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NATURALLY OCCURRING RADIONUCLIDES AND THEIR RADIOLOGICAL RISK ASSESSMENT IN RIVER SEDIMENTS FROM THE DITRAU ALKALINE MASSIF

Valentin Nicolae COȚAC[1]*, Ovidiu Gabriel IANCU[1], Nicușor NECULA[2,3], Marius Cristian SANDU[1], Aurelia Andreea LOGHIN[1,4], Adriana ION[5], & Sergiu LOGHIN[1]

[1]Department of Geology, "Al. I. Cuza" University, 20A Carol I Blv., 700505, Iași, România, cotacvalentin@gmail.com, ogiancu@uaic.ro, cristi2sandu@yahoo.com, scarlataureliaandreea@yahoo.com.
[2]Tulnici Research Station, „Alexandru Ioan Cuza" University of Iași, Iași, Romania, neculanicusor93@gmail.com.
[3]Department of Geography, Faculty of Geography and Geology, „Alexandru Ioan Cuza" University of Iași, Romania.
[4]Interdisciplinary research laboratories in the geochemistry of rural areas, RA-07, Mădârjac Station for Geographic research and Environmental quality monitoring, Iasi, „Alexandru Ioan Cuza" University of Iași, Iași, Romania.
[5] Geological Institute of Romania, Radiometry Laboratory, Bucharest, Romania, adi75riana@yahoo.com
[*]Corresponding author cotacvalentin@gmail.com.

Abstract: Naturally occurring ^{238}U, ^{232}Th and ^{40}K radionuclides within river bed sediments of Jolotca and Ditrău rivers from Ditrău Alkaline Massif (DAM) and their environmental risk and spatial distribution have been analyzed. The DAM metamorphic formations have been the subject of multiple studies due to their structure and high variety of mineral species. This led to the execution of many mining operations. River bed sediment samples have been collected from two of the main drainage basins of DAM, Ditrău and Jolotca rivers. The samples were analyzed using gamma-ray spectrometry in order to determine the concentration of the naturally occurring radionuclides and the risk parameters such as RLI (Representative level index), AGDE (Annual gonadal dose equivalent), H_{ex} (External hazard index), H_{in} (Internal hazard index) and D_R (absorbed gamma dose rates in air). ^{238}U, ^{232}Th and ^{40}K show values higher than the Upper Continental Crust (UCC) and other studies from around the world. D_R, AGDE and RLI are higher than the global average and the safe limits. These values are a consequence of the geological context which determined the presence of heavy minerals and Th and U bearing minerals.

Keywords: Riverbed sediments, radionuclides, Ditrău, Jolotca, radiological hazard, uranium deposits.

1. INTRODUCTION

The main objective of this study is the determination of the spatial distribution of the naturally occurring radionuclides ^{238}U, ^{232}Th and ^{40}K in the river-bed sediments of the Jolotca and Ditrău rivers from the Ditrău Alkaline Massif (DAM) and their associated radiological risk assessment.

U and Th bearing minerals have been previously described in the DAM (Hîrtopanu et al., 2010; Hîrtopanu et al., 2013b): Zircon grains with high Th-content 'Monazite Group', Thorite, Thorogummite, Thorianite, Uraninite, Aeschynite-(Y), Cheralite-Monazite-Huttonite series, Betafite, Polycrase (Y), Pyrochlore Group (Uranpyrochlore, Yttropyrochlore (Y) varieties), Yttrobetafite (Y).

In Romania, significant uranium concentrations have been reported in the Apuseni Mountains, Eastern Carpathians and Banat Mountains. Going through history, the exploration and mining of Uranium was the responsibility of Rare Metals Enterprise which later became Rare Metals Direction. This was subsequently incorporated by the National Uranium Company S.A. which is currently responsible for mining operations (Dahlkamp et al., 2016).

The elements discussed in this study e.g.: Thorium (Th) and Uranium (U), show an abundance of 10.5 ppm and 2.7 ppm respectively in the Upper Continental Crust (UCC) (Rudnick & Gao, 2013). U is a metallic element and is present as U^{4+} in igneous

rocks, as well as Th which is a rare element and has similar properties in the same state as Th^{4+} being close to light rare earth elements (LREE). Another naturally occurring isotope in the study area is ^{40}K and it is found in all potassium minerals. In the UCC potassium has a concentration of 2.8%, being a major element of the feldspar series, feldspathoids and micas (Ion et al., 2022; Rudnick & Gao, 2013).

Water can be polluted from different sources and different categories, such as agricultural chemicals, pesticides, and improper management of the city drainage systems that can contaminate the aquifers with waste from factories or mining activity, radioactive contamination being possible.

The radionuclides can be found either in solution, but most of them could be associated with riverbed sediments. The chemical and physical properties of the minerals from riverbed sediments are highly dependent of the natural context and the geological evolution of the outcropping formations. The mineral concentration is affected by the hydrological and geological conditions such as precipitations, weathering and geological context (Kawabata, 1959; Guagliardi et al., 2013).

Intruding in the Eastern Carpathian arc the Ditrău alkaline Massif is one of the few syenitic Massifs in Europe, displaying unique mineralizations. The genesis of the Massif has been theorized by many authors, most of them inclining towards a multi-stage model of different magmatic phases (Constantinescu et al., 2010).

The Ditrău alkaline Massif (DAM) has been the subject of many studies, the mining interest and rare mineralizations within the wide petrographic variety of the DAM has attracted even mining explorations in the communist era.

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2. GEOLOGICAL SETTING

The Ditrău Alkaline Massif is located at the western slope of the Eastern Carpathians, near Ditrău, Lăzarea and Gheorgheni localities (Figure 1). The DAM is believed to be an intrusive body with an internal zonal structure, generated in the pre-Alpine metamorphic rocks of the Bucovinean nappe complex near the Neogene-Quaternary volcanic arc of the Călimani-Gurghiu-Harghita Mountain range (Ianovici, 1938; Kräutner & Bindea, 1998). The massif is located at the inner boundary of the Mesozoic crystalline zone, within the Tulgheș Group (Constantinescu et al., 2010). Based on detailed geochemical studies published by Dallmeyer et al. (1997), the intrusion of the Ditrău Alkaline Massif has been related to mantle plume activity prior to Jurassic rifting within the Eastern Carpathian Orogen. Based on K-Ar and $^{39}Ar/^{40}Ar$ data, Kräutner & Bindea (1998) proposed the emplacement of DAM between Carnian and Aptian (231 to 110 Ma). Pană et al. (2000) carried a precise U-Pb zircon dating of the syenite phase from the Ditrău Massif. Morogan et al. (2000) proposed that the whole complex was derived from basanitic magmas with OIB- character, created by low degrees of melting of asthenospheric garnet lherzolite. Gyula (2017) suggested that DAM is the product of three main geological processes: hornblendites intrusion in the Middle Triassic, the intrusion of magmatic red syenites in the Middle Jurassic and general alkaline metasomatosis in the Lower Cretaceous.

