cs is very important anthropogenic radionuclide, which allows inclusion in geobiochemical environmental cycles, since its half

life is relatively long (30.2 years) as well. Therefore, for useful information on the background radiation in an area, it is necessary to investigate and follow up environmental radioactivity.

The term heavy metal often refers to the group of elements that have been associated with contamination, toxicity and pollution. Heavy metals also come from natural or anthropogenic sources. The main natural sources are geological degradation i.e. rock weathering and thermal springs. Recent surveys confirmed that the anthropogenic sources cause pollution effects through the various inputs: mining, metallurgical, chemical and heavy industries (including their waste discharges) (Alijagić and Šajn 2011; Liang et al. 2017; Ogundele et al. 2017; Pandey et al. 2014; Serbula et al. 2017; Stafilov et al. 2010; Yaylalı-Abanuz 2011), vehicle emissions (Hu et al. 2013; Li et al. 2001; Ordóñez et al. 2015; Shi et al. 2008; Wei et al. 2015) and agronomic practices, such as organic and mineral fertilization, application of pesticides. (Barać et al. 2016a; Esmaeili et al. 2014; Montagne et al. 2007; Nziguheba and Smolders 2007; Rodríguez et al. 2008).

Environmental pollution by persistent heavy metals can induce harmful effects on ground waters, agricultural production, food safety and consequently human health, because soil is most important ecosystem for human survival and development. Therefore, determination of heavy metals content and its spatial distributions in soils could partially help in identifying, monitoring and assessing the potential source of pollution in an area.

Recent studies have reported some data on environmental status of Serbia, but in various fields of interest pointing out various sources of contamination and pollution of certain areas (Borgna et al. 2009; Barać et al. 2016b; Ćujić et al. 2017; Dragović et al. 2014; Gulan et al. 2013; Milenković et al. 2015; Momčilović et al. 2010; Serbula et al. 2014; Tanić et al. 2014, 2016). The earlier two studies conducted in Southern Serbia were related to some other contaminated areas, and they investigated specific problems such as evaluation of the radioactivity and heavy metals in mining sites (Todorovic et al. 2012; Popovic et al. 2008).

Natural background radiation and radioactive emissions from nuclear facilities (Chernobyl, Fukushima) are the matter of public concern. Cancer risk from low doses of ionizing radiation is still the focus of a long-standing controversy in radiation protection (Körblein and Hoffmann 2006). The interest of the population about background radiation levels and the potential implications on health started with the increasing risk of cancer incidence and mortality in Serbia over the past years (Dimitrova et al. 2017; Durakovic 2001; Jia et al. 2005; Mihajlović et al. 2013; Slijepcevic et al. 2016).

Materials and methods

Study area

A study area covers Toplica region, situated between 42°52′–43°24′N and 20°56′–21°50′E in the South Serbia (Fig. 1). According to the administrative regionalization, Toplica region comprises four municipalities: Prokuplje, Kuršumlija, Blace and Žitoradja, where live 90.600 inhabitants, according to data from the 2011 census. Toplica region occupies an area of 3055 km^2 (Macejka et al. 1999); it is limited by the river South Morava on the east and by Kopaonik mountain on the west. Northern border of region formed mountains Veliki and Mali Jastrebac, while the southern boundary follows the highest parts of the mountains: Radan, Vidojevica and Pasjača. Average altitude of Toplica is 482 m, and percent of agricultural land is 10.9% according to data from 2012 (Valjarević et al. 2014).

Toplica region is very attractive in order to develop tourism, since three famous spas (Lukovska banja, Kuršumlijska banja and Prolom banja) belong to this region. In particular, affirmation of tourism is Devil's Town, unique tall stones formation, which was nominated for "New seven wonders of nature" (Valjarević et al. 2015). Secondly, it is necessary to mention that growing interest of scientists, inhabitants and visitors attracts archaeological excavations from the Neolithic period which are still ongoing. The first archaeological investigation in this area started in 1927 (Kuzmanović-Cvetković 1998). Toplica region is also important fruit-growing and agricultural area in Serbia.

All above-mentioned studies conducted in Serbia consider the environmental levels of radionuclides and various heavy metals in order to outline areas of potential toxicity. Nevertheless, such studies have not been conducted so far in Toplica region, and therefore,

