THORIUM (Th) CONCENTRATIONS IN SOIL OF TUZLA'S URBAN AREA

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The concentrations of the thorium (Th) radioactive element, was determined in 129 samples by a high-sophisticated instrumental method (ICP-MS). The geochemical - pedogeographic soil researches (soil sampling) were made in the urban area of Tuzla (on the area of about 100 km^2), in the proper network of 1x1 km, and according to URGE instructions. The thorium concentrations (Th) are in the range from 4.1 to 15.6 ppm, with a median of 8.9 ppm. The concentrations had been compared to the value of the median, because there is still no ordinance of the limited values for radioactive elements in soils. The increased concentrations are mainly related to the western, southwestern, southern and southeastern parts of the researched area. The geological settings (lignite, quartz sands and sandstones) can be genetically correlated with increased thorium concentrations and may be one of the sources of the soil contamination. Another potential source of soil contamination is the thermal power plant "Tuzla", that burns coal, where the ash and slag are deposited in its immediate vicinity. Also, the large number of individual home furnaces, which are using fossil fuels (lignite and brown coal) and are contributing to the soil contamination shouldn't be ignored.
Key words: radioactive element (Th), soil, increased concentrations, environment, Tuzla.

INTRODUCTION

The area of Tuzla geographically belongs to the region of north-eastern Bosnia, i.e. to the subregion of the Spreča-Majevica region. Tuzla is located in the valley of the Jala river. From the northeast, it's surrounded by medium high mountain morphostructure of Majevica, and from the south by the Spreča valley. The urban area of Tuzla is located between 18°56' and 18°79' E and 44°48 'and 44°60' N, at an altitude from 202 and 480 m. The urban area of Tuzla covers about 98.37 km^2 and it's located on the northern slope of the Dinarid mountain system, and is generally mildly tilted towards the Gornja Spreča valley (Stjepić Srkalović, 2015). There are about 110,979 inhabitants living in 66 settlements in this area (Census, 2013).

The area of Tuzla and it's wider surrounding is marked by the processes of urbanization and deruralization, industrialization and deagrarization, which are contributing mostly to the pollution, degradation and devastation of soil (Stjepić Srkalović, et al, 2016). Due to the correct data interpretation, the geological and pedogeographic characteristics of the researched area had to be considered.

The main goal of the research was to determine to what extent the urban area of Tuzla is contaminated with the radioactive element thorium (Th). It is a lithophile element, but it can also be dispersed in the environment by burning fossil fuels (especially coal), by metallurgic processes for high-temperature materials, IT technology, etc. Thorium is a

radioactive element that deposits in the bones and can cause bone cancer, even years after exposure. Thorium compounds are moderately toxic.

The thorium concentrations given and discussed in the paper are a part of the results obtained within the scientific-research project "Concentration of heavy metals in the city of Tuzla soil" supported by the Federal Ministry of Education and Science.

GEOLOGICAL SETTINGS AND PEDOGEOGRAPHIC CHARACTERISTICS

Geological settings

The oldest structures belong to the Tuzla's lower miocene formations in which organogenic limestones are prevailing ("slavinovićki" limestones and dolomites) with sporadic marls. Above them, the clasts were deposited with characteristic reddish coloring sandstones and conglomerates, building the "red" series. The continuation of the sedimentation cycle is made of a "trakasta" series, where the salt formation with accompanying dolomite, anhydrite and tufts are developed. The organogenic limestones, clays, marly clays, sands and subsidiary conglomerates are belonging to the youngest miocene products. The development of the lower pliocene is characterized by the deposition of several seams of lignite (main, base and top seams). Vertical development of the pliocene formation has the characteristics of rhythmicity: quartz sand, clays (slate and alevrite) and lignite. Quaternary formations were developed along the streams in the form of proluvial depositions (debris) and as precipitated terrace and alluvial sediments (sand and pebbles) (Fig. 1) (Čičić, 1988, Stjepić Srkalović, et al. 2017).