Recent studies are postulating a multi staged magmatic evolution on DAM (Klötzli et al., 2022, 2023) based on the nepheline syenites collected form the area. The authors distinguished three magmatic events that took place in the Upper Triassic as a result of a rift-related tectonic setting on the southwestern margin of the European Craton: 1. intrusion of the Ghiduț suite – dated at 231.1±0,8 Ma; 2. intrusion of the Ditrău suite – 230.7 ±0,2 Ma; 3. intrusion of the Lăzarea suite – 224,9±1.1 Ma. The center of the Ditrău Alkaline Massif was formed by nepheline syenite, surrounded by syenite and monzonite. North-western and north-eastern flanks are composed of alkali diorite, alkali granite, monzodiorites, monzosyenites, and hornblende gabbro/hornblendite (Ion, 2012). In the Jolotca area there are small discrete ultramafic bodies: kaersutite-bearing peridotite, olivine pyroxenite and hornblendite and alkali gabbros, the latter being also known from drill-cores in the Ditrău s.s. area (Constantinescu et al., 2010; Morogan et al., 2000). Hornblende gabbro/hornblendite and diorite are the earliest intrusive phase, and are incorporated within younger syenite and granite (Dallmeyer et al., 1997; Morogan et al., 2000). All of these rocks are cut by later stage dykes with a wide variety of compositions including tinguaite, phonolite, aplite, nepheline syenite, microsyenite, and later lamprophyre (Streckeisen 1952, 1954; Codarcea et al. 1958; Streckeisen & Hunziker, 1974; Anastasiu & Constantinescu, 1982; Anastasiu et al., 1994).

DAM is enriched in rare earth elements (REE), niobium, and molybdenum, monazite being the main REE-bearing phase (Hîrtopanu 2019; Honour et al., 2018). As of Borcos et al. (1983) three distinct mineralizations are found in the DAM: Jolotca-Ditrău (pneumatolytic-hydrothermal Mo-Pb-Zn + Au, Ag

deposit), Aurora-Ditrău (hydrothermal Mo deposit) and Ditrău (alluvial Ti, Zr deposit, zircon, ilmenite, titanite, magnetite and monazite being the main minerals found).

The first data on mineralization were provided by Ianovici (1933, 1938), who described occurrences of sphalerite, galena, pyrite, chalcopyrite and goethite in the Jolotca valley. He also identified several other minerals in the area: Y-allanite, xenotime, molybdenite, pyrochlore, baddeleyite and rhönite. The mineralization from Jolotca-Ditrău consists of oxides, sulfides, carbonates, phosphates and subordinate silicates and native elements, i.e. isocubanite, mackinawite, valleriite, native silver, anatase, brookite, Mn-rich ilmenite, pseudobrookite, lillianite (Constantinescu & Anastasiu, 2004). Sequential formation is suggested by all these aspects of the mineralization formed during the main stages (pneumatolytic and hydrothermal). This is also indicated by the presence of several mineral

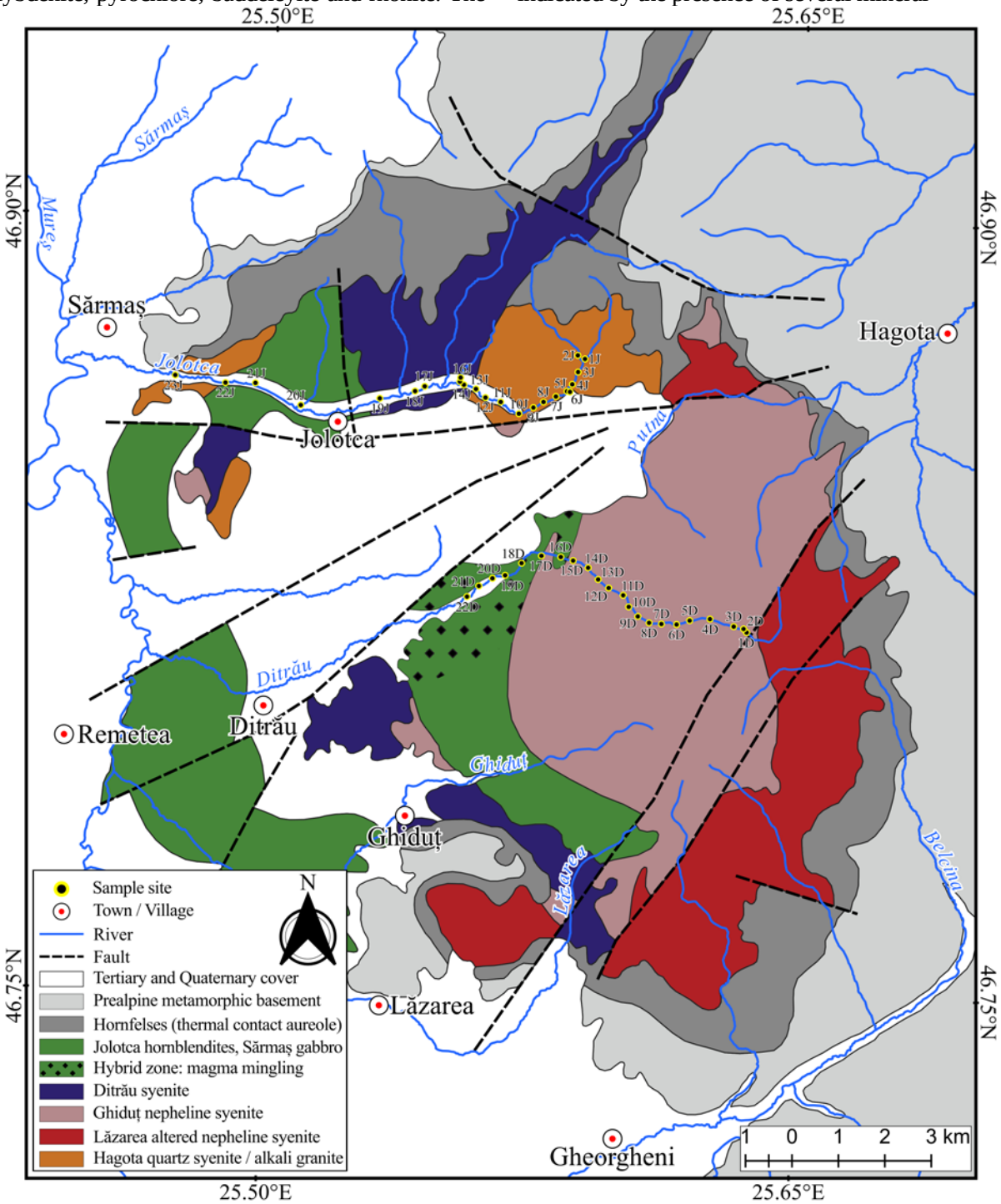

Figure 1. Geological map of the Ditrău Massif with the sampling points (modified after Anastasiu & Constantinescu, 1982; Kräutner & Bindea, 1998).