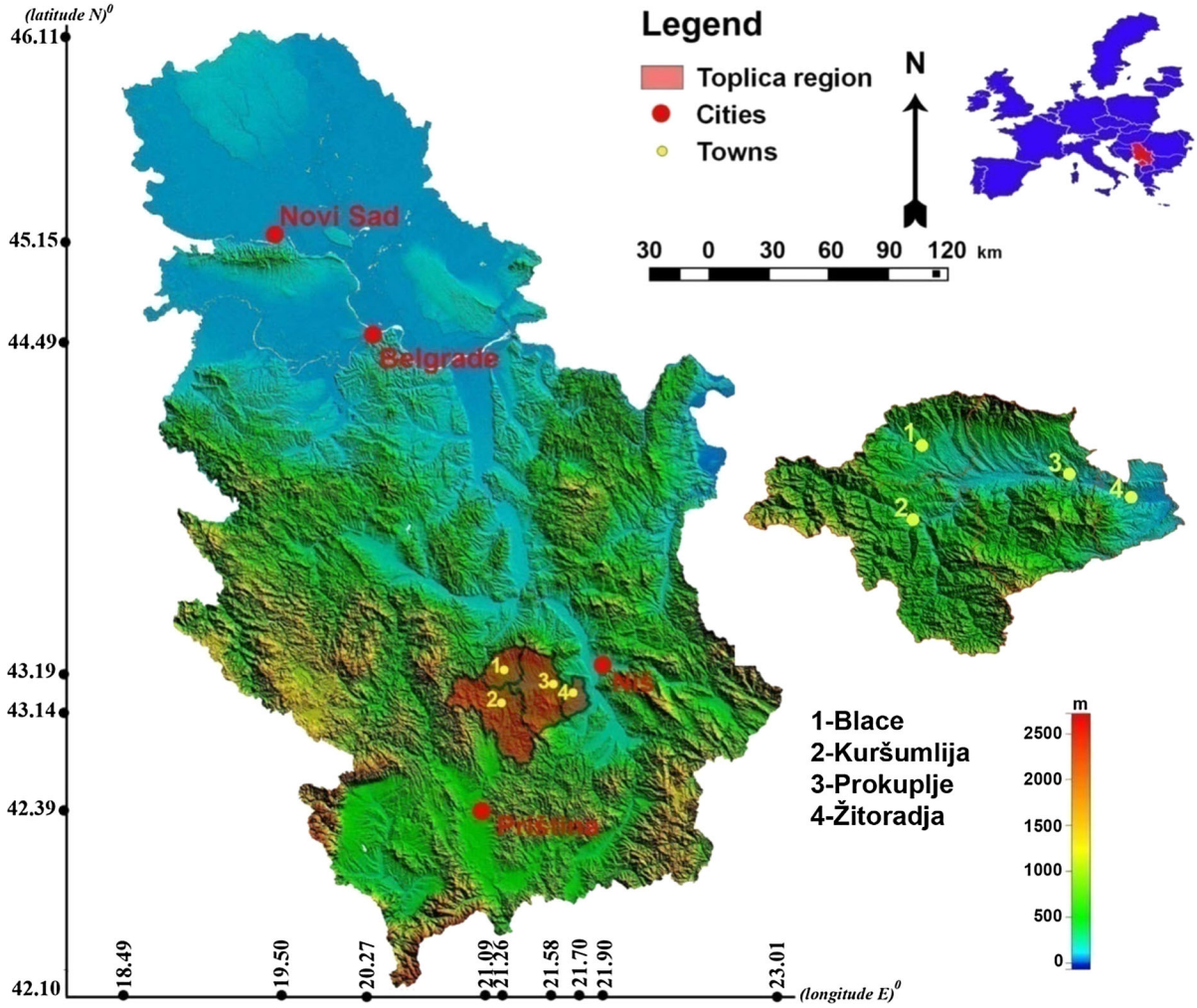

Fig. 1 Map of study area with sampling locations

the distributions of these elements in the natural and polluted soils of this territory are unknown. For this reason, this study was aimed to provide a contribution to a database on the radioactivity and heavy metal status, i.e., natural background of soil as basis for a wide variety of environmental applications as well as an approach to assess the relationship between geochemistry and the health of ecosystems. Also, the information of trace elements in the soil could be of great interest for agriculture (Wilcke et al. 1998) as well as for management and land use planning.

Therefore, this is the first environmental assessment study for Toplica region carried out to find out environmental level of radioactivity and heavy metals in soil and the potential risks to population health for both residents and visitors. External exposure to radiation was evaluated through dose and risk assessments. To assess the potential contamination by heavy metals in the soils enrichment factor (EF), the geoaccumulation index (I_{geo}), pollution index (PI) and pollution load index (PLI) were determined.

Geology

The geological structure of the region consists of magmatic, sedimentary rocks and metamorphic rocks of a different age (from Precambrian to Quaternary). The Rhodopes are considered as the oldest mountains of the Balkan Peninsula and Serbia; they are built of the archaic and Paleozoic crystalline schist, but also

from the metamorphic rocks. Since Rhodopes consist of old solid rocks, they have been only marginally affected by tangential tectonic movements; opposite to them, newly mountain range of Dinaridi (Kopaonik) formed on the west from Rhodopes (Dimitrijevic and Karamata 1966).

The main types of crystalline schists are andesite, fine-grained gneisses, amphibolites, magmatites, leptinoliths, mica schists, quartzite, marble, amphibole schist, pegmatite and mica rocks. Andesite and fine-grained gneisses underlie all other rocks. Green shale and metamorphosed gabbro found on the mountain Jastrebac belong to the Cambrian rocks, while low metamorphosed rocks from Devon period have been discovered in tectonic contacts of crystalline shale, serpentinised peridotite and Senonian sediments (Geological Atlas of Serbia 2002). From the Mesozoic era, the oldest rocks are related to Middle Triassic and widespread northwest of Kursumlija. The rocks formed during the Late Jurassic are positioned in the west of the region in the form of mass or elongated, but discontinuous zones having the direction of the NNW–SSE are presented by basic and ultra basic metamorphites and diabase-chert formation (Dimitrijevic and Karamata 1966). During the Tertiary, today's territory of Toplica region has been affected by intense volcanic activity. The beginning of volcanic activity is related to the upper Oligocene. There are some volcanic rocks on the west on the slopes of Kopaonik mountain. Also, there are three old volcanic calderas: caldera Devil's Town, the Gaitan and Tulare caldera. The largest of them, Devil's Town caldera with a diameter of 25 km belongs to the Toplica region (Jovanović 1972).

Climatic

Atlantic Ocean has a great influence on the climate of the region, western parts of the Toplica region receiving a significantly greater amount of rainfall (649.6 mm) in comparison with eastern parts (571.6 mm). The climate of the region is also affected by the continental air mass and the air mass coming from North Africa, that brings warm and dry weather during the summer. The mean annual air temperature is 11 °C, with a relative humidity of 75%.

Soil sampling and preparation

Systematic random sampling of undisturbed soil in Toplica region was carried out in April 2016. Forty-one samples were taken from municipalities as follows: eight from Prokuplje, nineteen from Kuršumlija, eight from Blace and six from Žitorađa. Global Positioning System (GPS, GARMIN eTrex 30x) was used for determining geographical coordinates; sampling elevations ranged from 222 to 962 m. Soil samples were collected simultaneously for radioactivity and heavy metal analysis, because both are hazardous and toxic elements; most of them are classified as either "known" or "probable" human carcinogens according to United States Environmental Protection Agency (US EPA) and the International Agency for Research on Cancer (IARC). The samples were taken up to 15 cm soil depth applying the template method where each sample was composed from sub-samples taken from 1 m^2 square area with a stainless steel spade according to IAEA recommendations (IAEA 2004). When the stones and rest of vegetation were removed, samples were packed to polyethylene bags and transported to laboratory; all samples were prepared for analysis by air-drying to constant weight, and by homogenizing up to granulation less than 2 mm.

Methods of determining radioactivity and heavy metal in soil

Gamma spectrometry analysis

Gamma spectrometry measurements of samples were taken 40 days after hermetically sealing in Marinelli beakers. Each of prepared soil samples was measured on HPGe detector (GEM30-70, ORTEC) in duration of 6 h. Detector has relative efficiency of 30% and energy resolution of 1.85 keV FWHM for ^{60}Co at 1.33 MeV. Detector calibration was done using a calibration source of a Marinelli mixture by Chech Metrological Institute (type MBSS 2 containing eleven radionuclides: ^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{137}Cs, ^{113}Sn, ^{85}Sr, ^{88}Y, ^{203}Hg and ^{152}Eu). In order to reduce the background, detector was protected by 10 cm lead. After background subtraction, activity concentration of radionuclides was determined considering the area of total absorption line, time of measurement, mass of sample, full energy peak

efficiency and absolute intensity of transition (Gulan et al. 2017). Gamma energy and intensity (yield) values for radionuclides or their progenies used in gamma spectrometry analysis are presented in Table S1. The activities of ^{226}Ra and ^{232}Th were determined as a weighted average activity obtained from gamma-ray lines of their decay products.

Determination of heavy metals content

Total heavy metal concentrations in soil samples were determined by microwave-assisted digestion in accordance with the USEPA Method 3051A using Milestone Ethos 1 microwave sample preparation system. Briefly, 0.5 g of dried and ground soil samples was measured into vessels equipped with controlled pressure relief mechanism. Nine milliliters of concentrated nitric acid and 1 ml of concentrated hydrochloric acid were added subsequently into the vessels. Vessels were sealed and placed in the microwave system. The temperature of the samples was risen to 180 °C in 10 min and remained at 180 °C for 15 min. At the end of the microwave program, the vessels were allowed to cool before being uncapped. After uncapping, samples were filtered and quantitatively transferred in 50-ml flasks and diluted with deionized water.

Analysis was subsequently performed using ICP-OES (Varian Vista Pro-axial). Quality control was periodically carried out with IRMM BCR reference materials CRM-141R and CRM-142R. Recoveries were within ± 10% of the certified values. Wavelengths used for analysis, method detection limits as well as certificated reference materials recoveries are given in Table S2.

All reagents were analytical grade or better, and blank samples were included in each extraction procedure. All calibration standards were prepared in the same acid matrix used for soil samples.

