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COPPER (Cu) DISTRIBUTION IN TUZLA'S TOPSOILS

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ABSTRACT

The main goal of the research was to determine to which extent the copper (Cu) is dominant in the topsoils of Tuzla's area. Considering the defined goal, the detailed soil analyze for the presence of this element in the area of Tuzla, was carried out. The terrain work was based on soil sampling (240 samples) from the area of about 303 km^2. The sampling network for the urban part of the town was 1x1 km, and for the rural part 1,5x1,5 km and according to URGE instructions. The Cu concentrations are obtained by the most sophisticated laboratory method (ICP-MS), with a highly sensitive detection threshold (0.02 to 10,000 ppm). Elevated concentrations of copper in the Tuzla's topsoil are recorded in 64 samples. The copper concentrations in these samples ranges from 50 ppm to 156,1 ppm. Highly exceeded concentrations are recorded in samples No: 64, 66, 163, 170, 171, 182, 187, 195, 214 and 249a, located mostly in the western part of the Tuzla. The increased concentrations copper are primarily a consequence of anthropogenic impacts in enviroment.

Key words: *copper (Cu), soil, concentration, distribution, Tuzla.*

INTRODUCTION

The area of the city 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. Tuzla's area is located between 18°55' and 18°9' E and 44°48 'and 44°67' N, at an altitude from 200 m at the lowest point at the Jala riverbed up to 600 m at the east and northeast border of the city. The area of Tuzla covers about 303 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. There are about 110,979 inhabitants living in 66 settlements in the researched area [1].
The soil pollution, degradation and devastation is a result of urbanization and deruralization, industrialization and deagrarization processes, which are contributing mostly to Tuzla city and its wider surroundings. The geological and pedogeographic characteristics of the researched area had to be considered, due to the correct data interpretation.

The main goal of the research was to determine to which extent the copper (Cu) is dominant in the soil of Tuzla's area. Considering the defined goal, the detailed soil analyze for the presence of this element in the area of Tuzla, was carried out. On the research results basis of the presence and quantity of the mentioned element, it has been concluded that the copper concentrations have been exceeded in the central and western parts of the researched area.

Pollution generates heavy metals contamination for urban and agricultural soils. Heavy metals also occur naturally, but rarely at toxic levels. Potentially contaminated soils may occur at old landfill sites (particularly those that accepted industrial wastes), old orchards that used insecticides containing arsenic as an active ingredient, fields that had past applications of waste water or municipal sludge, areas in or around mining waste piles and tailings, industrial areas where chemicals may have been dumped on the ground, or in areas downwind from industrial sites [2]. When using the contaminated soil to produce food by various crop plants, as the easy entry of these elements in the food chain, which increases the risk to human health [3].

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 "layered" 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.