generations. There are also important discontinuities marked by brecciation intervals. The REE mineralization (Nb-Th minerals) can be considered to be genetically related to the alkaline rocks, as the mineralogical and geochemical data show a common geochemical trend for the OIB setting of the REE, Ca and Nb with Th. Regarding the REE minerals identified in the Ditrău complex, they are part of the following six classes: REE(Y), Th, U – Carbonates; Nb, Ta, REE(Y), Ti, Zr, Th, Sn, U – Oxides; REE(Y) – Phosphates; REE(Y), Nb, Th, U, Zr, Pb, Ti – Silicates; Halides and Tellurides (Hîrtopanu et al., 2013a; Hîrtopanu, 2019) The main tectonic event present in our study area is the Sărmaș-Joseni crustal fault. From north to south crosses the Gheorgheni Basin and it could be described as a border between the crystallin Mesozoic area in the east and the Neogene pyroclastic deposits in the west (Pál-Molnár, 2010).

In this study, the naturally occurring radionuclides of river bed sediments along the Jolotca and Ditrău rivers were analyzed (Figure 1). The Ditrău River flows from east to west through different petrographical types. With a length of 16 km, firstly goes through of nepheline syenite zone, next through a gabbro hybrid zone and at the end the Pliocene-Pleistocene sedimentary area. The syenites are composed of alkali feldspar, nepheline, sodalite, amphibole and biotite, with secondary minerals such as zircon and monazite. The gabbro hybrid zone, known as the magma mixing zone, is described as gabbro with nepheline syenite veins forming rounded to sub-angular gabbroic enclaves (Honour et al., 2018). Jolotca River flows from east to west through different petrological types. The river has approximately a length of 15 km, emerging and passing first through the granitoid area and next through the hornblendites and the syenite deposits, respectively, as in the end to once again go over the granitoid deposits while exiting the study area. From a petrographically point of view, the granites are light gray with hints of light red and their main mineral components are quartz, K-feldspar, plagioclase, biotite and amphibole. The syenites zone consists mainly of syenite-monzosyenite and their mineral composition includes feldspar, orthoclase and microcline supplemented by rare minerals such as titanite, apatite, zircon. Most minerals from the black hornblendites include hornblende, titanite, biotite with plagioclase, apatite and pyrite (Gyula, 1998; Krautner & Bindea, 1998; Pál-Molnár et al., 2015).

3. MATERIAL AND METHODS

3.1. Sample collection and preparation

Sampling was conducted in July 2018. GPS coordinates were taken, and approximately 1 kg of sediment was sampled at each point and stored in zip-lock bags. Sampling points for both rivers covered all petrographic units and maintained a maximum distance of 500 m between each point, depending on terrain geomorphology.

A total number of 45 river sediment samples were collected from both rivers, 23 on the Jolotca river and 22 on the Ditrău river. The samples were air dried and sieved through 6 different sieves 4mm>2mm>0.5mm>0.25mm>0.125mm>0.063mm. After ensuring that pebbles, organic matter, and other debris were removed, we placed approximately 300 grams of homogenized, sieved, and air-dried sediment sample into a plastic zip-lock bag for analysis.

3.2. Analytical method

To determine the concentration of natural radionuclides, we used gamma-ray spectrometry with a high-purity germanium (HPGe) detector. The HPGe detector has a relative efficiency of 26% with a resolution of 1.80 keV for ^{60}Co at 1332 keV energy line and 0.800 keV for ^{57}Co at energy line of 122 keV: peak/ Compton ratio of 56:1 at 1.33 MeV and it was coupled to the conventional electronics connected to a multichannel analyzer (MCA-DSPEC jr.2.0-ORTEC).

In order to achieve complete equilibrium between ^{226}Ra and ^{222}Rn, the samples were rested in their containers for 30 days, the counting time for each sample was 12000 seconds.

For the data acquisition, an analyzer emulation software (MAESTRO-32) for storage was used, display and online analysis of the acquired γ-spectra.

To isolate the detector from background radiation, a 10 cm thick lead plate was used to surround the detector. The calibration has been done using a multi-element standard that contained radionuclides with known activities, also (IAEA, 2003) reference materials were used, such as RGU−1, RGTh−1, and RGK−1.

The resultant gamma-ray spectra have been analyzed off-line by means of a dedicated software: Gamma Vision-32.

^{238}U activity concentrations were determined using gamma-ray emissions of ^{214}Pb at 352 keV and 295 keV, ^{214}Bi at 609 keV and 1120 keV, ^{226}Ra at 186 keV. ^{232}Th-series, the emissions of ^{228}Ac at 338.4 keV and 911.2 keV was used, for ^{212}Bi at 727 keV and for ^{208}Tl at 860 keV. The activity concentration of ^{40}K was determined directly, from its emission at 1460 KeV γ-line.

3.2.1 Spatial distributions maps

Spatial distribution maps were realized in ArcGIS 10.2 software using Inverse Distance Weighting (IDW) as a data interpolation method.

3.2.2 Calculated parameters

a. Absorbed gamma dose rate (D_R)

The absorbed gamma dose rate depends on the natural specific activity concentration of natural radionuclides such as ^{238}U, ^{232}Th and ^{40}K, and is described as the amount of energy from ionising radiation absorbed per unit mass of matter per unit time (Ravisankar et al., 2015).

The D_R due to terrestrial gamma rays in the air at 1 m above the ground has been calculated for ^{238}U, ^{232}Th and ^{40}K according to UNSCEAR (2000).

