

1 **ENVIROMENTAL RISK ASSESSMENT FROM RADIOACTIVITY AND HEAVY**
2 **METALS IN SOIL OF TOPLICA REGION, SOUTH SERBIA**

3 Vladica Stevanović^a, Ljiljana Gulan^a, Biljana Milenković^{b,1}, Aleksandar Valjarević^a, Tijana
4 Zeremski^c, Ivana Penjišević^a

5 *^aFaculty of Natural Science and Mathematics, University of Priština, Lole Ribara 29,*
6 *38220KosovskaMitrovica, Serbia*

7 *^bFaculty of Science, University of Kragujevac, Radoja Domanovića 12, 34000 Kragujevac, Serbia*

8 *^cInstitute of Field & Vegetable Crops, Maksima Gorkog 30, 21000 Novi Sad, Serbia*

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¹**Corresponding author:** Biljana Milenkovic
Tel:+381 34336223; fax: +381 34335040
E-mail address: bmilenkovic@kg.ac.rs (B. Milenkovic)

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14 **ABSTRACT**

15 Activity levels of natural and artificial radionuclides and content of ten heavy metals (As, Cd, Co, Cr, Cu, Mn, Ni,
16 Pb, Zn and Hg) were investigated in 41 soil samples collected from Toplica region located in the south part of
17 Serbia. Radioactivity was determined by gamma spectrometry using HPGe detector. The obtained mean activity
18 concentrations \pm standard deviations of radionuclides ^{226}Ra , ^{232}Th , ^{40}K and ^{137}Cs were 29.9 ± 9.4 , 36.6 ± 11.5 ,
19 492 ± 181 and $13.4\pm 18.7\text{Bq kg}^{-1}$, respectively. According to Shapiro-Wilk normality test, activity concentrations of
20 ^{226}Ra and ^{232}Th were consistent with normal distribution. External exposure from radioactivity was estimated
21 through dose and radiation risk assessments. Concentrations of heavy metals were measured by using ICP-OES and
22 their health risks were then determined. Enrichment by heavy metals and pollution level in soils were evaluated
23 using the enrichment factor (EF), the geoaccumulation index (I_{geo}), pollution index (PI) and pollution load index
24 (PLI). Based on GIS approach the spatial distribution maps of radionuclides and heavy metal contents were
25 made. Spearman correlation coefficient was used for correlation analysis between radionuclide activity
26 concentrations and heavy metal contents.

27 **Keywords:** radionuclides, heavy metals, spatial distribution, environmental risk, GIS

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29 **1. Introduction**

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31 Permanent background radiation arises from natural (terrestrial and cosmic) and anthropogenic sources (UNSCEAR
32 2008). Main contributors to natural radiation are terrestrial radionuclide ^{40}K and radionuclides of the ^{238}U and ^{232}Th
33 series. The external exposure of population due to background radiation mainly coming up from soil. Since they
34 originated from various geological formations, knowledge about levels and spatial distribution of these
35 radionuclides is substantially for possible risk assessment to gamma ray exposure. As well, fission product ^{137}Cs is
36 very important anthropogenic radionuclide, which allows inclusion in geo-bio-chemical environmental cycles, since
37 it's half-life is relatively long (30.2 y). Therefore, for useful information of background radiation in an area is
38 necessary to investigate and follow up environment radioactivity.

39 The term heavy metal is often refers to the group of elements that have been associated with contamination,
40 toxicity and pollution. Similarly as radionuclides, heavy metals are natural or anthropogenic origin. The main
41 natural sources come from geological degradation, i.e. rock weathering and from thermal springs. Recent surveys
42 confirmed that the anthropogenic sources cause pollution effects through the various inputs: mining, metallurgical,
43 chemical and heavy industries (including their waste discharges) (Alijagić and Šajn 2011; Liang et al. 2017;
44 Ogundele et al.2017; Pandey et al. 2014; Serbula et al. 2017; Stafilov et al. 2010;Yaylah-Abanuz 2011), vehicle
45 emissions (Hu et al. 2013; Li et al. 2001; Ordóñez et al.2015; Shi et al. 2008; Wei et al. 2015) and agronomic
46 practices, such as organic and mineral fertilization, application of pesticides, etc.(Barać et al. 2016a; Esmaeili et al.
47 2014; Montagne et al. 2007; Nziguheba and Smolders 2007; Rodríguez et al.2008).

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

52 Recent studies gave some data about environmental state of Serbia, but in various field of interest pointing out
53 various sources of contamination and pollution of certain areas (Borgna et al. 2009; Barać et al. 2016b; Čujić et al.
54 2017; Dragović et al. 2014; Gulan et al. 2013; Milenković et al. 2015; Momčilović et al. 2010; Serbula et al. 2014;
55 Tanić et al. 2014, 2016).The earlier two studies in Southern Serbia were related to some other contaminated areas
56 and they dealt with specific problems such as evaluation of the radioactivity and heavy metals in mining sites
57 (Todorovic et al. 2012; Popovic et al. 2008).

58 Natural background radiation and radioactive emissions from nuclear facilities (Chernobyl, Fukushima) are the
59 matter of public concern. Cancer risk from low doses of ionizing radiation is still the focus of a long-standing
60 controversy in radiation protection (Körblein and Hoffmann 2006).The interest of the population about background
61 radiation levels and the potential implications on health startedwith the increasing risk of cancer incidence and
62 mortality in Serbia over the past years (Dimitrova et al. 2017; Durakovic 2001; Jia et al. 2005; Mihajlović et al.
63 2013; Slijepcevic et al. 2016).