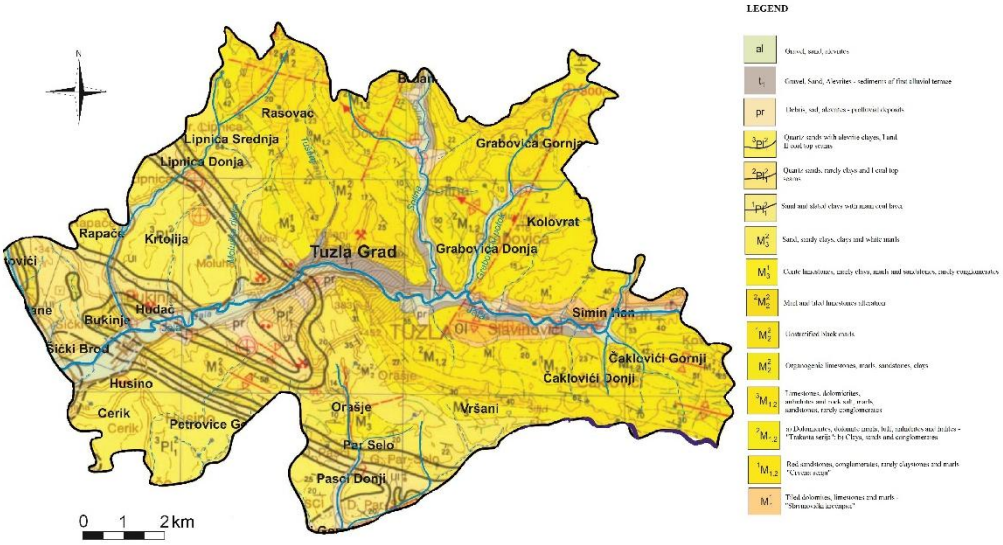

Fig. 1: Geological map of the Tuzla's urban area (Čičić, 1988).

Pedogeographic characteristics

On the pedological map (R - 1: 50 000) of the Tuzla's urban area, there are 16 (mostly automorphic) soil types (Stjepić Srkalović, 2015) (Fig. 2). The most common types of soil in the researched area are yellowish-brown soils on sands and sandstones, brown degraded soil on clays and loams, brown medium deep and deep soil on limestones, grey-brown carbonate soil, grey-brown deeply-soaked soils, pelosols and vertisols. It should be noted that high percentage of this soils is covered with urban infrastructure and isn't used for agricultural purposes.

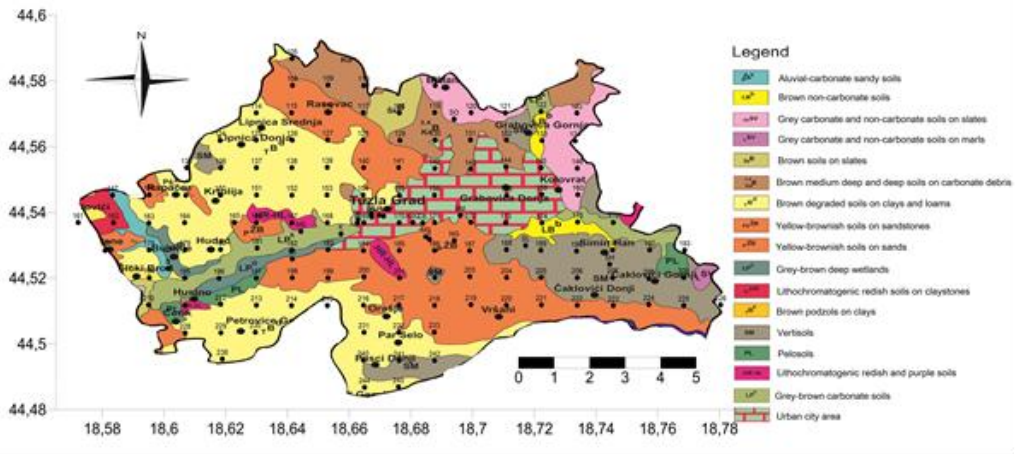

Fig. 2: Pedological map of the Tuzla's urban area

METHODS AND RESEARCH RESULTS

Research methods

The methods of research and laboratory testing included the analysis of previous research findings, terrain observation, sample preparation for laboratory testing, laboratory research and textual and graphical processing of results.

Terrain work was based on soil sampling (129 samples) from the area of about 100 km^2 (urban part of Tuzla) (Fig. 3). The samples were collected according the composite sampling scheme (Fig. 4), i.e. 5 subsamples collected from the corners and the center of the square made 1 sample. Samples were taken from a depth of about 30 cm and stored in PVC bags with the specified number, location, coordinates and other data.