The samples were analyzed for total mercury content using Direct Mercury Analyzer DMA 80 Milestone, which combines techniques of thermal decomposition, catalytic conversion, amalgamation and atomic absorption spectrophotometry (λ = 253.65 nm) in solid soil samples in accordance with US EPA Method 7473. The limit of detection for total mercury content was 0.0033 mg kg^{-1}. Quality control was periodically carried out with IRMM BCR reference materials 143R, and deviations were within ± 5% of the certified values.

GIS analysis

Geographical Information System (GIS) and data modeling in combination with environmental analysis are very powerful tools for calculating and describing some properties of environmental data in an area of interest. GIS software Quantum Geographical Information System (QGIS) and System for Automated Geoscientific Analyses (SAGA), with tools for geospatial calculations (Bíl et al. 2012; Frechtling 1999; Wu and Chen 2016), were used for representing activity concentration of radionuclides and heavy metal contents in analyzed soils. Territory of Toplica region with borders of four municipalities was cropped for future manipulating of vectorized data in GIS. Raster data for heavy metals and radionuclides were georeferenced, and all positions (sampling locations) were digitalized in QGIS. Ordinary kriging method was employed through QGIS and SAGA (GIS) of Spatial Analyst. The priority is given to ordinary kriging and semi-ordinary kriging, since it includes autocorrelation (statistical relationship) between the measured points, although there are a few other methods. Accordingly, the weights are based not only on the distance between the measured points and the prediction of location, but also on their overall spatial arrangement. It also minimizes the variance of the error of estimation.

Radiation dose and risk assessment

Radiation dose assessment

By using A_{Ra}, A_{Th} and A_K, as the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in soil, respectively (hereinafter), and dose coefficients recommended by UNSCEAR (UNSCEAR 2008), the absorbed dose rates $\dot{D}$ (nGy h^{-1}) in the air due to natural radionuclides were computed according to the following formula:

$$\dot{D} = 0.462 \times A_{Ra} + 0.604 \times A_{Th} + 0.0417 \times A_K \quad (1)$$

The calculated values of $\dot{D}$ (nGy h^{-1}) were converted to effective doses D_E (μSv y^{-1}) by multiplying with 0.7 Sv Gy^{-1} (conversion coefficient) and 1750 h (annual time for exposure outdoors) as follows:

$$D_E = 1226 \times \dot{D} \quad (2)$$

The absorbed dose rate due to the presence of artificial radionuclide ^{137}Cs in soil was computed using dose rate per unit of ^{137}Cs activity concentration of 0.03 nGy h^{-1}(Bq kg^{-1})$^{-1}$ (Nenadović et al. 2011).

Since gonads are reproductive organs sensitive to radiation, the calculation of annual gonadal dose equivalent G (μSv y^{-1}) was done using the above-mentioned activity concentrations of radionuclides A_{Ra}, A_{Th}, A_K, according to formula:

$$G = 3.09 \times A_{Ra} + 4.18 \times A_{Th} + 0.314 \times A_K \quad (3)$$

Radiation risk assessment

Using the D_E (μSv) and life expectancy LE (estimated to 70 years), excess lifetime cancer risk ELCR was calculated according to following formula (Taskin et al. 2009):

$$\mathrm{ELCR} = D_E \times \mathrm{LE} \times \mathrm{RF} \quad (4)$$

where RF is fatal cancer risk per Sievert (5.5×10^{-2} Sv^{-1}) for stochastic effects of radiation (ICRP 2007).

Since natural radionuclides are not uniformly distributed in soil environment, radium equivalent activity Ra_{eq} was introduced to represent a weighted sum of A_{Ra}, A_{Th} and A_K. Presuming that activity concentrations of these radionuclides produce the same dose rates, Ra_{eq} was calculated according to the formula (Huy and Luyen 2006) as follows:

$$Ra_{eq} = A_{Ra} + 1.43 \times A_{Th} + 0.077 \times A_K \quad (5)$$

For estimation gamma radiation hazard associated with the natural radionuclide, representative gamma index $I_{\gamma r}$ was used according to the equation:

$$I_{\gamma r} = \frac{A_{Ra}}{150\,\frac{Bq}{kg}} + \frac{A_{Th}}{100\,\frac{Bq}{kg}} + \frac{A_K}{1500\,\frac{Bq}{kg}} \leq 1 \quad (6)$$

A widely used external hazard index H_{ex} is a modified quantity of Ra_{eq} (H_{ex} equal to unity corresponds to Ra_{eq} of 370 Bq kg^{-1}). It is a useful norm for safety standard regulation in radiation protection, and it is calculated by the following equation (Bertka and Mathew 1985; Papastefanou et al. 2005):

$$H_{ex} = \frac{A_{Ra}}{370} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \quad (7)$$

Enrichment and pollution assessment

Enrichment factors (EFs) were estimated to rate the possible anthropogenic contamination caused by heavy metals in soils. EF was determined as the concentration ratio of an examined metal to a reference metal in each sample, divided by the concentration ratio of their background values based on the following equation:

$$\mathrm{EF} = \frac{(C_i/C_{ref})_{sample}}{(B_i/B_{ref})_{background}} \quad (8)$$

where C_i is the measured concentration of the ith heavy metal (mg kg^{-1}), C_{ref} is the measured concentration of reference metal for normalization (mg kg^{-1}), B_i is the background value of European concentrations (mg kg^{-1}), and B_{ref} is background concentration of the reference metal of the soil in the same region (Salminen et al. 2005). Metals such as Al, Fe, Sc, Mn and Ti were commonly used as reference metals (Szolnoki et al. 2013). In this study, Mn was tested as geochemical normalizer, because of its relatively high concentration and stability in the crust (Tasdemir and Kural 2005). To assess the degree of metal pollution, the EF of each element was calculated and classified into 5 contamination categories: EF $<$ 2, minimal enrichment; $2 \leq \mathrm{EF} < 5$, moderate enrichment; $5 \leq \mathrm{EF} < 20$, significant enrichment, $20 \leq \mathrm{EF} < 40$, very high enrichment and EF $\geq$ 40, extremely high enrichment (Sutherland 2000).

The geoaccumulation index (I_{geo}), pollution index (PI) and pollution load index (PLI) were determined to estimate the pollution level of heavy metal. The geoaccumulation index (I_{geo}) was proposed by Muller (1969) to assess the degree of heavy metal contamination in the soils. It was calculated according to the following equation:

$$I_{geo} = \log_2\left[\frac{C_i}{1.5B_i}\right] \quad (9)$$

According to contamination degree, I_{geo} is classified into six classes as follows: $I_{geo} < 0$, practically uncontaminated (Class 0); $0 < I_{geo} < 1$, uncontaminated to moderately contaminated (Class 1); $1 < I_{geo} < 2$, moderately contaminated (Class 2); $2 < I_{geo} < 3$, moderately to heavily contaminated (Class 3); $3 < I_{geo} < 4$, heavily contaminated (Class

4); $4 < I_{geo} < 5$, heavily to extremely contaminated (Class 5); $I_{geo} > 5$, extremely contaminated (Class 6) (Wei and Yang 2010).