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65 **2. Materials and methods**

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67 2.1 Study area

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69 A study area covers Toplica region, situated between 42°52'–43°24' N and 20°56'–21°50' E in the South Serbia
70 (Fig.1). According to the administrative regionalization Toplica region comprises four municipalities: Prokuplje,
71 Kuršumlija, Blace and Žitoradja, where live 90.600 inhabitants, according to data from the 2011 census. Toplica
72 region occupies an area of 3055 km² (Maćejka 1999); it is limited by the river South Morava on the East, and by
73 Mount Kopaonik on the West. Northern border of region formed mountains Veliki and Mali Jastrebac, while the
74 southern boundary follows the highest parts of the mountains: Radan, Vidojevica and Pasjača. Average altitude of
75 Toplica is 482 m, and percent of agricultural land is 10.9% according to data from 2012 (Valjarević et al. 2014).

76 Toplica region is very attractive in order to develop tourism, since three famous spas (Lukovska banja,
77 Kuršumlijska banja and Prolom banja) belong to this region. Especially affirmation of tourism is Devil's Town,
78 unique tall stones formation, which was nominated for "New seven wonders of nature" (Valjarević et al. 2015).
79 Secondly, it is necessary to mention that growing interest of scientists, inhabitants and visitors attract archaeological
80 excavations from the Neolithic period which are still ongoing. The first archaeological investigation in this area
81 started in 1927 (Kuzmanović 2006). Toplica region is also important fruit growing and agricultural area in Serbia.

82 All abovementioned studies conducted in Serbia consider the environmental levels of radionuclides and various
83 heavy metals in order to outline areas of potential toxicity. Nevertheless, such studies have not been conducted so
84 far in Toplica region and therefore, the distributions of these elements in the natural and polluted soils of this
85 territory are unknown. For this reason, this study was aimed to provide a contribution to a data-base on the
86 radioactivity and heavy metal status, i.e. natural background of soil as basis for a wide variety of environmental
87 applications as well as an approach to assess the relationship between geochemistry and the health of ecosystems.
88 Also, the information of trace elements in the soil could be of great interest for agriculture (Wilcke et al. 1998) as
89 well as for management and land use planning.

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

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96 2.1.1 Geology

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98 The geological structure of the region consists of magmatic, sedimentary rocks, and metamorphic rocks of a
99 different age (from Precambrian to Quaternary). The Rhodopes are considered as the oldest mountains of the Balkan
100 Peninsula and Serbia; they are built of the archaic and Paleozoic crystalline schist, but also from the metamorphic
101 rocks. Since Rhodopes consist of old solid rocks, they have been only marginally affected by tangential tectonic
102 movements; opposite to them, newly mountain range of Dinaridi (Kopaonik) formed on the west from Rhodopes
103 (Dimitrijevic and Karamata 1966).

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

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118 2.1.2 Climatic

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120 Atlantic Ocean has a great influence on the climate of the region; western parts of the Toplica region receiving a
121 significantly greater amount of rainfall (649.6 mm) in comparison to eastern parts (571.6 mm). The climate of the

122 region is also affected by continental and air mass from North Africa, bringing a warm and dry weather during the
123 summer. The mean annual air temperature is 11 °C, with a relative humidity of 75%.

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125 2.2 Soil sampling and preparation

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127 Systematic random sampling of undisturbed soil in Toplica region was carried out in April 2016. Forty-one samples
128 were taken from municipalities as follows: eight from Prokuplje, nineteen from Kuršumlija, eight from Blace and
129 six from Žitorađa. Global Positioning System (GPS, GARMIN eTrex 30x) was used for determining geographical
130 coordinates; sampling elevations ranged from 222–962 m. Soil samples were collected simultaneously for
131 radioactivity and heavy metal analysis, because both are hazardous and toxic elements; most of them are classified
132 as either “known” or “probable” human carcinogens according to United States Environmental Protection Agency
133 (U.S. EPA) and the International Agency for Research on Cancer (IARC). The samples were taken up to 15 cm soil
134 depth applying the template method where each sample was composed from sub-samples taken from 1 m² square area
135 with a stainless steel spade according to IAEA recommendations (IAEA 2004). When the stones and rest of
136 vegetation were removed, samples were packed to polyethylene bags and transported to laboratory; all samples were
137 prepared for analysis by air-drying to constant weight, and by homogenizing up to granulation less than 2mm.

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139 2.3 Methods of determination radioactivity and heavy metal in soil

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141 2.3.1 Gamma spectrometry analysis

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143 Gamma spectrometry measurements of samples were performed 40 days after hermetically sealing in Marinelli
144 beakers. Each of prepared soil samples were measured on HPGe detector (GEM30-70, ORTEC) in duration of
145 6h. Detector has relative efficiency of 30% and energy resolution of 1.85 keV FWHM for ⁶⁰Co at 1.33 MeV.
146 Detector calibration was done using a calibration source of a Marinelli mixture by Czech Metrological Institute
147 (type MBSS 2 containing eleven radionuclides: ²⁴¹Am, ¹⁰⁹Cd, ¹³⁹Ce, ⁵⁷Co, ⁶⁰Co, ¹³⁷Cs, ¹¹³Sn, ⁸⁵Sr, ⁸⁸Y, ²⁰³Hg and
148 ¹⁵²Eu). In order to reduce the background, detector was protected by 10 cm lead. After background subtraction,
149 activity concentration of radionuclides was determined considering the area of total absorption line, time of