Soil sampling was conducted according to the geochemical expert group (The Urban Geochemistry Project (URGE)) (Ottesen, et al, 2008).

Preparation of soil samples for laboratory analysis (sowing, drying, grinding, weighing) was carried out on the Faculty of mining, geology and civil engineering of the University of Tuzla.

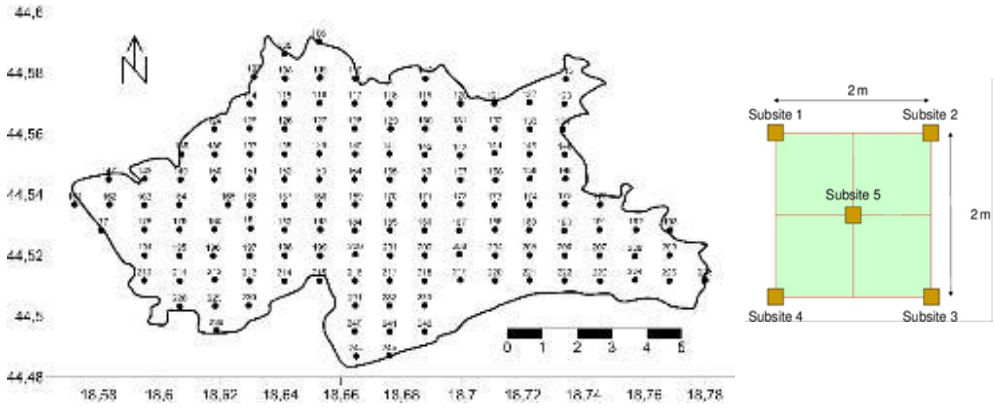

Fig. 3, 4: Sample locations and soil sampling scheme

Laboratory analysis was performed at Bureau Veritas Commodities Canada Ltd., Laboratory in Vancouver - Canada, by Ultra trace ICP-MS method (Inductively Coupled Plasma - Mass Spectrometry), code MA250. The detection limit of this method for thorium is 0,1 – 4.000 ppm.

The graphical processing of the results was made in the Golden Software Surfer 12 software package.

Research results

Thorium concentrations were analyzed in 129 soil samples collected in the urban part of Tuzla and shown in Table 1. Graphic display of the thorium concentration in the soil of the urban part of Tuzla is shown in Fig. 5.

Table 1. Thorium (Th) concentrations in soil of Tuzla's urban area

Sample No.	Th in ppm	Sample No.	Th in ppm	Sample No.	Th in ppm	Sample No.	Th in ppm
105	5.5	142	**10.4**	175	**9.0**	207	6.6
108	6.6	143	6.2	176	7.2	208	7.4
109	6.3	144	8.8	177	6.3	209	8.5
110	8.0	145	**11.8**	178	**14.6**	210	**10.7**
112	6.7	146	**9.7**	179	8.1	211	8.8
114	8.4	147	**9.0**	180	8.3	212	**13.3**
115	6.8	148	**12.4**	181	8.9	213	**13.3**
116	5.4	149	**9.9**	182	7.3	214	**11.3**
117	8.8	150	**12.5**	183	**9.6**	215	**12.8**
118	6.0	151	**10.6**	184	8.5	216	**12.6**
119	9.8	152	**10.3**	185	8.1	217	8.3
120	6.8	153	8.3	186	8.5	218	**11.3**
121	7.1	154	6.6	187	7.7	219	**9.1**

122	7.7	155	6.4	188	**9.1**	220	8.3
123	7.7	156	8.5	189	6.0	221	8.8
124	7.6	158	**9.2**	190	**9.6**	222	**9.2**
125	4.9	159	**9.5**	191	8.0	223	**9.1**
126	7.5	160	**10.9**	192	7.5	224	**15.0**
127	8.0	161	**11.8**	193	**10.3**	225	**9.8**
128	**10.5**	162	**12.3**	194	7.9	226	**9.9**
129	**9.2**	163	**10.5**	195	6.6	228	**15.6**
130	7.1	164	**10.9**	196	**10.5**	229	**15.6**
131	7.4	165	7.0	197	8.3	230	**13.7**
132	6.6	166	**9.9**	198	**12.2**	231	**13.0**
133	**11.3**	167	**10.8**	199	**12.4**	232	**9.5**
134	6.3	168	**9.7**	200	**9.2**	233	**12.7**
135	9.2	169	**10.1**	201	8.5	238	**12.5**
136	8.1	170	**9.0**	202	6.4	240	**9.5**
137	**9.1**	171	8.5	203	7.1	241	**10.2**
138	8.4	172	8.7	204	**9.9**	242	**11.7**
139	8.0	173	8.7	205	8.4	244	**9.5**
140	6.9	174	**9.8**	206	8.2	245	**9.5**
Median							8,9
Avg.							9,18