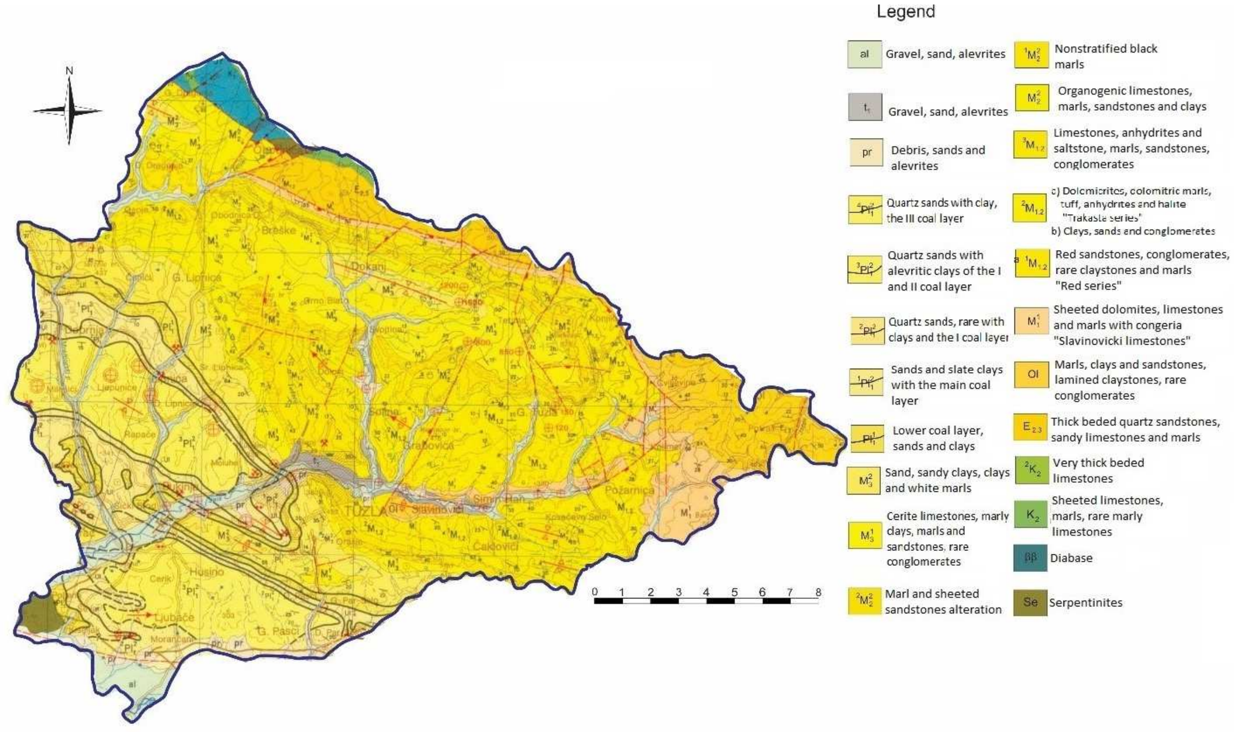

Figure 1 Geological map of the Tuzla's area

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) (Figure 1) [4].

Pedogeographic characteristics

On the pedological map (R - 1: 50 000) of the Tuzla's urban area, there are 25 (automorphic and hydromorphic) soil types [1,5] (Figure 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.