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

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155 2.3.2 Determination of heavy metals content

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157 Total heavy metal concentrations in soil samples was determined by microwave assisted digestion in accordance to
158 the USEPA Method 3051A using Milestone Ethos 1 microwave sample preparation system. Briefly, 0.5 g of dried
159 and ground soil samples were measured into vessels equipped with controlled pressure relief mechanism. 9 ml of
160 concentrated nitric acid and 1 ml of concentrated hydrochloric acid were added subsequently into the vessels.
161 Vessels were sealed and placed in the microwave system. The temperature of the samples was risen to 180 °C in 10
162 minutes and remained at 180°C for 15 minutes. At the end of the microwave program, the vessels were allowed to
163 cool before being uncapped. After uncapping, samples were filtered and quantitatively transferred in 50 ml flasks
164 and diluted with deionized water.

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

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

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

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177 2.3.3 GIS analysis

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GIS (Geographical Information System) and modeling of data is a very powerful tool for calculating and describing some properties of environmental data in an area. GIS software QGIS (Quantum Geographical Information System) and SAGA (System for Automated Geoscientific Analyses), with tools for geo-spatial calculations (Bil 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 geo-referenced 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.

2.4 Radiation dose and risk assessment

2.4.1 Radiation dose assessment

By using the 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 the following formula:

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

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:

$$D_E = 1.226 \cdot \dot{D} \quad (2)$$

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

208 Since gonads are reproductive organs sensitive to radiation, the calculation of annual gonadal dose equivalent G
209 ($\mu\text{Sv y}^{-1}$) was done using abovementioned activity concentrations of radionuclides A_{Ra}, A_{Th}, A_K , according to
210 formula:

$$211 \quad G = 3.09 \cdot A_{Ra} + 4.18 \cdot A_{Th} + 0.314 \cdot A_K \quad (3)$$

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213 2.4.2 Radiation risk assessment

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

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$$218 \quad ELCR = D_E \cdot LE \cdot RF \quad (4)$$

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220 where fatal cancer risk per Sievert, RF amounts $5.5 \cdot 10^{-2} \text{ Sv}^{-1}$ for stochastic effects of radiation to the whole
221 population (ICRP 2007).

222 Since natural radionuclides are not uniformly distributed in soil environment, radium equivalent activity Ra_{eq}
223 was introduced to represents a weighted sum of A_{Ra}, A_{Th} and A_K . Presuming that activity concentrations of these
224 radionuclides produce the same dose rates, Ra_{eq} was calculated according to formula (Huy and Luyen 2008):

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$$226 \quad Ra_{eq} = A_{Ra} + 1.43 \cdot A_{Th} + 0.077 \cdot A_K \quad (5)$$

227 For estimation gamma radiation hazard associated with the natural radionuclide, representative gamma index
228 $I_{\gamma r}$ was used according to equation:

$$229 \quad I_{\gamma r} = \frac{A_{Ra}}{150 \frac{\text{Bq}}{\text{kg}}} + \frac{A_{Th}}{100 \frac{\text{Bq}}{\text{kg}}} + \frac{A_K}{1500 \frac{\text{Bq}}{\text{kg}}} \leq 1 \quad (6)$$

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

233
$$H_{ex} = \frac{A_{Ra}}{370} + \frac{A_{Th}}{259} + \frac{A_K}{4810} \quad (7)$$

234

235 **2.5 Enrichment and pollution assessment**

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

240
$$EF = \frac{(C_i/C_{ref})_{sample}}{(B_i/B_{ref})_{background}} \quad (8)$$

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

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

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

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

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

260 The pollution index (PI) was calculated as the ratio of concentration of each metal in the soil sample to the
261 background value. The obtained PI was classified as low ($PI \leq 1$), middle ($1 < PI \leq 3$) or high ($PI > 3$) (Chen et al.
262 2005).

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

$$265 \quad PLI = (PI_1 \times PI_2 \times PI_3 \times \dots \times PI_n)^{1/n} \quad (10)$$

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

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270 2.6 Health risk assessment from heavy metals

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

$$277 \quad ADD_{ing} = C \times \frac{IngR \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (11)$$

$$278 \quad ADD_{in} = C \times \frac{InhR \times EF \times ED}{PEF \times BW \times AT} \quad (12)$$

$$279 \quad ADD_{dermal} = C \times \frac{SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (13)$$

280 where ADD_{ing} , ADD_{in} and ADD_{dermal} are the average daily intake from soil ingestion, inhalation and dermal
281 absorption in $mg \text{ kg}^{-1} \text{ day}^{-1}$; C is the concentration of metal in soil ($mg \text{ kg}^{-1}$); $IngR$ and $InhR$ are the ingestion and
282 inhalation rate of soil, respectively ($mg \text{ day}^{-1}$, $m^3 \text{ day}^{-1}$); EF is the exposure frequency (day year^{-1}); ED is exposure

283 duration (year); BW is the body weight of exposed individual (kg); AT is the averaging time (day); PEF is the
284 emission factor ($\text{m}^3 \text{kg}^{-1}$); SA is the surface area of the exposed skin (cm^2); AF is the adherence factor ($\text{mg cm}^{-2} \text{day}^{-1}$);
285 ABS is the dermal absorption factor (unitless). Data for all these parameters for children (aged 1–17) and adults
286 (aged 18–) are presented in Table S3 (Qing et al. 2015; Haribala et al. 2016).