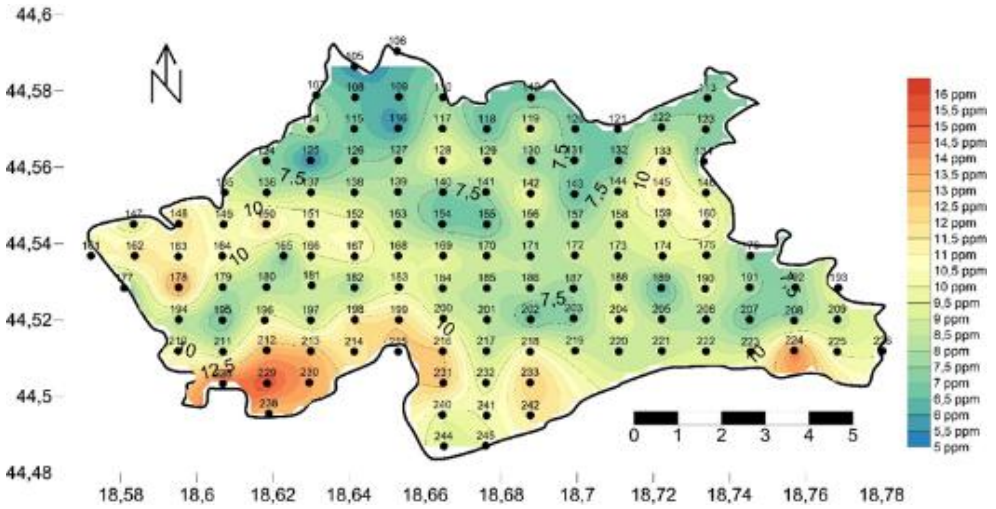

Fig. 5: Thorium concentrations in Tuzla's urban area soil samples

DISCUSSION

Thorium (Th) is a radioactive actinoid metal. The average thorium content in the magmatic rocks is of a wide range (ultramafites -0.005 ppm, neutral rocks -7 ppm and acid rocks -18 ppm). In sedimentary rocks, the average content of thorium for sand is 5.5 ppm, while in carbonate rocks it is 1.7 ppm (Šorša, Halamić, 2014).

Thorium can be found in a seventy-one mineral, of which four minerals contain more than 70% of thorium (thorianite - ThO_2; thorogummite -$Th(SiO_4)_{1-x}(OH)_{4x}$; hutonite - $ThSiO_4$ and thorite - $ThSiO_4$). The highest content of the thorium is in the thorianite - 87.88% (Emsley, 1991).

Considering that thorium mostly appears in alteration-resistant minerals, its geochemical mobility is very small (Šorša, Halamić, 2014). The average value of thorium in soils is about 13 ppm. In soils, it's mostly accumulated from the parent rocks (geological settings) (Halamić, Miko, 2009).

The range of thorium concentrations in the investigated area is in the range from 4.1 to 15.6 ppm, with a median of 8.9 ppm (Tab. 1 and Fig. 5). The increased concentrations, in relation to the median, were determined in 62 samples collected in the Tuzla's urban area. The maximum concentrations of thorium were recorded in the western, southwestern, southern and southeastern parts of the researched area. Soil samples No. 228 and 229 (southwestern part of the investigated area) have reached a thorium concentration of 15.6 ppm, while in 33 samples the thorium concentrations were from 10 to 15 ppm.

The increased concentrations of thorium at these sites may be due to the geological settings of the terrain, i.e. the composition of the parent rocks that directly affects the soil composition. The parent rocks are characterized by the alteration of lignite and poorly bounded quartz sand, which can be genetically linked to radioactive elements.