The activity concentration of the radionuclides is converted into the dose rate in $Bq \cdot kg^{-1}$ using the following conversion factors 0.462 $nGy \cdot h^{-1}$ for ^{238}U, 0.604 $nGy \cdot h^{-1}$ for ^{232}Th, and 0.042 $nGy \cdot h^{-1}$ for ^{40}K. If the conversion factors are known, and on the basis of UNSCEAR (2000), the absorbed gamma dose rate (D_R) can be calculated using the following equation:

$$D_R = 0.462A_U + 0.604A_{Th} + 0.042A_K \ [nGy \cdot h^{-1}]$$

A_U, A_{Th} and A_K are the specific activities of ^{238}U, ^{232}Th and ^{40}K ($Bq \cdot kg^{-1}$).

b. Annual effective dose equivalent (AEDE)

The annual effective dose rate or AEDE represents a calculated parameter based on the data from UNSCEAR (2000), where the conversion factor from the absorbed dose in the air is 0.7 $SvGy^{-1}$ and the outdoor occupancy factor equals 0.2. This parameter (AEDE rate in $mSvy^{-1}$) was calculated by the following formulas based on (UNSCEAR, 2000):

$$AEDE = D_R(nGy \cdot h^{-1}) \cdot 8760h \cdot 0.2 \cdot 0.7\ SvGy^{-1} * 10^{-6}$$

$$AEDE = D_R \cdot 0.00123\ [mSvy^{-1}]$$

Table 1. Statistical parameters for the concentrations of radionuclides in the samples from Ditrău and Jolotca rivers.

Parameter		Min	Max	Mean
River		**Jolotca**		
^{238}U	[$Bq \cdot kg^{-1}$]	12.35	61.13	33.89
^{232}Th		26.88	68.41	43.29
^{40}K		482.02	1871.74	1042.40
U/UCC	ppm/UCC	0.37	1.83	1.02
Th/UCC		0.63	1.60	1.02
K/UCC	%/UCC	0.66	2.58	1.44
River		**Ditrău**		
^{238}U	[$Bq \cdot kg^{-1}$]	19.02	68.67	43.22
^{232}Th		29.27	73.81	49.86
^{40}K		1245.74	1831.05	1484.85
U/UCC	ppm/UCC	0.57	2.06	1.30
Th/UCC		0.69	1.73	1.17
K/UCC	%/UCC	1.72	2.52	2.04

c. Radium equivalent activity (Raeq)

Radium equivalent activity or Raeq is a calculated parameter to quantify and express gamma output from mixtures of radionuclides in a material (Tufail, 2012). It is described by Farai & Ademola (2005), as a common parameter that can be used to compare the activity concentrations of building materials that contain K, Th or U.

The following equation can be used to obtain the Raeq (Beretka & Mathew, 1985):

$$Raeq = A_U + 1.43A_{Th} + 0.077A_K \ [Bq \cdot kg^{-1}]$$

d. Representative level index (RLI)

The representative level index or RLI is used to determine the level of gamma radiation hazard associated with the natural radionuclides such as ^{238}U, ^{232}Th and ^{40}K in the sediments and has been determined using the following formula (Alam et al., 1999; Ravisankar et al., 2015):

$$RLI = (1: 150A_U) + (1: 100A_{Th}) + (1: 1500A_K)$$

A_U, A_{Th} and A_K are the specific activities of ^{238}U, ^{232}Th and ^{40}K ($Bq \cdot kg^{-1}$). The RLI should be below 1 to maintain a lower level of radioactivity.

e. Annual gonadal dose equivalent (AGDE)

Annual gonadal dose equivalent or AGDE can be explained as a yearly dose received by reproductive organs, bone marrows and bone surface cells (UNSCEAR, 2000). The annual gonadal dose equivalent due to naturally occurring radionuclide activities has been calculated using the following formula:

$$AGDE = 3.09A_U + 4.18A_{Th} + 0.314A_K \ [\mu Svy^{-1}]$$

A_U, A_{Th} and A_K are the specific activities of ^{238}U, ^{232}Th and ^{40}K ($Bq \cdot kg^{-1}$).

f. Internal hazard index (H_{in})

The internal hazard index, or H_{in} for short, is a calculated parameter that reflects the internal exposure to radon and its products. Radon and its products are very dangerous to the organs of the respiratory tract. H_{in} is computed using the equation (Beretka & Mathew, 1985; Ravisankar et al., 2015, Sandu et al., 2020):

$$H_{in} = (A_U: 185\ Bq \cdot kg^{-1}) + (A_{Th}: 259\ Bq \cdot kg^{-1}) + (A_K: 4810\ Bq \cdot kg^{-1})$$

A_U, A_{Th} and A_K are the specific activities of ^{238}U, ^{232}Th and ^{40}K ($Bq \cdot kg^{-1}$). The value of H_{in} must be lower than 1 (UNSCEAR, 2000).

g. External hazard index (H_{ex})

External hazard or short H_{ex} is the calculated parameter that reflects the external radiation exposure attributed to gamma radiation and is used to approximate and determine the potential radiological risk produced by the radionuclides in sediments. H_{ex} is calculated using the formula (Beretka & Mathew, 1985; Ravisankar et al., 2015):

$$H_{ex} = (A_U: 370\ Bq \cdot kg^{-1}) + (A_{Th}: 259\ Bq \cdot kg^{-1}) +$$

(A_K: 4810 Bq·kg^{-1})

A_U, A_{Th} and A_K are the specific activities of ^{238}U, ^{232}Th and ^{40}K (Bq·kg^{-1}). The value of H_{ex} must be lower than 1 (UNSCEAR, 2000).

4. RESULTS

The main results of our analysis are shown in Table 1 and Table 2. It can be observed that ^{238}U varies from 12.35 [Bq·kg^{-1}] to 61.13 [Bq·kg^{-1}] with an average value of 33.89 [Bq·kg^{-1}] in the samples from Jolotca river. The samples from Ditrău river show values from 19.02 [Bq·kg^{-1}] to 68.67 [Bq·kg^{-1}] with an average value of 43.22 [Bq·kg^{-1}].

^{232}Th shows values ranging from 26.88 [Bq·kg^{-1}] to 68.41 [Bq·kg^{-1}] with an average of

Table 2. Concentrations of naturally occurring radionuclides in the samples from Ditrău and Jolotca rivers.