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

$$290 \quad HI = \sum_{i=1}^n HQ_i = \sum_{i=1}^n \frac{ADD}{RfD_i} \quad (14)$$

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

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294 **3. Results and discussion**

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296 **3.1 Environmental risk assessment of radioactivity**

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298 Spatial distributions of radionuclides ^{226}Ra , ^{232}Th , ^{40}K and ^{137}Cs based on GIS approach are presented in Fig. 2a-
299 d, respectively. According to data in Table S4 and Figures 2a-b, the uneven, but quite similar spatial distributions of
300 radionuclides ^{226}Ra and ^{232}Th is evident; it confirms their common origin and occurrence in nature. High values of
301 these radionuclides noticed in the North-West parts of Toplica region, correspond to above-mentioned intrusion of
302 volcanic rocks on the slopes of Kopaonik mountain. For this reason, considering the same origin, the spatial
303 distribution of radionuclide ^{40}K is similar to the other natural radionuclides ^{226}Ra and ^{232}Th . The distribution of ^{137}Cs
304 is skewed which is typical for anthropogenic contamination. An explanation of inhomogeneous radionuclide
305 distribution could be different dispersion pattern of ^{137}Cs released after Chernobyl accident. However, according to
306 Figures 2c-d, the spatial distributions of radionuclides ^{40}K and ^{137}Cs seem to be the opposite, which can be explained
307 by the slow migration of caesium in potassium-rich soils (Van der Stricht and Kirchmann 2001) and through
308 different soil types (Sohlenius et al. 2013). Besides, obtained low values of ^{137}Cs at higher altitudes could be
309 influenced by enhanced soil erosion (Mitrović et al. 2016); they can be related to the fact that surface soils are

310 subjected to the “wash of” effect (Gulan et al. 2013) and the type of vegetation (Zhiyanski et al. 2008). It could be
311 concluded that the highest values of ^{137}Cs activity concentrations correspond to locations with decomposed plant
312 materials.

313 Shapiro-Wilk’s normality test performed using SPSS 20.0 software was found that activity concentrations of
314 ^{226}Ra and ^{232}Th were normally distributed. Descriptive statistics of determined activity concentrations of
315 radionuclides are presented in Table 1. The worldwide average concentrations of radionuclides in soil (UNSCEAR
316 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
317 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
318 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
319 Bq kg⁻¹) is higher than the worldwide average. The lowest values of radionuclide’s activities were measured in
320 location of Devil's Town; this sample is very interesting, since it was sampled near spring of acidic water (pH=3.5)
321 (Stevanović 2005). Mean relative ratio $^{226}\text{Ra}/^{232}\text{Th}$, $^{226}\text{Ra}/^{40}\text{K}$ and $^{232}\text{Th}/^{40}\text{K}$ was 0.82, 0.06 and 0.07, respectively.

322 It is notable from Table 4 that levels of natural radionuclides are similar to data obtained from studies previously
323 conducted in Serbia, with exception to the higher values of a mountain area, Kopaonik (granodiorite massif).
324 Radionuclide ^{137}Cs is very inhomogeneously distributed all over Serbia due to its anthropogenic origin. Results are
325 comparable with more recent studies conducted in Belgrade (Janković-Mandić et al. 2014) and Stara Planina
326 (Vranjes et al. 2016) confirming presence of ^{137}Cs in the environment but with decreasing tendency.

327 Descriptive statistics of results were shown in Table 1; the values of \dot{D} varied from 2.4–99.8 nGy h⁻¹ with a mean
328 value of 56.4 nGy h⁻¹. An average contribution of particular radionuclide to total dose rate amounted 25.5% (range
329 17–64%) for ^{226}Ra , 38.7% (range 23–44%) for ^{232}Th and 35.8% (range 13–47%) for ^{40}K .

330 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
331 external exposure to natural terrestrial radiation.

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

335 The values of annual gonadal dose equivalent varied from 16.2–712.3 μSv y⁻¹; a mean value was calculated to be
336 400 μSv y⁻¹. As the organs of interest, UNSCEAR consider the activity of bone marrow and bone surface cells when
337 estimating dose equivalent (UNSCEAR 1988).

338 The values of *ELCR* ranged from $0.11 \cdot 10^{-4}$ – $4.71 \cdot 10^{-4}$ (Table 1); a mean value of $2.66 \cdot 10^{-4}$ is slightly higher than
339 worldwide mean of $2.54 \cdot 10^{-4}$.

340 The maximum calculated value of 209.4 Bq kg^{-1} is lower than the recommended value of 370 Bq kg^{-1} (ICRP
341 1990).