The soils which had been developed on this parent material are alluvial-carbonate sandy soils (Bukinje, Šićki Brod), brown degraded soil on clay and loams (Petrovice Gornje, Par Selo, Pasci Donji), yellowish-brown soils on sands and sandstones (Par Selo, Čaklovići Donji) and vertisols (Pasci Donji, Čaklovići Donji) (Fig. 2). It is evident that most of the sites are located above the coal layer, which can also be the cause of increased thorium concentrations in soil samples.

Also, the anthropogenic influence on dispersion of this radioactive element into the environment, i.e. by burning fossil fuels shouldn't be ignored. Into the environment, this metal is scattered by fossil fuels combustion (especially coal), by the usage in metallurgy, IT technology, etc. All types of coal are naturally radioactive. The members of the Uranium (U) and Thorium (Th) series are concentrated by burning in thermal power plants at about 1,700°C (Kovač, Marović, 2008). The main increase of natural radioactivity, that is contained in coal, is generated during its combustion in thermal power plants. Because of the concentration of radionuclides in ashes and slag, there is a significant environmental pollution caused by natural radionuclides, i.e. by the technologically conditioned increase of natural radioactivity (Kljajić, et al, 1995). The urban area under slag and ashes is not insignificant, especially when considering that it has a negative effect, not only on the ground below the landfill, but also within a radius of 5km. One of the additional problems is the position of these landfills, which are in the valleys of the streams and rivers, and as recipients, they transport pollutants downstream (Stjepić Srkalović, et al, 2016).

The production process of the power plant "Tuzla" and the uncontrolled burning of coal in a large number of individual home furnaces, combined with meteorological

conditions (thermal inversions), i.e., wind directions, have an impact on increasing the concentration of thorium in this area.

The dispersion of the pollutants depends on the wind speed and intensity. According to the annual values, the highest wind frequencies that are occurring in the area of Tuzla valley are the northeastern winds, which are represented by 17.5% and the southwestern winds with 13% (Tab. 2).

Table 2. Frequencies and medium speeds of certain wind directions in the Tuzla valley

Pravac	N	NE	E	SE	S	SW	W	NW	C
%	11,2	17,5	5,8	4,9	3,9	13,0	8,7	4,3	30,6
m/s	1,5	1,4	1,3	1,6	1,8	2,0	1,6	1,3	

Data source: Meteorološki godišnjaci, FHMZ, Sarajevo.

Figure 5 indicates that the elevated concentrations are mainly in the surrounding of the power plant "Tuzla". The elevated thorium concentrations in samples No. 148, 149, 150, 151, 152, 162, 163, 164, 167 and 178 (from 9.9 to 14.6 ppm) are related to samples taken near landfills and slags of Divkovići I and II, indicating that these areas, even after recultivation pose a threat to the environment and human health.

Elevated thorium concentrations in the southern part of the investigated area (samples No. 212, 213, 214, 215, 216, 222, 223, 224, 225, 226, 228, 229, 230, 231, 232, 233, 238, 240, 241, 244, 245) ranging from 9.1 to 15.6 ppm (Fig. 5, tab. 1) are related to samples taken near power plant "Tuzla" and the open pit mine "Dubrave", from which, they were most probably scattered by air streams into the surrounding areas and deposited in the soil.

CONCLUSION

Thorium concentrations were analyzed in 129 soil samples, collected in the urban part of Tuzla. The thorium concentration is in the range from 4.1 to 15.6 ppm. Since the legal regulations on soils on the territory of Bosnia and Herzegovina (and beyond) have no limited values for any radioactive element, the value of the median (8.9 ppm) was taken as the limiting boundary.

The increased concentrations in relation to the median, were determined in 62 samples, collected in the urban area of Tuzla. The maximum concentrations of thorium were recorded in the western, southwestern, southern and southeastern parts of the researched area.

One of the potential sources of thorium is certainly the parent rock (lignite, poorly bounded quartz sands) that are genetically linked to radioactive elements. Another source is of anthropogenic character, and is related to the combustion of fossil fuels in power plant "Tuzla", as well as the surrounding individual facilities with furnaces, which can be seen in the paper results. This source of contamination is also indicated by a network of increased concentrations in samples, located in the western and southern parts of the researched area.

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SUMMARY

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