Sample ID	River	^{238}U	^{232}Th	^{40}K		^{238}U	^{232}Th	^{40}K
		[Bq·kg^{-1}]				ppm		%
1J		25.688	37.5144	688.6		2.08	9.24	2.2
2J		32.2335	39.9098	723.03		2.61	9.83	2.31
3J		33.9625	41.615	738.68		2.75	10.25	2.36
4J		19.019	26.8772	795.02		1.54	6.62	2.54
5J		25.935	33.698	826.32		2.1	8.3	2.64
6J		20.3775	32.277	726.16		1.65	7.95	2.32
7J		26.0585	33.8198	766.85		2.11	8.33	2.45
8J		61.1325	68.411	857.62		4.95	16.85	2.74
9J		29.887	37.5956	892.05		2.42	9.26	2.85
10J		28.5285	36.2558	985.95		2.31	8.93	3.15
11J		12.35	30.4906	482.02		1	7.51	1.54
12J	**Jolotca**	21.6125	29.435	1314.6		1.75	7.25	4.2
13J		49.894	57.3272	1665.16		4.04	14.12	5.32
14J		47.5475	55.013	1158.1		3.85	13.55	3.7
15J		49.2765	52.6582	973.43		3.99	12.97	3.11
16J		38.532	46.1216	1305.21		3.12	11.36	4.17
17J		51.9935	63.4578	1108.02		4.21	15.63	3.54
18J		34.086	41.7368	1549.35		2.76	10.28	4.95
19J		31.369	39.0572	1449.19		2.54	9.62	4.63
20J		42.1135	49.6538	1295.82		3.41	12.23	4.14
21J		51.129	58.5452	1568.13		4.14	14.42	5.01
22J		49.894	57.3272	1871.74		4.04	14.12	5.98
23J		56.316	63.6608	1743.41		4.56	15.68	5.57
1D		28.158	36.9866	1314.6		2.28	9.11	4.2
2D		32.2335	37.8798	1349.03		2.61	9.33	4.31
3D		33.9625	39.585	1364.68		2.75	9.75	4.36
4D		19.019	29.2726	1421.02		1.54	7.21	4.54
5D		50.635	56.028	1452.32		4.1	13.8	4.64
6D		57.4275	62.727	1352.16		4.65	15.45	4.32
7D		50.7585	60.2098	1705.85		4.11	14.83	5.45
8D		45.0775	50.547	1796.62		3.65	12.45	5.74
9D		42.237	47.7456	1831.05		3.42	11.76	5.85
10D		38.4085	43.9698	1611.95		3.11	10.83	5.15
11D		36.803	42.3864	1734.02		2.98	10.44	5.54
12D	**Ditrău**	39.8905	50.7094	1627.6		3.23	12.49	5.2
13D		37.544	43.1172	1665.16		3.04	10.62	5.32
14D		47.5475	52.983	1471.1		3.85	13.05	4.7
15D		51.7465	57.1242	1599.43		4.19	14.07	5.11
16D		38.532	44.0916	1305.21		3.12	10.86	4.17
17D		49.153	54.5664	1421.02		3.98	13.44	4.54
18D		68.666	73.8108	1549.35		5.56	18.18	4.95
19D		68.419	73.5672	1449.19		5.54	18.12	4.63
20D		49.5235	63.0518	1295.82		4.01	15.53	4.14
21D		51.129	56.5152	1245.74		4.14	13.92	3.98
22D		49.894	47.1772	1317.73		4.04	11.62	4.21

Conversion: specific activity (Bq)–concentration (ppm) (IAEA, 2003). 1 ppm U = 12.35 Bq. 1 ppm Th = 4.06 Bq. 1% K = 313 Bq

43.29 [Bq·kg^{-1}] in the samples from Jolotca river, while the samples from Ditrău river contain values ranging from 29.27 [Bq·kg^{-1}] to 73.81 [Bq·kg^{-1}] with an average value of 49.86 [Bq·kg^{-1}].

Regarding ^{40}K isotope, samples taken from Jolotca river exhibit values ranging from 482.02 [Bq·kg^{-1}] to 1871.74 [Bq·kg^{-1}] with an average value of 1042.40 [Bq·kg^{-1}]. Meanwhile, samples from Ditrău river have levels ranging from 1245.74 [Bq·kg^{-1}] to 1831.05 [Bq·kg^{-1}] with an average value of 1484.85 [Bq·kg^{-1}].

Radium equivalent activity or Ra_{eq} was calculated for all the samples (Figure 2a). It shows an average value of 185.98 [Bq·kg^{-1}] with a maximum of 281.59 [Bq·kg^{-1}] for the samples from the Jolotca river and an average of 232.99 [Bq·kg^{-1}] with a maximum value of 293.51 [Bq·kg−1] for the samples from Ditrău River.

The Absorbed gamma dose rate (D_R) was calculated for all the samples (Figure 2b). On average, the samples from Jolotca river showed a value of 90.50 [nGy·h^{-1}], with the highest value of