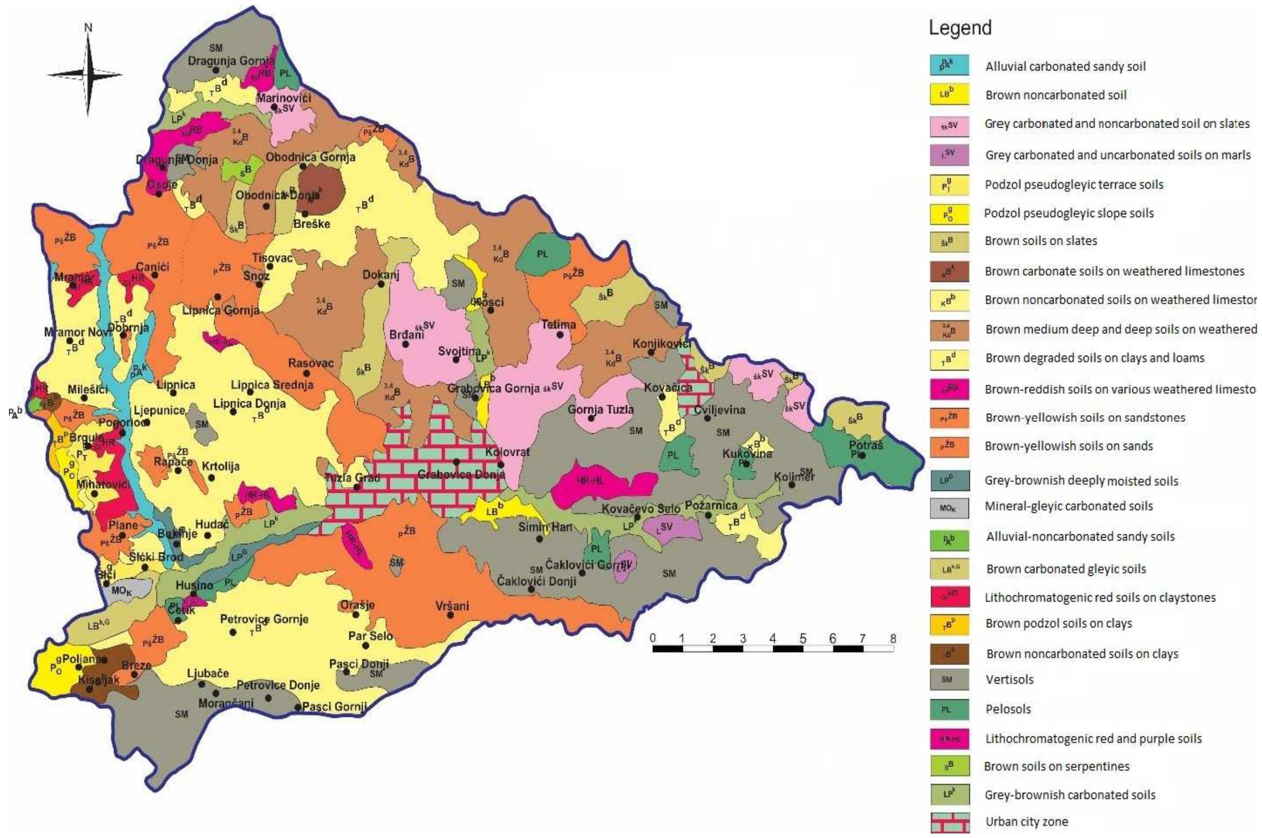

Figure 2 Pedological map of the Tuzla's area

Accumulation of copper in soils is mainly due to anthropogenic origin, such as mining or industrial activities. Agricultural use of products containing copper is also common, especially in pesticides applied in vineyards and orchards [6].

Deep sandy and light loamy soils are much more likely to be Cu deficient than medium or heavy textured soils. The parent material forming these soils may contain low Cu concentrations. Cu is strongly bound to organic matter too. As organic matter increases, the probability of Cu deficiency increases. Manure and straw from previous crops can also tie up Cu. Copper availability is also reduced as pH increases [7].

According to *„Pravilnik o utvrđivanju dozvoljenih količina štetnih i opasnih tvari u zemljištu i metode njihovog ispitivanja"* the highest allowed concentration of copper in sandy soils is 50 ppm, in silty-loam soils 65 ppm and in clayey soils is 80 ppm (Table 1). In Bosnia and Herzegovina, for organic agriculture the limited value of the copper in the soil is 50 ppm, and maximally allowed concentration of copper in organic fertilizers is 300 ppm [8].

Table 1 The limited values of copper concentrations in soil

Heavy metal	Sandy soil (ppm)	Silty-loam soil (ppm)	Cleyey soil (ppm)
Cu	50	65	80

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 (240 samples) from the area of about 303 km^2 (within the borders of the city of Tuzla) (Fig. 3). The sampling network for the urban part of the town was 1x1 km, and for the rural part 1,5x1,5 km. The samples located near the east border of Tuzla (southwestern slopes of the Majevica Mt.) were not collected due to mines. Samples marked with an "a" after an order number (246a-268a) are control samples taken mostly near schools in the urban part of Tuzla.

The samples were collected from the designated locations by a process of composite sampling. Five soil subsamples were taken and mixed together at each sampling (Figure 4). Samples were taken from a depth of about 30 cm and stored in PVC bags with the specified number, location and coordinates. These composite soil samples, weighing about 0.5 kg each, were dispatched to a laboratory and prepared for chemical analyses.

Soil sampling was conducted according to the geochemical expert group (The Urban Geochemistry Project (URGE)) [9].