The pollution index (PI) was calculated as the ratio of concentration of each metal in the soil sample to the background value. The obtained PI was classified as low ($PI \leq 1$), middle ($1 < PI \leq 3$) and high ($PI > 3$) (Chen et al. 2005).

The pollution load index (PLI) was determined to give an estimation of the pollution level for the entire sampling location.

$$PLI = (PI_1 \times PI_2 \times PI_3 \times \cdots \times PI_n)^{1/n} \quad (10)$$

According to value of the PLI, soils can be classified as unpolluted (< 1), unpolluted to moderately polluted (1–2), moderately polluted (2–3), moderately to highly polluted (3–4), highly polluted (4–5) and very highly polluted (> 5) (Chen et al. 2015).

Health risk assessment of heavy metals

Health risk assessment of heavy metals in soil was used to quantify non-carcinogenic risk to population using the hazard quotient (HQ) and the hazard index (HI). US Environmental Protection Agency (USEPA 2001) developed health risk assessment model used in this study. Human beings are exposed to soil heavy metals through three pathways: ingestion, air inhalation and dermal contact. The average daily doses (ADDs) from these tree main paths are obtained using the following equations:

$$ADD_{ing} = C \times \frac{IngR \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (11)$$

$$ADD_{inh} = C \times \frac{InhR \times EF \times ED}{PEF \times BW \times AT} \quad (12)$$

$$ADD_{dermal} = C \times \frac{SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (13)$$

where ADD_{ing}, ADD_{inh} and ADD_{dermal} are the average daily intake from soil ingestion, inhalation and dermal absorption in mg kg^{-1} day^{-1}; C is the concentration of metal in soil (mg kg^{-1}); IngR and InhR are the ingestion and inhalation rate of soil, respectively (mg day^{-1}, m^3 day^{-1}); EF is the exposure frequency (day $year^{-1}$); ED is exposure duration (year); BW is the body weight of exposed individual (kg); AT is the averaging time (day); PEF is the emission factor (m^3 kg^{-1}); SA is the surface area of the exposed skin (cm^2); AF is the adherence factor (mg cm^{-2} day^{-1}); ABS is the dermal absorption factor (unitless). Data for all these parameters for children (aged 1–17) and adults (aged 18–) are presented in Table S3 (Qing et al. 2015; Haribala et al. 2016).

The calculated average daily doses for each metal and exposure pathway are divided by the reference dose (RfD) to give a non-cancer risk or hazard quotient (HQ). Assessment of the health risk of various exposure pathways was done using the sum of HQs, well known as the hazard index (HI). The HI is calculated as follows:

$$HI = \sum_{i=1}^{n} HQ_i = \sum_{i=1}^{n} \frac{ADD}{RfD_i} \quad (14)$$

where i corresponds to the ith element. The value of $HI < 1$ suggests that harmful health effects are uncertain and the risk increases as HI increases. If $HI > 1$, there is concern for chronic effects.

Results and discussion

Environmental risk assessment of radioactivity

Spatial distributions of radionuclides ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs based on GIS approach are presented in Fig. 2a–d, respectively. According to data in Table S4 and Fig. 2a–b, the uneven, but quite similar spatial distributions of radionuclides ^{226}Ra and ^{232}Th are evident; it confirms their common origin and occurrence in nature. High values of these radionuclides noticed in the north–west parts of Toplica region correspond to the above-mentioned intrusion of volcanic rocks on the slopes of Kopaonik mountain. For this reason, considering the same origin, the spatial distribution of radionuclide ^{40}K is similar to the other natural radionuclides ^{226}Ra and ^{232}Th. The distribution of ^{137}Cs is skewed which is typical for anthropogenic contamination. An explanation of inhomogeneous radiocesium distribution could be different dispersion pattern of ^{137}Cs released after Chernobyl accident. However, according to Fig. 2c–d, the spatial distributions of radionuclides ^{40}K and ^{137}Cs seem to be the opposite, which can be explained by the

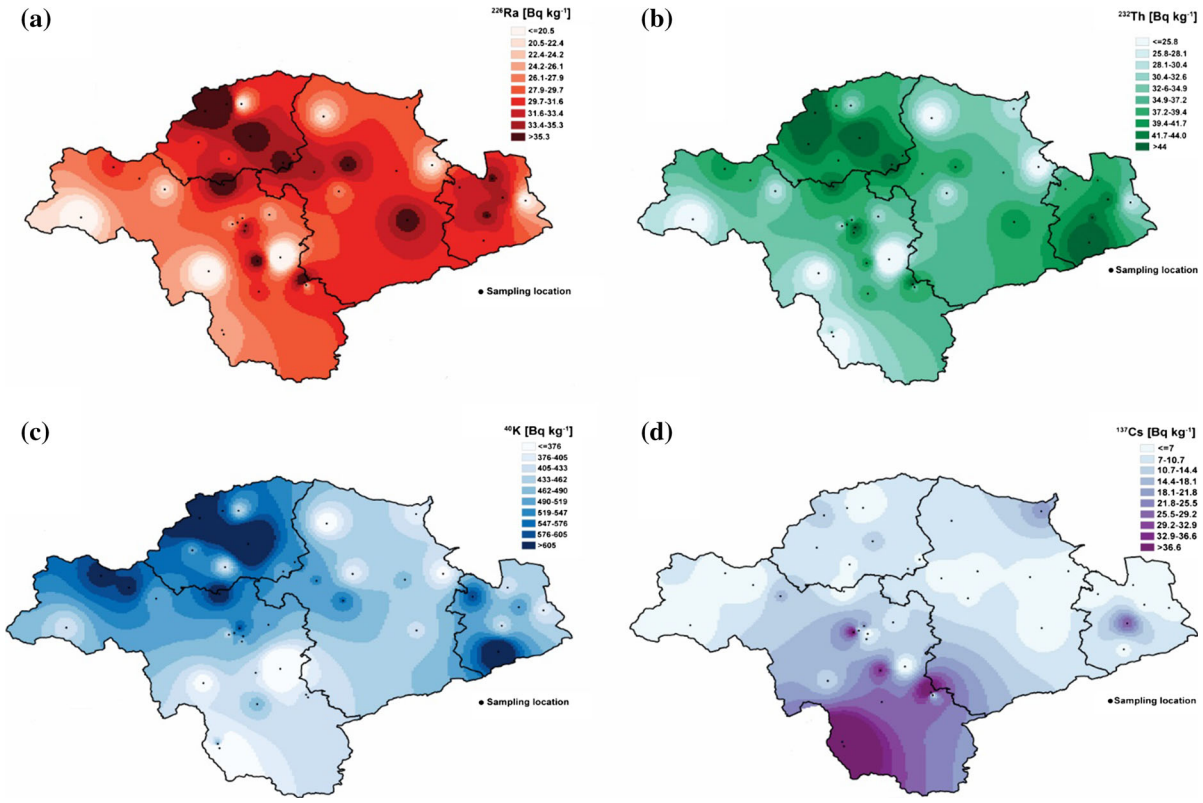

Fig. 2 Spatial distribution of radionuclides ^{226}Ra, ^{232}Th, ^{40}K and ^{137}Cs

slow migration of cesium in potassium-rich soils (Van der Stricht and Kirchmann 2001) and through different soil types (Sohlenius et al. 2013). Besides, obtained low values of ^{137}Cs at higher altitudes could be influenced by enhanced soil erosion (Mitrović et al. 2016); they can be related to the fact that surface soils are subjected to the "wash of" effect (Gulan et al. 2013) and the type of vegetation (Zhiyanski et al. 2008). It could be concluded that the highest values of ^{137}Cs activity concentrations correspond to locations with decomposed plant materials.