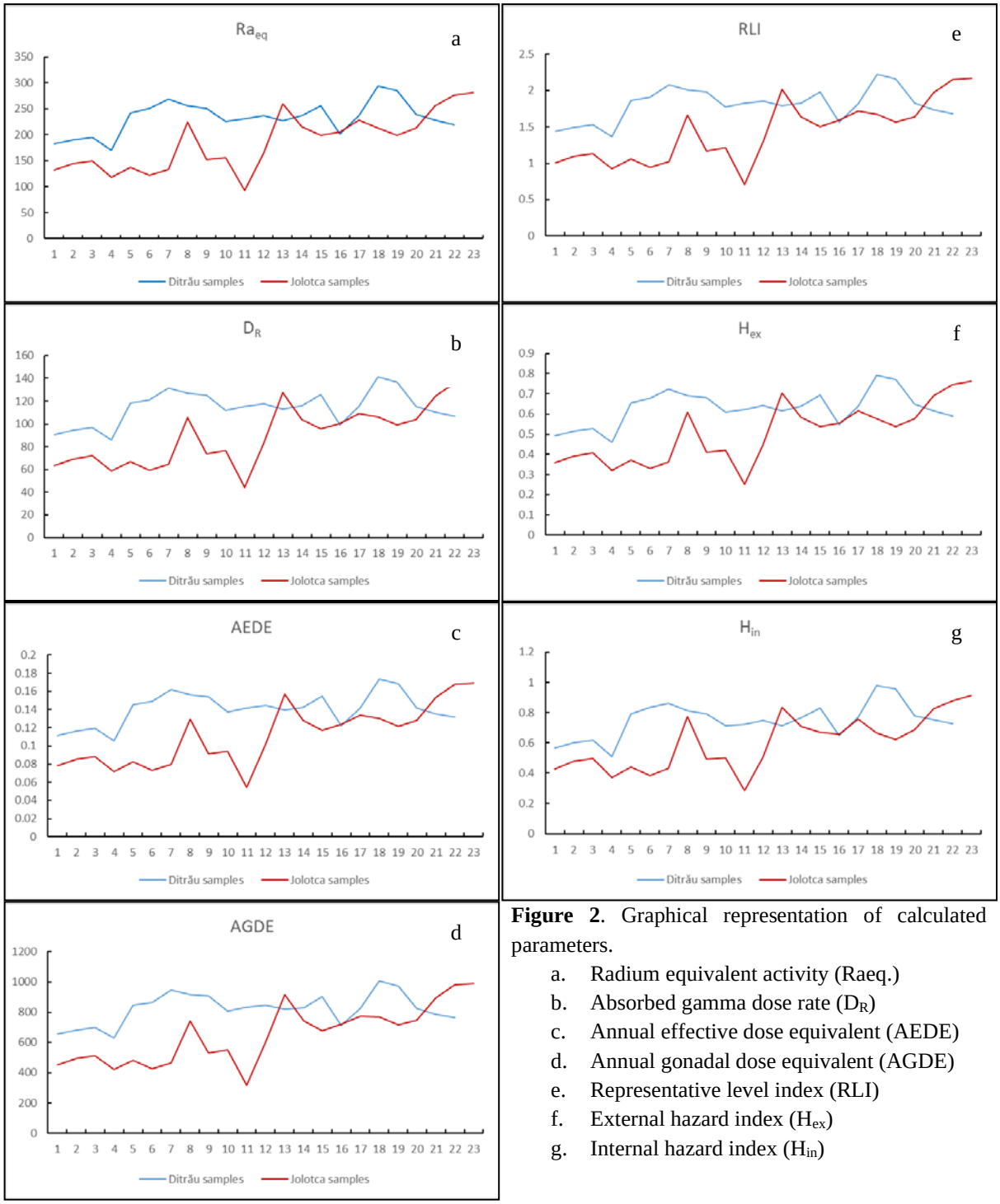

Figure 2. Graphical representation of calculated parameters.

a. Radium equivalent activity (Raeq.)
b. Absorbed gamma dose rate (D_R)
c. Annual effective dose equivalent (AEDE)
d. Annual gonadal dose equivalent (AGDE)
e. Representative level index (RLI)
f. External hazard index (H_{ex})
g. Internal hazard index (H_{in})

137.69 [nGy·h^{-1}]. Meanwhile, the samples from Ditrău river had an average value of 114.35 [nGy·h^{-1}] and the highest value of 141.37 [nGy·h^{-1}].

The annual effective dose rate or AEDE (Figure 2c) shows an average value of 0.11 [mSvy^{-1}] with a maximum value of 0.16 [mSvy^{-1}] for the samples from Jolotca river, and for the samples from Ditrău river an average value of 0.14 [mSvy^{-1}] and a maximum value of 0.17 [mSvy^{-1}].

Annual gonadal dose equivalent or AGDE (Figure 2d) shows an average value of 648.26 [μSvy^{-1}] with a maximum value of 987.54 [μSvy^{-1}] for the samples from Jolotca river, and for the samples from Ditrău river an average value of 821.46 [μSvy^{-1}] with a max value of 1007.20 [μSvy^{-1}].

The representative level index or RLI (Figure 2e) shows an average value of 1.43 and a maximum value of 2.1 for the samples from Jolotca river. On the other hand, the samples taken from Ditrău river have an average value of 1.8 and a maximum value of 2.22. Figure 2f presents the calculation of external hazard or short H_{ex} for all the samples. The average value for the samples from Jolotca river is 0.5, with a maximum value of 0.76. On the other hand, the average value for the samples from Ditrău river is 0.62, with a maximum value of 0.79.

An internal hazard index, also known as H_{in}, was calculated for all the samples and presented in Figure 2g. The results show that the samples from Jolotca river have an average H_{in} value of 0.6, with a maximum value of 0.91. Meanwhile, the samples collected from Ditrău river have an average H_{in} value of 0.75, with a maximum value of 0.97.

5. DISCUSSIONS

5.1. Comparison to the UCC values and Spatial distribution

When comparing our sample values of U, Th and K to those of UCC (Rudnick & Gao, 2013), we observe a clear trend of enrichment in all radionuclides (Figure 3).

The UCC average values are 2.7 ppm for U, 10.5 ppm for Th and 2.32% for K.

In the case of ^{238}U, the average in our samples is 43.22 [Bq·kg^{-1}] for Ditrău river and 33.89 [Bq·kg^{-1}] for Jolotca river (Figure 4). Th is 49.86 [Bq·kg^{-1}] for Ditrău river and 43.29 [Bq·kg^{-1}] for Jolotca river (Figure 5). For K we have an average value of 1484.85 [Bq·kg^{-1}] for Ditrău river and 1042.40 [Bq·kg^{-1}] for Jolotca river (Figure 6). This is predominantly due to the mineralogy of the Massif and the presence of minerals such as monazite - $(Ce,La,Nd,Th)(PO_4, SiO_4)$, Thorite - (Th, U) SiO_4, Thorogummite - $(Th,U)[(SiO_4)(OH)_4]$, Uraninite - UO_2, Cheralite - $CaTh(PO_4)_2$, Chevkinite-(Ce) – $(Ce_4(Ti,Fe^{2+},Fe^{3+})_5O_8(Si_2O_7)_2$, Pyrochlore Group (Uranpyrochlore variety) – $(Ca,U,Ce)_2(Nb,Ti,Ta)_2O_6(OH,F)$ (Hirtopanu et al., 2010; Sándor Szakáll, 2010; Honour et al., 2018). This may be one of the reasons of high Th and U concentrations.

After comparing our results with the calculated values for UCC, we have determined that the values from Jolotca river are close to the normal UCC parameters, exception making K which reaches slightly higher average values K/UCC ratio = 1.44 (Figures 4, 5, 6). Analyzing the riverbed sediments from Ditrău basin we have observed that all three parameters exceed the UCC average values. K/UCC ratio = 2; Th/UCC ratio = 1,17; U/UCC ratio = 1,30.

When comparing to other studies from around the world (Table 3) we can observe a clear difference. All naturally occurring radionuclides show higher values in our study exception being ^{232}Th that shows higher values in another study in Romania.

^{238}U in Ditrău river shows higher values than all the other studies, in Jolotca river we have lower concentrations, 2 other studies show higher values. ^{40}K show higher values even double when compared to some studies from around the world.