The 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. Laboratory analysis was performed at Bureau Veritas Commodities Canada Ltd., Laboratory in Vancouver - Canada, by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). The limit detection of this method for copper is 0.02 to 10.000 ppm. The graphical processing of the results was made in the Golden Software Surfer 13 software package.

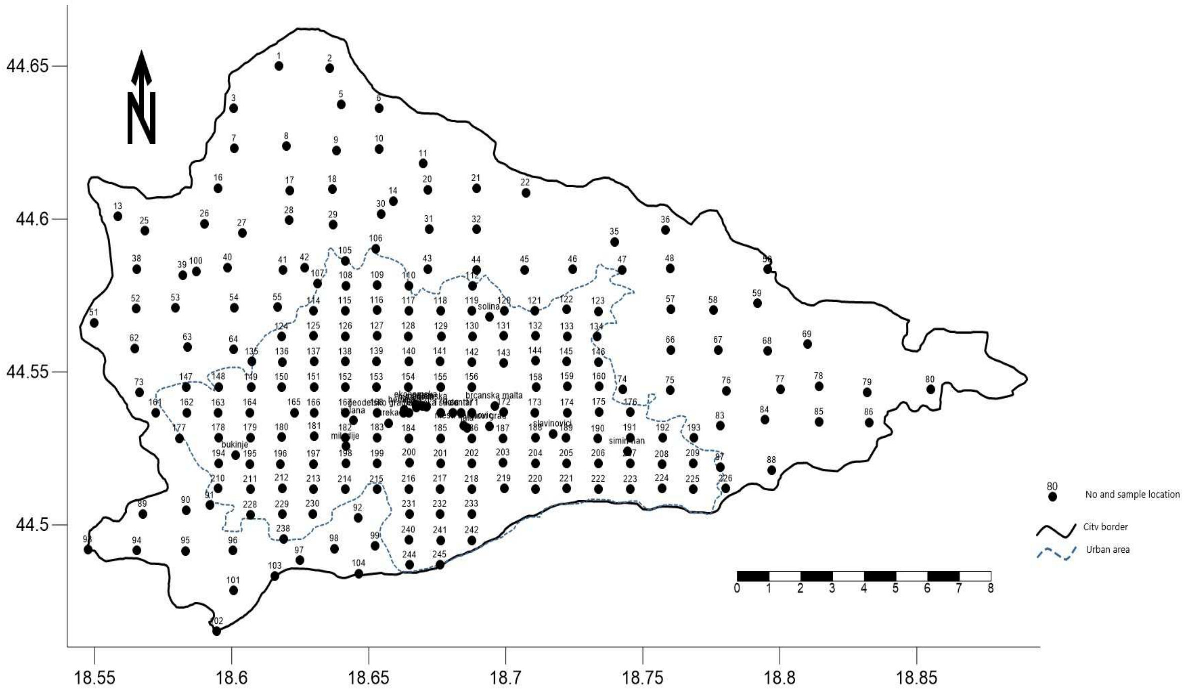

Figure.3 Sample locations

RESEARCH RESULTS

The copper concentrations were analyzed in 240 soil samples collected in the city of Tuzla and shown in Table 2. The map of copper concentrations in the Tuzla's soil is shown in Figure 4.

Table 2 Copper concentrations in Tuzla's topsoil

No.	Cu(ppm)	No.	Cu(ppm)	No.	Cu(ppm)	No.	Cu(ppm)	No.	Cu(ppm)	No.	Cu(ppm)
1	**59.7**	53	**57.6**	106	**60.3**	152	6.1	198	46.2	250a	47.5
2	**64.4**	54	26	107	26.2	153	45.4	199	**68.5**	251a	**61.2**
3	39.6	55	24.4	105	**66.2**	154	37.9	200	**78.7**	252a	**55.2**
5	39.3	57	28.2	108	**53.4**	155	**66.2**	201	23.5	253a	**78.5**
6	**58**	58	28.6	109	**66.5**	156	49.8	202	**53.8**	254a	**58**
7	43.7	59	50.8	110	46.1	158	**55.7**	203	**59.6**	255a	**61.2**
8	46.3	62	39.8	112	37.2	159	**50.3**	204	43.9	256a	45.2
9	25.5	63	27.4	114	24.4	160	44.3	205	41.9	257a	36.5