Shapiro–Wilk normality test performed using SPSS 20.0 software was found that activity concentrations of ^{226}Ra and ^{232}Th were normally distributed. Descriptive statistics of determined activity concentrations of radionuclides are presented in Table 1. The worldwide average concentrations of radionuclides in soil (UNSCEAR 2008) are given as follows: 32, 45 and 412 Bq kg^{-1} for ^{226}Ra, ^{232}Th and ^{40}K, respectively. The mean values of measured specific activity for ^{226}Ra (29.9 Bq kg^{-1}) and ^{232}Th (36.6 Bq kg^{-1}) are lower than the worldwide average values. There is a great variation (7–1053 Bq kg^{-1}) in the values of specific activities of ^{40}K, and the mean value (492 Bq kg^{-1}) is higher than the worldwide average. The lowest values of radionuclide's activities were measured in the location of Devil's Town; this sample is very interesting, since it was sampled near spring of acidic water (pH = 3.5) (Stevanović 2005). Mean relative ratio ^{226}Ra/^{232}Th, ^{226}Ra/^{40}K and ^{232}Th/^{40}K was 0.82, 0.06 and 0.07, respectively.

It is notable from Table 2 that levels of natural radionuclides are similar to data obtained from studies previously conducted in Serbia, with exception to the higher values of a mountain area, Kopaonik (granodiorite massif). Radionuclide ^{137}Cs is very inhomogeneously distributed all over Serbia due to its anthropogenic origin. Results are comparable with more recent studies conducted in Belgrade (Janković-Mandić et al. 2014) and Stara Planina (Vranješ et al. 2016) confirming the presence of ^{137}Cs in the environment but with a decreasing tendency.

Table 1 Descriptive statistics of radionuclides, doses and radiation risk assessment

	Radioactivity				Dose estimation				Radiation risk assessment			
	^{226}Ra (Bq kg^{-1})	^{232}Th	^{40}K	^{137}Cs	$\dot{D}$ (nGy h^{-1})	D_E (μSv y^{-1})	D_{ECs}	G	ELCR 10^{-4}	Ra_{eq} (Bq kg^{-1})	$I_{\gamma r}$	H_{ex}
Min	3.3	0.9	7.2	0.01	2.4	2.9	0.0	16.2	0.1	5.1	0.04	0.01
Max	48.2	58.9	1053	83.3	99.8	122.4	3.1	712.3	4.7	209.4	1.6	0.6
Median	30.7	38.7	481	6.6	58.5	71.8	0.2	417.4	2.8	124.7	0.9	0.3
Mean	29.9	36.6	492	13.4	56.4	69.2	0.5	399.8	2.7	120.1	0.9	0.3
SD	9.4	11.5	181	18.7	17.1	21.0	0.7	121.9	0.8	36.3	0.3	0.1
Skewness	− 0.44	− 0.69	0.89	2.38	− 0.25	− 0.25	2.38	− 0.21	− 0.25	− 0.34	− 0.24	− 0.34

Descriptive statistics of results are shown in Table 1; the values of $\dot{D}$ varied from 2.4 to 99.8 nGy h^{-1} with a mean value of 56.4 nGy h^{-1}. An average contribution of particular radionuclide to total dose rate amounted to 25.5% (range 17–64%) for ^{226}Ra, 38.7% (range 23–44%) for ^{232}Th and 35.8% (range 13–47%) for ^{40}K.

The mean value of 69.2 μSv y^{-1}for D_E is very close to worldwide average (66 μSv y^{-1}) (UNSCEAR 2008) for external exposure to natural terrestrial radiation.

It was calculated that annual effective dose from ^{137}Cs, D_{ECs} (μSv y^{-1}) varied from 0 to 3.1 μSv y^{-1} (mean 0.5 μSv y^{-1}). Therefore, a contribution to effective dose from ^{137}Cs in soil is negligible in comparison to the same one from natural radionuclides, since it amounted in average 0.8% (a maximum value was 5%).

The values of annual gonadal dose equivalent varied from 16.2 to 712.3 μSv y^{-1}; a mean value was calculated to be 400 μSv y^{-1}. As the organs of interest, UNSCEAR considers the activity of bone marrow and bone surface cells when estimating dose equivalent (UNSCEAR 1988).

The values of ELCR ranged from 0.11 × 10^{-4} to 4.71 × 10^{-4} (Table 1); a mean value of 2.66 × 10^{-4} is slightly higher than the worldwide mean of 2.54 × 10^{-4}.

The maximum calculated value of 209.4 Bq kg^{-1} is lower than the recommended value of 370 Bq kg^{-1} (ICRP 1990).

The calculated mean value of $I_{\gamma r}$ was 0.89, but 13 locations have value over 1.

The radiation hazard is insignificant if H_{ex} is less than one. Since the maximum calculated value was 0.56, the criterion was satisfied.

Environmental risk assessment of heavy metals

As natural constituents of soils, heavy metals concentration varies depending on parental materials. Also, as a consequence of human activities such as distribution of fertilizers, pesticides, industries, waste disposal and air pollution, concentration of heavy metal in soils was increased. Spatial distributions of measured heavy metal concentrations are presented in Fig. 3a–j.

The average value of Cr in Toplica region is comparable to previously measured values in urban areas of Serbia (Gulan et al. 2017; Milenković et al. 2015; Dugalic et al. 2010), and it is higher than that in the industrial area (Table 2). The average values of heavy metals: Cr, Cu, Mn and Zn obtained in this study are in the range of results reported for urban parks in Belgrade (Kuzmanoski et al. 2014) and are comparable with values from other areas in Serbia. Average Mn content in Serbia is higher than in European countries, while elevated Ni occurs in soils formed of ultrabasic or basic rocks (Pavlović et al. 2017) which are mainly located in areas of Western Serbia (Dragović et al. 2008; Dugalic et al. 2010). It can be seen from Table S4 that more than half of sampling locations have Ni concentrations above the maximum allowable concentration (50 mg kg^{-1}). Concentrations of Cu are significantly higher only in the vicinity of cooper smelting plant (Nikolić et al. 2011), and concentrations of Pb and Zn are higher nearby Pb–Zn mine (Gulan et al. 2013). The concentrations of dangerous and harmful elements As, Cd and Hg in Toplica region are below the maximum allowable concentrations (25, 3 and 2 mg kg^{-1}, respectively), but As is slightly higher than those measured in urban area (Crnković et al. 2006; Milenković et al. 2015;

Table 2 Mean values of radioactivity and heavy metals—comparison with other studies in Serbia