5.2 Risk assessment

Absorbed gamma dose rate (DR)

Absorbed gamma dose rate average on a

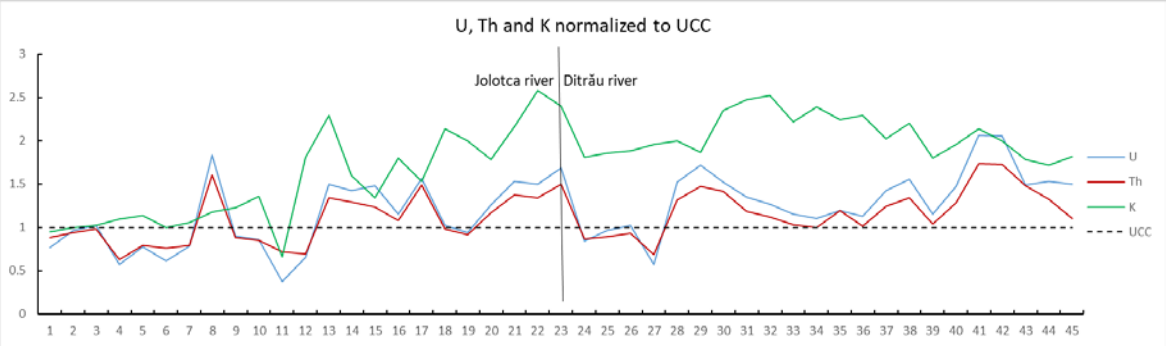

Figure 3. River distribution of U, Th and K (normalized to the UCC)

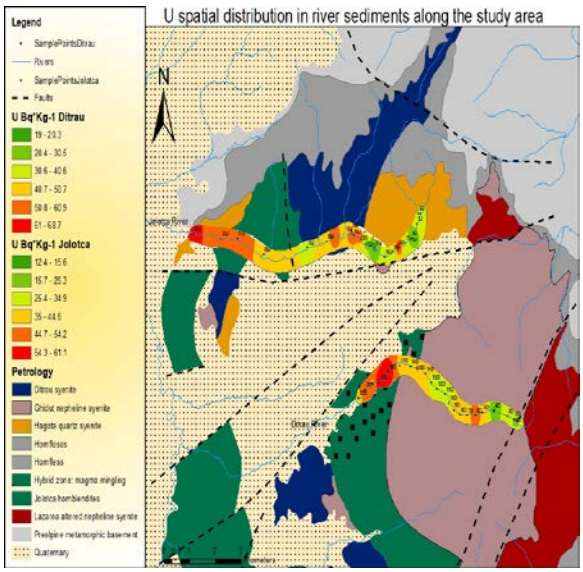

Figure 4. Spatial distribution of U in river sediments along the study area.

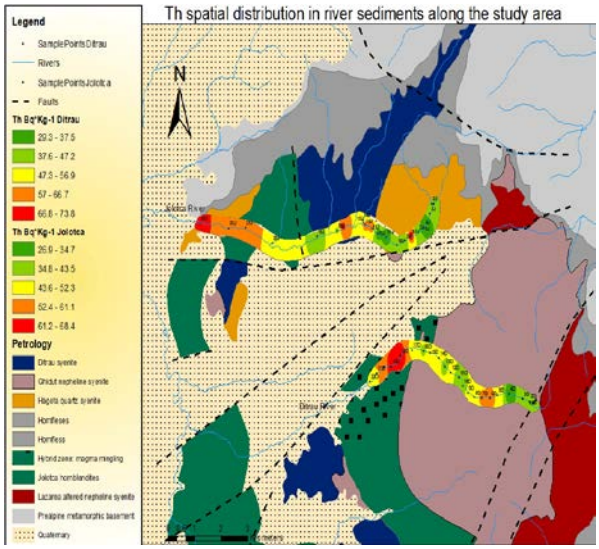

Figure 5. Spatial distribution of Th in river sediments along the study area.

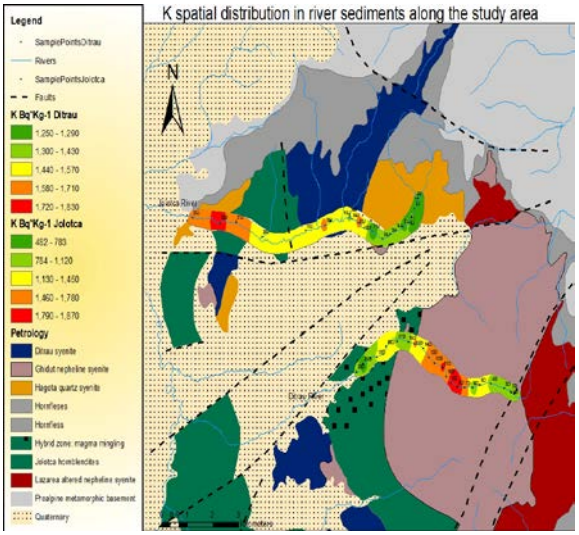

Figure 6. Spatial distribution of K in river sediments along the study area.

worldwide level = 84 nGy·h^{-1} (UNSCEAR, 2000) (Figure 7). All the samples from Ditrău river exceed this value, the average being 113 nGy·h^{-1}. The DR values for the Jolotca River (Figure 8) are due to the presence of U, Th and K bearing minerals and the fact that the sediments and geodynamics of the river provide good solubility and transport throughout the massif.

Table 3. Average concentrations of naturally occurring radionuclides from different studies.

Country	River	^{238}U	^{232}Th	^{40}K	Source
		[Bq·kg^{-1}]			
Romania	Bradul	33.36	39.94	675.45	Sandu et al., 2020
U.S.A.	Reedy	38	45	609	Powell, 2007
Bangladesh	Karnaphuli	37.9	65.5	272	Chowdhury, 1999
Bangladesh	Shango	25.4	57.5	255	Chowdhury, 1999
Romania	Primătar	23.54	37.44	278.75	Sandu, 2020
India	Ponnaiyar	6.43	52.76	395.67	Ramasamy, 2011
Romania	V. Seacă	37.14	55.86	818.18	Sandu et al., 2020
Romania	Ditrău	43.22	49.86	1484.85	This study
Romania	Jolotca	33.89	43.29	1042.4	This study

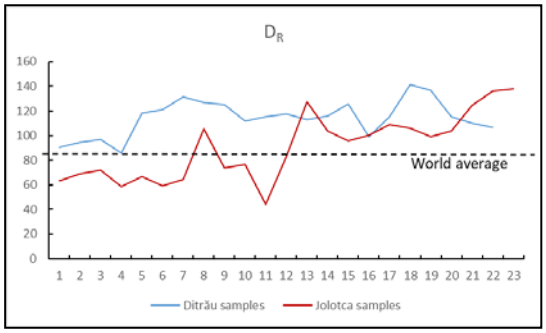

Figure 7. The concentrations of Dr in river sediments compared to worldwide values