10	40.1	64	**136.6**	115	**56.7**	161	32.6	206	**57.1**	258a	30.2
11	25.5	66	**85.5**	116	**67.4**	162	26.7	207	41.3	259a	**53.8**
13	10.1	67	28.1	117	42.3	163	**115.1**	208	**53.5**	260a	42.3
14	26.5	68	46.8	118	51.2	164	**59.7**	209	38	261a	34.4
15	20.6	69	29.2	119	38.9	165	7	210	35.6	262a	43.8
16	35.4	71	34.6	120	**65.9**	166	27.4	211	**70.7**	263a	37.7
17	35.9	72	22.9	121	49.6	167	**59**	212	29.7	264a	37.3
18	24.3	73	32.3	122	29.2	168	18.8	213	35.7	265a	47.5
19	30.3	74	34.4	123	42.1	169	24.8	214	**138.7**	266a	**61.2**
19a	38.4	75	41.6	124	7.7	170	**124.4**	215	38.1	267a	**55.2**
20	30.1	76	34.7	125	10.2	171	**99.1**	216	21.6	268a	**78.5**
21	35.8	77	32.8	126	**60.4**	172	48.4	217	**53.7**	Avg	43,52
22	40	78	34.8	127	**52.9**	173	**61.8**	218	26.4		
25	6.8	79	48.2	128	46.5	174	**54.7**	219	**56.2**		
26	39.6	80	26.5	129	40.6	175	**51.1**	220	**61.3**		
27	42	83	36.4	130	**51.8**	176	**58.4**	221	41.6		
28	42.2	84	41.3	131	47.1	177	7.6	222	**60.6**		
29	40	85	50.8	132	49.7	178	42.6	223	44.8		
30	24.3	86	47.3	133	45.6	179	**67.8**	224	19.8		
31	43.8	87	46.2	134	45.4	180	24.3	225	18.4		
32	32.6	88	27.2	135	36	181	35	226	**58.5**		
35	28.8	89	41.3	136	21.7	182	**82.5**	228	32.2		
36	33.9	90	57.4	137	13.7	183	**69.9**	229	26.1		
38	13.9	91	43.9	138	25.3	184	31.7	230	**50.7**		
39	25.2	92	47.9	139	26.5	185	**64.8**	231	33.3		
40	5.3	93	14.2	140	68.2	186	45.2	232	9.9		
41	39.5	94	19.3	141	43.8	187	**99.1**	233	8.8		
42	31.5	95	22	142	43.1	188	39.6	238	21.7		
43	35.5	96	42.2	143	63.7	189	48.7	240	16		
44	22	97	42.3	144	44.5	190	**56.4**	241	38.8		
45	24.1	98	26.2	145	52.5	191	43.1	242	32.2		
46	45.2	99	28	146	38.5	192	28	244	45.8		
47	27.9	100	20.7	147	102	193	43.1	245	**57.4**		
48	**52.8**	101	29.6	148	49.8	194	47.6	246a	**70.6**		
50	**50.8**	102	45.5	149	41.5	195	**156.1**	247a	46.1		
51	30.3	103	29.7	150	26.4	196	50.4	248a	43.7		
52	**73.9**	104	25.1	151	26.3	197	24.3	249a	**116.1**		