Area/town in Serbia	As (mg kg^{-1})	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Hg	^{226}Ra (Bq kg^{-1})	^{232}Th	^{40}K	^{137}Cs	References
Industrial area															
Coal-fired power plant	–	0.2	13.4	32.2	18.2	610	55.9	24.1	79.6	–	–	–	–	–	Ćujić et al. (2017)
Coal-fired power plant	–	–	–	–	–	–	–	–	–	–	31.3	32.8	577	–	Tanić et al. (2016)
Cooper smelting plant	59.08	2.92	–	–	913.33	1070	36.83	86.67	–	0.133	–	–	–	–	Nikolić et al. (2011)
Steel plant	–	2.75	25.5	56.3	31.8	740	80.2	40.6	77.6	–	–	–	–	–	Dragović et al. (2014)
Pb–Zn mine	91.7	5.2	15.9	85.3	93.3	1410	151.9	5080	1258	–	40.6	48	743.2	81	Gulan et al. (2013)
Urban area															
Belgrade	7.2	–	–	32.1	28.3	–	68	55.5	118	–	–	–	–	–	Crnković et al. (2006)
Belgrade	–	–	–	–	–	–	–	–	–	–	33.6	39.3	508	–	Janković-Mandić and Dragović (2010)
Belgrade	–	–	–	–	–	–	–	–	–	–	–	–	–	23	Janković-Mandić et al. (2014)
Priština	79.74	0.61	15.05	101.46	43.25	788.67	113.72	113.03	124.69	–	23.7	35.1	375.4	–	Gulan et al. (2017)
Čačak**	–	–	–	–	–	–	–	–	–	–	26.77	35.06	433.77	42.84	Papić et al. (2014)
Čačak**	10.15	0.24	–	22.92	23.62	–	31.18	26.73	66.65	0.19	–	–	–	–	Papić and Vuković (2015)
Novi Sad**	–	1.63	14.7	3.53	22.3	450	25.1	27.4	110	–	–	–	–	–	Škrbić and Đurišić-Mladenović (2013)
Novi Sad	6.5	–	7.3	28	38.8	368.6	28.7	82.3	100.3	–	–	–	–	–	Mihailović et al. (2015)
Central Serbia	16.05	–	22.62	109.25	28.18	1090.43	80.1	47.14	127.6	–	33.5	50.3	425.8	40.2	Milenković et al. 2015
Western Serbia	138.39	0.65	31.34	108.1	22.72	1144.23	229.41	47.41	64.8	–	33.2	49.1	379	36.4	Dugalic et al. (2010)
Southern Serbia**	3.34	–	7.94	29.9	–	692	11.8	–	43	10.7	27	26	332	99	Popovic et al. (2008)
Mountain area															
Kopaonik	–	–	–	–	–	–	–	–	–	–	80	77	725	76.6	Mitrović et al. (2016)
Zlatibor	–	1.42	–	46.3	8.64	953	320	41.5	21.8	–	27.1*	17.9	142	232	Dragović et al. (2008)
Tara	–	–	–	–	–	–	–	–	–	–	30*	29	233	97.6	Mitrović et al. (2009)
Maljen	–	–	–	–	–	–	–	–	–	–	36*	34	297	161.5	Mitrović et al. (2009)
Stara Planina	–	–	–	–	–	–	–	–	–	–	40	50	461	8.7	Vranješ et al. (2016)
Lowland area															
Vojvodina	–	–	–	–	–	–	–	–	–	–	51*	53	554	–	Bikit et al. (2005)
Banat	1.33	–	–	9.68	47.02	–	7.14	4.48	20.05	–	–	–	–	–	Ninkov et al. (2012)
Toplica region**	17	0.12	19.4	100.3	39.9	735	117.8	47.3	110.7	0.11	29.9	36.6	492	13.4	This study

*Value of ^{238}U; **urban and rural areas

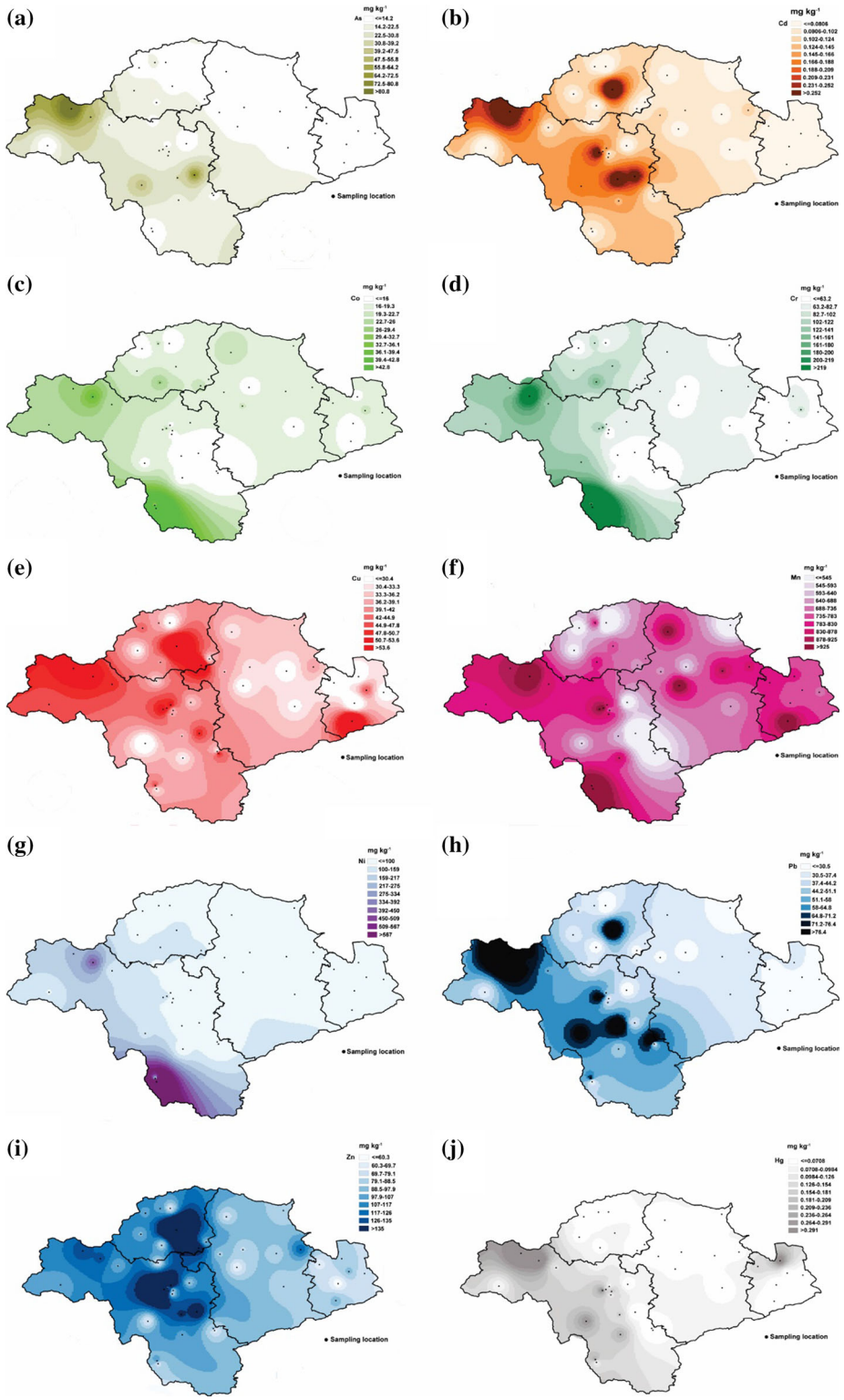

Fig. 3 Spatial distribution of heavy metal concentrations

Papić and Vuković 2015). Three locations on the eastern slopes of the mountain Kopaonik (NW Toplica region, Fig. 1) have elevated values of As which correspond to naturally acidic forest soils (Pavlović et al. 2017). According to the Water Management Plan of the Republic of Serbia, this position is marked for the construction of the storage reservoir "Selova" on the river Toplica (Kostadinov et al. 2008).