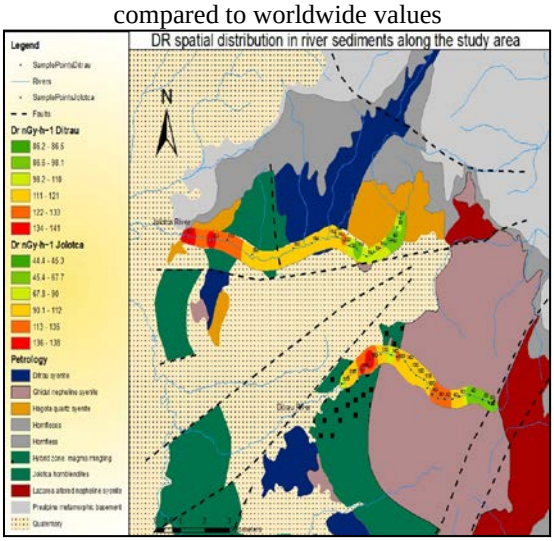

Figure 8. Spatial distribution of Dr in river sediments along the study area

Annual gonadal dose equivalent (AGDE)

The world average for AGDE is 300 μSvy^{-1} (UNSCEAR, 2000) (Figure 9). In the samples from both rivers, we can observe that even the minimum value is higher than the world average. For Ditrău

river, we have values ranging from 627.32 μSvy^{-1} to 1007.20 μSvy^{-1} with an average of 815.33 μSvy^{-1} and for the samples from Jolotca river, values that range from 316.96 μSvy^{-1} to 987.54 μSvy^{-1} with an average of 620.48 μSvy^{-1} (Figure 10).

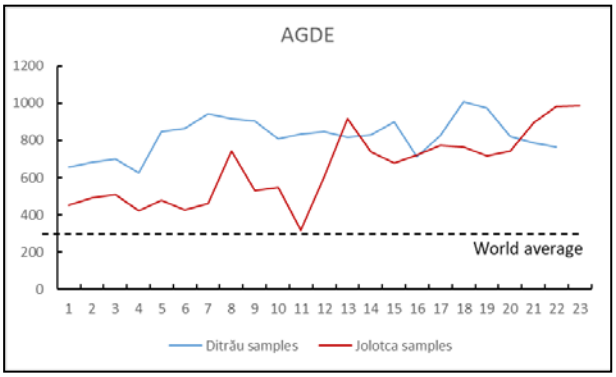

Figure 9. The concentrations of AGDE in river sediments compared to worldwide values.

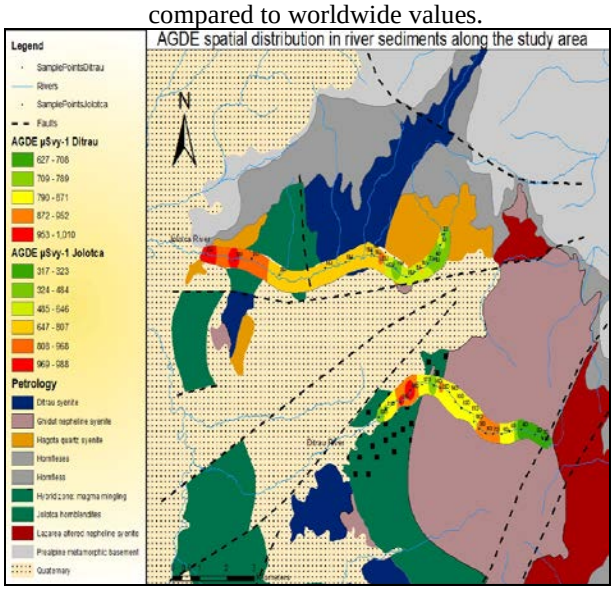

Figure 10. Spatial distribution of AGDE in river sediments along the study area.

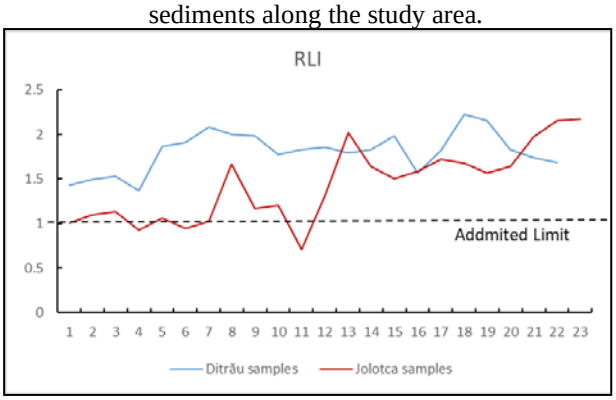

Figure 11. The concentrations of RLI in river sediments compared to worldwide values.

Representative level index (RLI)

Representative level index (RLI) shows values that exceed the acceptable limit of 1 (Figure 11), with values ranging from 1.36 to 2.22 with an average of 1.79 in the Ditrău samples and for the samples from Jolotca river values that range from 0.70 to 2.17 with an average of 1.37 (Figure 12).

The other calculated parameters for the risk assessment such as Annual effective dose equivalent (AEDE), External hazard index (H_{ex}) and Internal hazard index (H_{in}) do not exceed world averages.

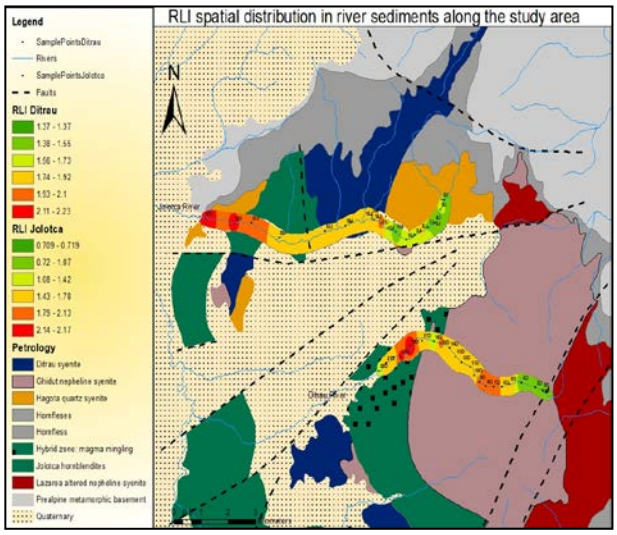

Figure 12. Spatial distribution of RLI in the samples from both rivers.

6. CONCLUSIONS

All naturally occurring radionuclides ^{238}U, ^{232}Th and ^{40}K show values well above the continental crust values and higher than those obtained in other studies. For ^{238}U and ^{232}Th the higher values are due to the minerals like xenotime, epidote, calcium and phosphate minerals bearing REE found in the surveyed area. On the other hand, the high ^{40}K values are due to the alkaline, K-feldspar-rich nature of the massif.

While the Absorbed gamma dose rate (D_R), Annual gonadal dose equivalent (AGDE) and Representative level index (RLI) show values well above the world average and acceptable limits, this can be attributed to the geological context, the presence of heavy minerals and the fact that in the studied area U and Th bearing minerals have been previously described.

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