342 The calculated mean value of I_{yr} was 0.89, but 13 locations have value over 1.

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

345

346 3.2 Environmental risk assessment from heavy metals

347

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

352 The average value of Cr in Toplica region is comparable to previously measured values in urban areas of Serbia
353 (Gulan et al. 2017; Milenković et al. 2015; Dugalic et al., 2010), and it is higher than that in the industrial area (Table
354 4). The average values of heavy metals: Cr, Cu, Mn and Zn obtained in this study are in the range of results reported
355 for urban parks in Belgrade (Kuzmanoski et al. 2014) and are comparable with values from other areas in Serbia.
356 Average Mn content in Serbia is higher than in European countries, while elevated Ni occurs in soils formed of
357 ultrabasic or basic rocks (Pavlović et al. 2017) which are mainly located in areas of Western Serbia (Dragović et al.
358 2008; Dugalic et al. 2010). It can be seen from Table S4 that more than half of sampling locations have Ni
359 concentrations above the maximum allowable (50 mg kg^{-1}). Concentrations of Cu are significantly higher only in
360 vicinity of copper smelting plant (Nikolić et al. 2011) and concentrations of Pb and Zn are higher nearby Pb-Zn mine
361 (Gulan et al. 2013). The concentrations of dangerous and harmful elements As, Cd and Hg in Toplica region are
362 below the maximum allowable concentrations (25 , 3 and 2 mg kg^{-1} , respectively), but As is slightly higher than those
363 measured in urban area (Crnković et al. 2006; Milenković et al. 2015; Papić and Vuković 2015). Three locations on
364 the eastern slopes of the mountain Kopaonik (NW Toplica region, Fig.1) have elevated values of As which
365 correspond to naturally acidic forest soils (Pavlović et al. 2017). According to the Water Management Plan of the

366 Republic of Serbia, this position is marked for construction of the storage reservoir "Selova" on the river Toplica
367 (Kostadinov et al. 2008).

368 Heavy metals enrichment factors calculated relative to background value (Mn was taken as the reference
369 element) are presented in Table 2. The EFs of As, Cd, Co, Cr, Cu, Ni, Pb, Zn and Hg were in the range of 0.16-
370 244.5; 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.
371 The mean EF values of Cd, Co and Hg less than 2 indicate that the metal derived completely from natural processes.
372 Metal enrichments were found in the next order As>Cu>Ni>Pb>Zn>Cr. The values for Cr, Cu, Ni, Pb and Zn
373 showed moderate enrichment suggesting anthropogenic impact on environment (Zhang and Liu 2002). With the
374 highest mean EF value of 7.3, As showed significant enrichment. According to mean values of EFs the soils in this
375 study were moderately affected by human activities. The EFs alone cannot precisely identify sources of analyzed
376 heavy metals in soils but they are useful to speculate on their anthropogenic or lithogenic origin. Reimann and de
377 Caritat (2005) reported that EFs are influenced by a number of factors and contamination is just one of them. In
378 differ to the enrichment factor I_{geo} and PI were calculated to evaluate the pollution level of heavy metal.

379 The calculated values of I_{geo} are shown in Table 2. The range values of I_{geo} for heavy metals were: -3.33 to 3.68
380 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
381 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
382 study soils were practically uncontaminated. Calculated I_{geo} values for As, Co, Mn, Pb, Zn and Hg indicate
383 uncontaminated to moderately contaminated soils while I_{geo} values for Cd, Cr and Ni indicate moderately
384 contaminated soils.

385 The mean values of PI are given in Table 2. The ranges of PI values were as follows: As (0.15-19.27), Cd (0.08-
386 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
387 (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
388 which indicates that the investigated soils are contaminated by heavy metals.

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

391

392 3.3 Health risk assessment from heavy metals

393

394 The results of the average daily doses via different pathways are listed in Table 2. RfD ($\text{mg kg}^{-1} \text{ day}^{-1}$) is the
395 maximum daily dose of a metal from a particular exposure pathway for human population during a lifetime, Table 3.

396 The results of HQs and HI by above mentioned metals in soils for adults and children via different pathways are
397 shown in Table 3. The various exposure pathways of metals for adults and children increased in the order inhalation
398 < dermal contact < ingestion. The contributions of HQ_{ing} to HI were 97.1 and 84.2 % for children and adults
399 proposing that ingestion was main exposure pathway. This result was comparable with other authors (Chabukdhara
400 and Nema 2013; Wei et al. 2015)

401 The calculated HI values for children and adults decreased in the following order: As > Cr > Pb > Ni > Cu > Hg >
402 Zn > Cd, Table 3. The total HI values were 0.73 and 0.18 for children and adults, respectively. According to USEPA
403 guidelines only values greater than 1 indicate that population may experience non-carcinogenic effects (USEPA
404 2001). Children have a greater tendency than adults because of intense body growth and their behavior.

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

408

409 3.4 Correlation analysis

410 Spearman correlation coefficients between heavy metals and radionuclides were presented in Table S5. The obtained
411 coefficients were performed using SPSS 20.0 software. The presented Spearman matrix has shown various levels of
412 correlation. The coefficient of 0.804 between activity concentrations of ^{226}Ra and ^{232}Th implies strong positive
413 correlation ($p \leq 0.01$). This result is in agreement with our previously published results (Gulan et al. 2017;
414 Milenkovic et al. 2015). Due to fact that ^{226}Ra and ^{232}Th have similar behavior throughout their transport this was
415 expected (Chandrasekaran et al. 2015).

416 Strong positive correlations at the 0.01 significance level among pairs of As-Cd, As-Pb, Cd-Pb, Cd-Zn, Cu-Zn,
417 Cr- Ni; Co is also strong positive correlated with Cr, Mn and Ni; as well as Pb with Zn and Hg are evident from
418 Table S5. This indicates their geogenic association and geochemical affinities in soils.