Heavy metals enrichment factors calculated relative to background value (Mn was taken as the reference element) are presented in Table 3. The EFs of As, Cd, Co, Cr, Cu, Ni, Pb, Zn and Hg were in the range of 0.16–244.5; 0.04–44.11; 0.19–4.83; 0.42–12.02; 0.71–87.8; 0.35–35.05; 0.50–51.31, 0.43–70.03 and 0.34–5.54, respectively. The mean EF values of Cd, Co and Hg less than 2 indicate that the metal derived completely from natural processes. Metal enrichments were found in the next order: As > Cu > Ni > Pb > Zn > Cr. The values for Cr, Cu, Ni, Pb and Zn showed a moderate enrichment suggesting anthropogenic impact on environment (Zhang and Liu 2002). With the highest mean EF value of 7.3, As showed significant enrichment. According to mean values of EFs, the soils in this study were moderately affected by human activities. The EFs alone cannot precisely identify sources of analyzed heavy metals in soils, but they are useful to speculate on their anthropogenic or lithogenic origin. Reimann and de Caritat (2005) reported that EFs are influenced by a number of factors and contamination is just one of them. On the contrary, I_{geo} and PI were calculated to assess the level of heavy metal pollution.

The calculated values of I_{geo} are shown in Table 3. The range values of I_{geo} for heavy metals were: − 3.33 to 3.68 for As, − 4.2 to 1.11 for Cd, − 3.72 to 3.28 for Co, − 2.62 to 4.72 for Cr, − 0.1 to 2.35 for Cu, − 4.99 to 1.13 for Mn, − 6.48 to 6.27 for Ni, − 1.3 to 3.3 for Pb, − 0.43 to 2.64 for Zn and − 4.35 to 3.12 for Hg. The mean I_{geo} of Cd showed that study soils were practically uncontaminated. Calculated I_{geo} values for As, Co, Mn, Pb, Zn and Hg indicate uncontaminated to moderately contaminated soils, while I_{geo} values for Cd, Cr and Ni indicate moderately contaminated soils.

The mean values of PI are given in Table 3. The ranges of PI values were as follows: As (0.15–19.27), Cd (0.08–3.24), Co (0.11–14.54), Cr (0.24–39.58), Cu (1.40–7.67), Mn (0.05–3.29), Ni (0.02–115.43), Pb (0.61–14.77), Zn (1.11–9.32) and Hg (0.60–6.46). The mean PI value for all investigated elements (except for Cd) was higher than 1 which indicates that the investigated soils are contaminated by heavy metals.

The PLI in all soil samples varied from 0.60 to 6.46 with the average of 2.37. This result indicates that the investigated area was moderately polluted by the heavy metals.

Health risk assessment of heavy metals

The results of the average daily doses via different pathways are listed in Table 3. RfD (mg kg^{-1} day^{-1}) is the maximum daily dose of a metal from a particular exposure pathway for human population during a lifetime, as shown in Table 4.

The results of HQs and HI by the above-mentioned metals in soils for adults and children via different pathways are shown in Table 4. The various exposure pathways of metals for adults and children increased in the order: inhalation < dermal contact < ingestion. The contributions of HQ_{ing} to HI were 97.1 and 84.2% for children and adults proposing that ingestion was main exposure pathway. This result was comparable with other authors (Chabukdhara and Nema 2013; Wei et al. 2015)

The calculated HI values for children and adults decreased in the following order: As > Cr > Pb > Ni > Cu > Hg > Zn > Cd, as shown in Table 4. The total HI values were 0.73 and 0.18 for children and adults, respectively. According to USEPA guidelines, only values greater than 1 indicate that population may experience non-carcinogenic effects (USEPA 2001). Children have a greater tendency than adults because of intense body growth and their behavior.

In the case of non-cancerogenic risk, HI values of As are higher than others but still below 1, and there is no possibility of adverse health effect. Arsenic cancerogenic risk was calculated in the study (Tepanosyan et al. 2017), where it has a defined cancer slope factor.

Correlation analysis

Spearman correlation coefficients between heavy metals and radionuclides are presented in Table S5. The obtained coefficients were performed using SPSS 20.0 software. The presented Spearman matrix has shown various levels of correlation. The coefficient of 0.804 between activity concentrations of ^{226}Ra and ^{232}Th implies strong positive correlation ($p \leq 0.01$).

Table 3 Concentrations, pollution indices and the average daily doses (ADDs) of soil metals for children and adults