419

420 4. Conclusion

421
422 This study was performed to assess environmental risk of radioactivity and heavy metals. The activity
423 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
424 Hg) in soil samples from Toplica region were obtained using HPGe gamma ray spectrometry and ICP-OES analysis
425 technique, respectively.

426 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
427 the worldwide average values. There is a great variation (7-1053 Bq kg⁻¹) in the values of specific activities of ^{40}K
428 and the mean value of 492 Bq kg⁻¹ is higher than the worldwide average. Dose assessment and radiological risk
429 assessment indicate that there was no significant risk for population of Toplica region.

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

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

436 The health risk assessment of heavy metals in soil was used to quantify non-carcinogenic risk to population using
437 the hazard quotient (HQ) and the hazard index (HI). The total HI values were 0.73 and 0.18 for children and adults,
438 respectively. According to USEPA guidelines only values greater than 1 indicate that population may experience
439 non-carcinogenic effects. The various exposure pathways of metals for adults and children increased in the order
440 inhalation < dermal contact < ingestion.

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

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

448

449

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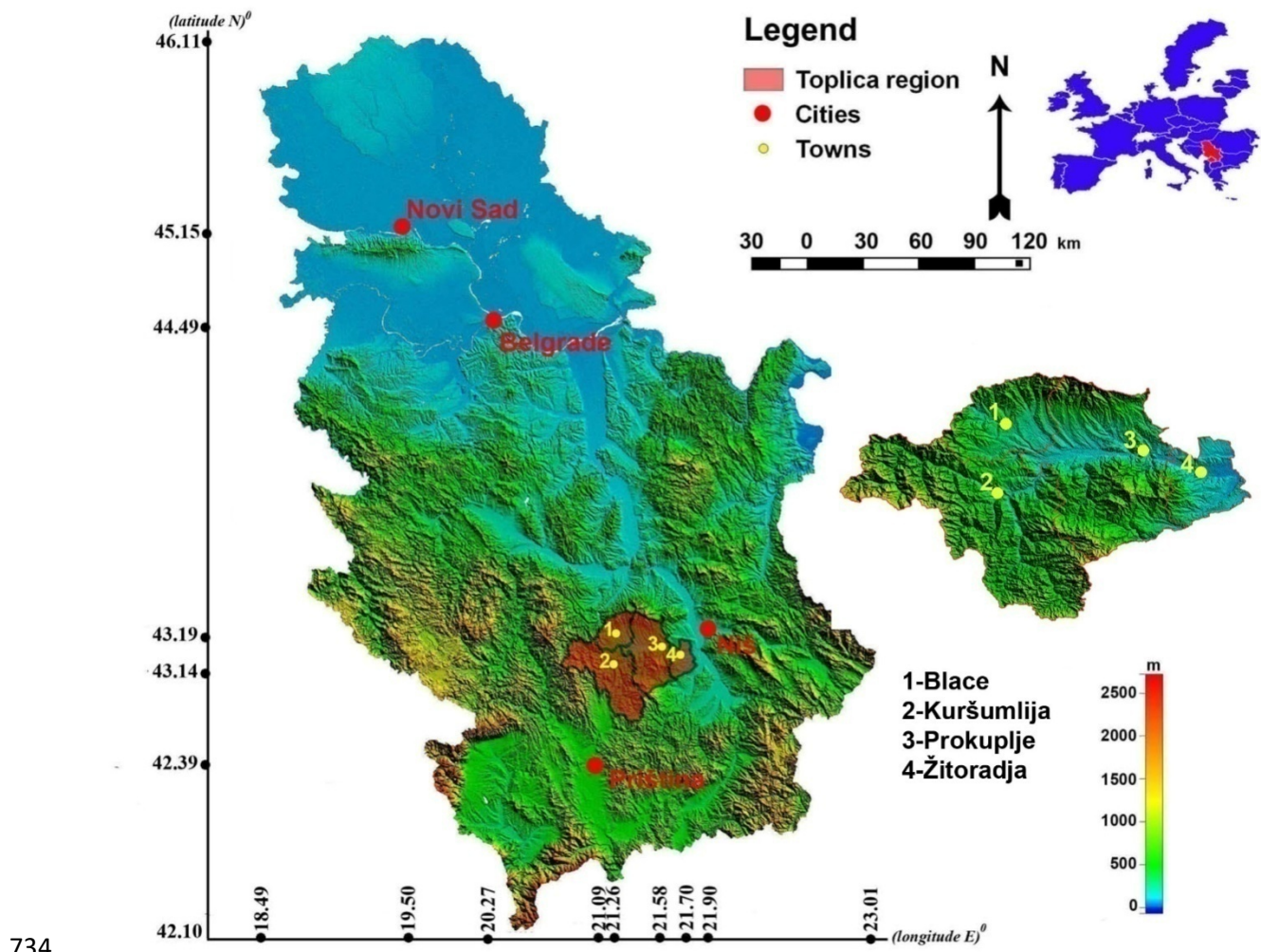
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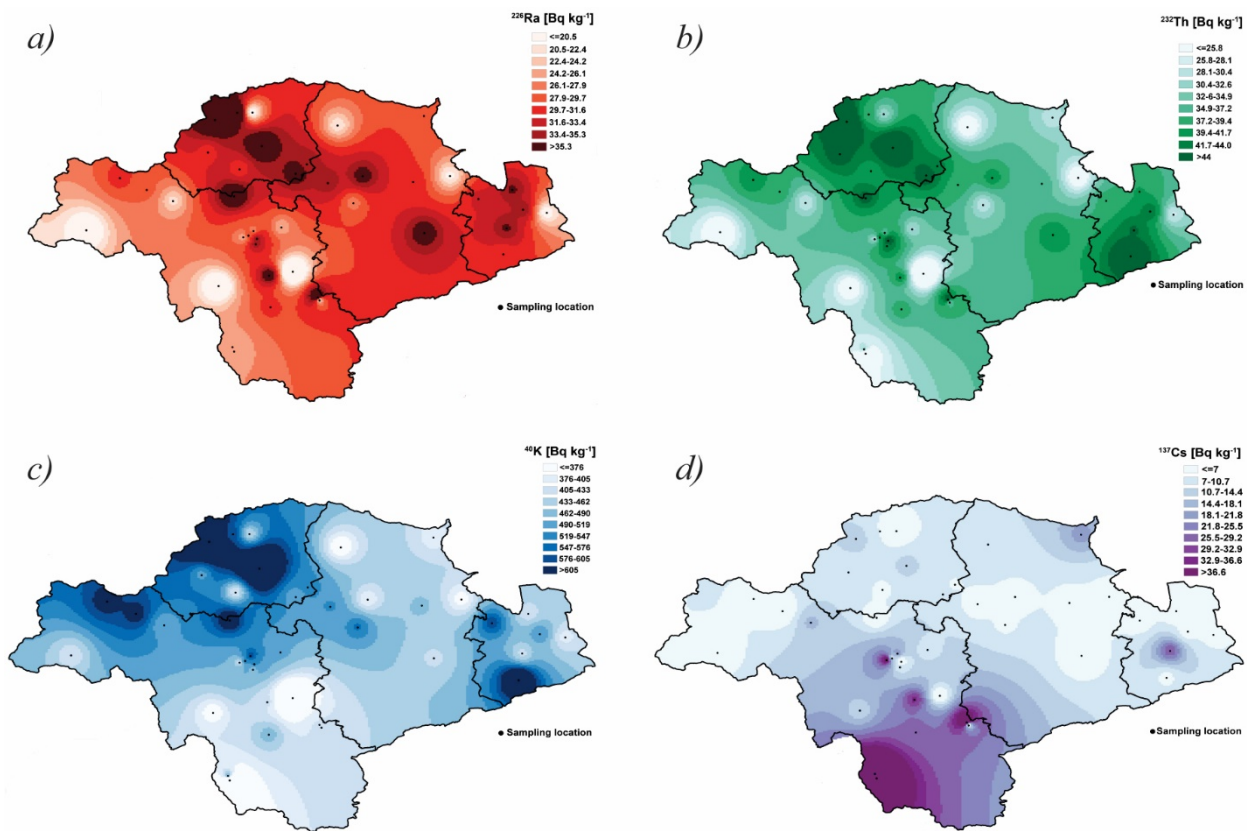
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Fig. 1 Map of study area with sampling locations

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Fig. 2 The spatial distribution of radionuclides ²²⁶Ra, ²³²Th, ⁴⁰K and ¹³⁷Cs

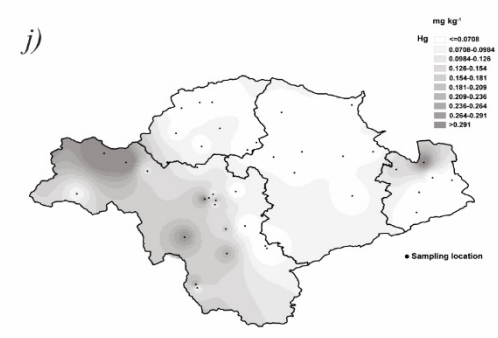
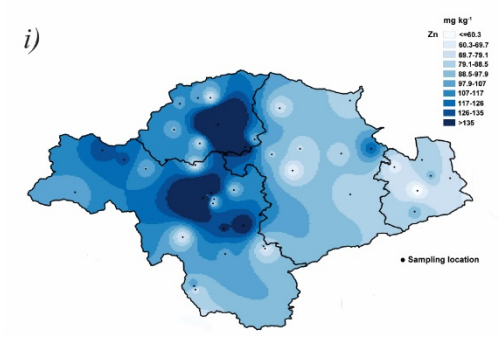
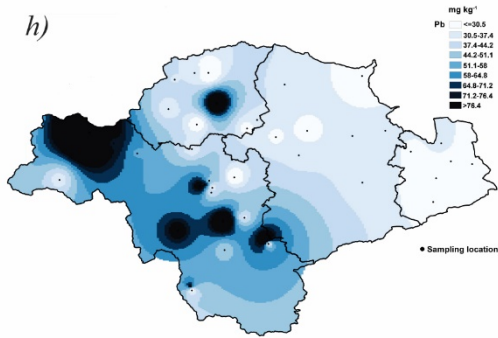
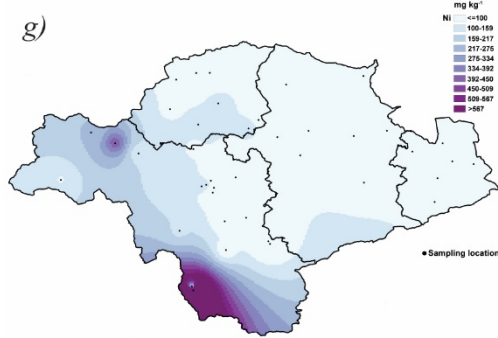
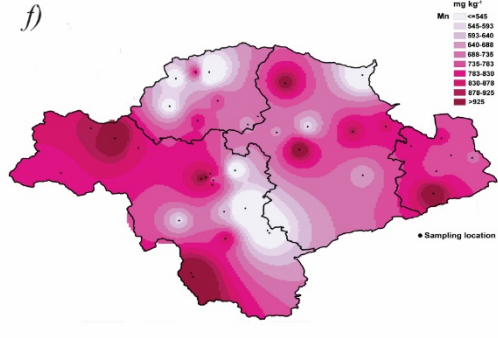
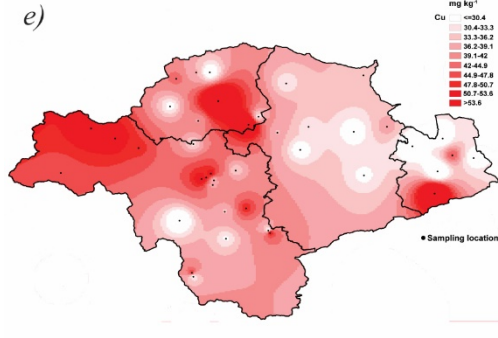
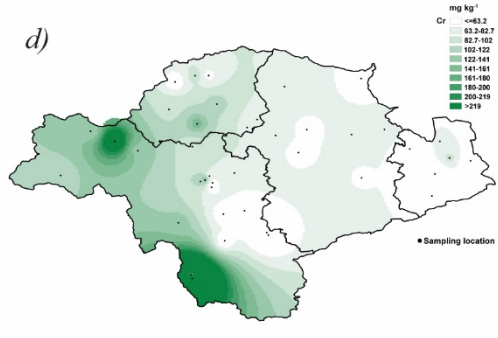
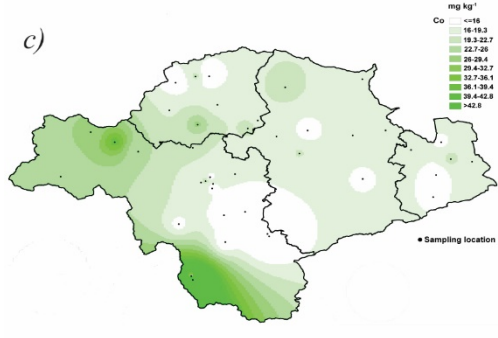
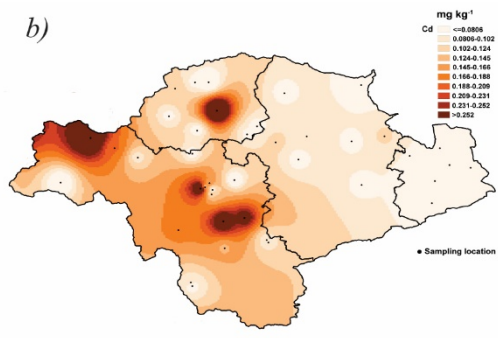
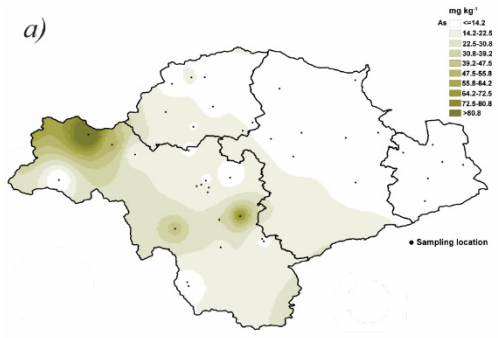


Fig. 3 The spatial distribution of heavy metal concentrations

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

	Radioactivity				\dot{D} (nGy h ⁻¹)	Dose estimation			$ELCR \cdot 10^{-4}$	Radiation risk assessment		
	²²⁶ Ra	²³² Th	⁴⁰ K	¹³⁷ Cs		D_E	D_{ECs}	G		Ra_{eq} (Bq kg ⁻¹)	I_{yr}	H_{ex}
	(Bq kg ⁻¹)					(μSv y ⁻¹)				(Bq kg ⁻¹)		
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

Table 2. Concentrations, pollution indices, and the average daily doses (ADDs) of soil metals for children and adults.

Element		C (mg ⁻¹ kg ⁻¹)	Pollution indices			ADD _{ing}		ADD _{inh}		ADD _{der}	
			<i>EF</i>	<i>I_{geo}</i>	<i>PI</i>	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 3.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

Table 4. Mean values of radioactivity and heavy metals - comparison with other studies in Serbia.

Area/ Town in Serbia		As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	Hg	²²⁶ Ra	²³² Th	⁴⁰ K	¹³⁷ Cs	Reference
mg kg ⁻¹												Bq kg ⁻¹				
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
Urban area	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
	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
Mountain area	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	Dugalić et al., 2010
	Southern Serbia**	3.34	-	7.94	29.9	-	692	11.8	-	43	10.7	27	26	332	99	Popović et al. 2008
	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
Lowland area	Maljen	-	-	-	-	-	-	-	-	-	-	36*	34	297	161.5	Mitrović et al. 2009
	StaraPlanina	-	-	-	-	-	-	-	-	-	-	40	50	461	8.7	Vranjes et al. 2016
	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 ²³⁸U

**- urban and rural area