Elements	C (mg^{-1} kg^{-1})	Pollution indices			ADD_{ing}		ADD_{inh}		ADD_{der}	
		EF	I_{geo}	*PI*	Child	Adult	Child	Adult	Child	Adult
As										
Mean	17	7.30	0.33	2.83	1.08E−04	2.32E−05	6.06E−09	3.42E−09	1.86E−07	2.49E−07
Min	0.89	0.16	− 3.33	0.15	5.71E−06	1.22E−06	3.19E−10	1.80E−10	9.82E−09	1.31E−08
Max	115.6	244.48	3.68	19.27	7.39E−04	1.58E−04	4.13E−08	2.33E−08	1.27E−06	1.70E−06
Cd										
Mean	0.12	1.49	− 1.33	0.83	7.66E−07	1.64E−07	4.28E−11	2.41E−11	1.32E−09	1.76E−09
Min	0.01	0.04	− 4.20	0.08	7.54E−08	1.62E−08	4.22E−12	2.38E−12	1.30E−10	1.73E−10
Max	0.47	44.11	1.11	3.24	3.01E−06	6.45E−07	1.68E−10	9.48E−11	5.17E−09	6.90E−09
Co										
Mean	19.4	1.52	0.60	2.77	1.24E−04	2.66E−05	6.93E−09	3.91E−09	2.13E−07	2.85E−07
Min	0.8	0.19	− 3.72	0.11	5.09E−06	1.09E−06	2.84E−10	1.60E−10	8.75E−09	1.17E−08
Max	101.8	4.83	3.28	14.54	6.51E−04	1.39E−04	3.64E−08	2.05E−08	1.12E−06	1.49E−06
Cr										
Mean	100.3	2.19	1.10	4.56	6.41E−04	1.37E−04	3.58E−08	2.02E−08	1.10E−06	1.47E−06
Min	5.4	0.42	− 2.62	0.24	3.44E−05	7.37E−06	1.92E−09	1.08E−09	5.92E−08	7.89E−08
Max	870.7	12.02	4.72	39.58	5.57E−03	1.19E−03	3.11E−07	1.75E−07	9.57E−06	1.28E−05
Cu										
Mean	39.9	3.94	1.05	3.33	2.55E−04	5.47E−05	1.43E−08	8.04E−09	4.39E−07	5.86E−07
Min	16.8	0.71	− 0.10	1.40	1.08E−04	2.31E−05	6.02E−09	3.39E−09	1.85E−07	2.47E−07
Max	92	87.80	2.35	7.67	5.88E−04	1.26E−04	3.29E−08	1.85E−08	1.01E−06	1.35E−06
Mn										
Mean	735		0.17	1.92	4.70E−03	1.01E−03	2.63E−07	1.48E−07	8.08E−06	1.08E−05
Min	18		− 4.99	0.05	1.16E−04	2.48E−05	6.46E−09	3.64E−09	1.99E−07	2.65E−07
Max	1258		1.13	3.29	8.04E−03	1.72E−03	4.49E−07	2.53E−07	1.38E−05	1.85E−05
Ni										
Mean	117.8	3.70	1.47	8.42	7.53E−04	1.61E−04	4.21E−08	2.37E−08	1.30E−06	1.73E−06
Min	0.23	0.35	− 6.48	0.02	1.50E−06	3.22E−07	8.38E−11	4.73E−11	2.58E−09	3.44E−09
Max	1616	35.05	6.27	115.43	1.03E−02	2.21E−03	5.77E−07	3.26E−07	1.78E−05	2.37E−05
Pb										
Mean	47.3	3.07	0.73	3.15	3.02E−04	6.48E−05	1.69E−08	9.52E−09	5.20E−07	6.93E−07
Min	9.2	0.50	−1.30	0.61	5.86E−05	1.26E−05	3.27E−09	1.85E−09	1.01E−07	1.34E−07
Max	221.5	51.31	3.30	14.77	1.42E−03	3.03E−04	7.91E−08	4.46E−08	2.44E−06	3.25E−06
Zn										
Mean	110.7	2.96	0.44	2.31	7.08E−04	1.52E−04	3.96E−08	2.23E−08	1.22E−06	1.62E−06
Min	53.5	0.43	− 0.43	1.11	3.42E−04	7.33E−05	1.91E−08	1.08E−08	5.88E−07	7.85E−07
Max	447.3	70.03	2.64	9.32	2.86E−03	6.13E−04	1.60E−07	9.01E−08	4.92E−06	6.56E−06
Hg										
Mean	0.11	1.47	0.27	2.91	6.88E−07	1.48E−07	3.85E−11	2.17E−11	1.18E−09	1.58E−09
Min	0.003	0.34	− 4.35	0.07	1.74E−08	3.73E−09	9.72E−13	5.48E−13	2.99E−11	3.99E−11
Max	0.48	5.54	3.12	13.04	3.08E−06	6.61E−07	1.72E−10	9.72E−11	5.30E−09	7.08E−09

Table 4 Chronic (non-carcinogenic) reference dose (RfD) and health risks of heavy metals in soils

Metals	RfD_{ing}	RfD_{inh}	RfD_{der}	HQ_{ing}		HQ_{inh}		HQ_{der}		HI	
	(mg kg^{-1} day^{-1})			Child	Adult	Child	Adult	Child	Adult	Child	Adult
As	3.00E−04	3.01E−04	1.23E−04	3.61E−01	7.74E−02	2.02E−05	1.14E−05	1.52E−03	2.02E−03	3.63E−01	7.95E−02
Cd	1.00E−03	2.86E−05	1.00E−05	7.66E−04	1.64E−04	1.50E−06	8.43E−07	1.32E−04	1.76E−04	8.99E−04	3.41E−04
Cr	3.00E−03	3.00E−03	6.00E−05	2.14E−01	4.58E−02	1.19E−05	6.73E−06	1.84E−02	2.45E−02	2.32E−01	7.03E−02
Cu	4.00E−02	4.02E−02	1.20E−02	6.38E−03	1.37E−03	3.57E−07	2.01E−07	3.66E−05	4.88E−05	6.42E−03	1.42E−03
Ni	2.00E−02	2.06E−02	5.40E−03	3.77E−02	8.07E−03	2.10E−06	1.19E−06	2.40E−04	3.20E−04	3.79E−02	8.39E−03
Pb	3.50E−03	3.52E−03	5.25E−04	8.63E−02	1.85E−02	4.82E−06	2.72E−06	9.90E−04	1.32E−03	8.73E−02	1.98E−02
Zn	3.00E−01	3.00E−01	6.00E−02	2.36E−03	5.06E−04	1.32E−07	7.44E−08	2.03E−05	2.71E−05	2.38E−03	5.33E−04
Hg	3.00E−04	8.57E−05	2.10E−05	2.29E−03	4.92E−04	4.49E−07	2.53E−07	5.64E−05	7.52E−05	2.35E−03	5.67E−04

This result is in agreement with our previously published results (Gulan et al. 2017; Milenkovic et al. 2015). Due to the fact that ^{226}Ra and ^{232}Th have similar behavior throughout their transport, this was expected (Chandrasekaran et al. 2015).

There are strong positive correlations at the 0.01 significance level among pairs of As–Cd, As–Pb, Cd–Pb, Cd–Zn, Cu–Zn, Cr–Ni; Co is also strong positive correlated with Cr, Mn and Ni; as well as Pb with Zn and Hg (Table S5). This indicates their geogenic association and geochemical affinities in soils.

Conclusion

This study was performed to assess environmental risk of radioactivity and heavy metals. The activity concentrations of ^{226}Ra, ^{232}Th, ^{40}K,^{137}Cs and the concentrations of metals (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn and Hg) in soil samples from Toplica region were obtained using HPGe gamma-ray spectrometry and ICP-OES analysis technique, respectively.

The mean values of measured specific activity for ^{226}Ra (29.9 Bq kg^{-1}) and ^{232}Th (36.6 Bq kg^{-1}) are lower than the worldwide average values. There is a great variation (7–1053 Bq kg^{-1}) in the values of specific activities of ^{40}K, and the mean value of 492 Bq kg^{-1} is higher than the worldwide average. Dose assessment and radiological risk assessment indicate that there is no significant risk for population of Toplica region.

The calculated enrichment factors (EFs) showed moderate metal enrichment in the following order: As > Cu > Ni > Pb > Zn > Cr. With the highest EF value of 7.3, As showed a significant enrichment. According to mean values of EFs, the soils in this study were moderately affected by human activities.

The pollution load index (PLI) was determined to give an estimation of the pollution level for the entire sampling location. The PLI in all soil samples varied from 0.60 to 6.46 with the average of 2.37. This result indicates that the investigated area was moderately polluted by the heavy metals.

The health risk assessment of heavy metals in soil was used to quantify non-carcinogenic risk to population using the hazard quotient (HQ) and the hazard index (HI). The total HI values were 0.73 and 0.18 for children and adults, respectively. According to USEPA guidelines, only values greater than 1 indicate

that population may experience non-carcinogenic effects. The various exposure pathways of metals for adults and children increased in the order: inhalation < dermal contact < ingestion.

Correlations between heavy metals and radionuclides were calculated by Spearman correlation coefficient. Strong positive correlation between radionuclides ^{226}Ra and ^{232}Th was observed.

This study presents the baseline information on the natural and artificial radioactivity and heavy metal contents in the investigated area. Toplica region is well known for its thermal spas. The obtained data not only can be used as a reference data for pollution monitoring but also can serve as a reference for further investigations of radon in spas and estimation of dose from inhalation. The study also provides a base for the local authority for further long-term monitoring of any anthropogenic contamination of either radioactivity or heavy metals.

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