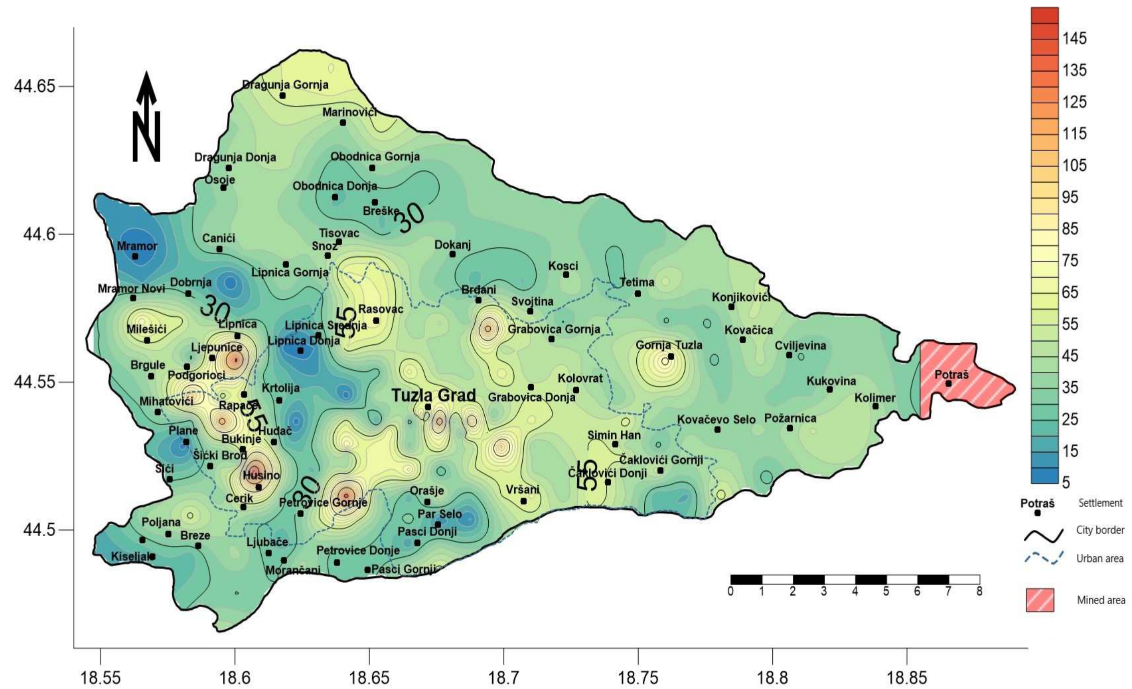

Figure 4 Copper (Cu) distribution in Tuzla's topsoil

DISCUSSION

Copper is a metal that occurs in four oxidation states (Cu, Cu^{1+}, Cu^{2+}, and Cu^{3+}) with Cu^{2+} being most common. The atomic number and atomic weight of copper are 29 and 63.546, respectively. Copper has a specific gravity of 8.96 g/cm^3 at 20°C, a melting point of 1083°C, and a boiling point of 2695°C [10].

Copper concentrations in soil vary considerably with soil type, soil amendments, distance from anthropogenic sources, distance from natural ore bodies, and composition of bedrock and parent material among other factors. In igneous rocks its average content is 55 ppm (ultramafic rocks 10 ppm, basalts 87 ppm, granodiorites 30 ppm and granites 10 ppm). The average content in shales is 45 ppm, in sandstones 5 ppm and in carbonates 4 ppm (Table 3) [10].

Concentration of copper in soils varies from 2 to 250 ppm, with median of 30 ppm. The quantity of Cu in the soil significantly depends on climate characteristics – the greatest concentrations are registered in tropical regions (laterite soils) and the smallest in temperate and cold climate zones. Major content of copper is registered in loamy soils while sandy soils contain relatively lower quantities of this element. Concentration of copper in soils is regulated both by pH values and the content of organic matter [11].

Table 3 Concentrations of Cu in rocks

Rocks					
igneous	Cu (ppm)	sedimentary	Cu (ppm)	metamorphic	Cu (ppm)
ultramafic	10	sandstones	5	shale	45
basalts	87	carbonates	4		
granodiorite	30				
granite	10				

Copper belongs to the substances which are essential for human health, e.g. by being part of enzymes involved in specific metabolic processes. However, it may be harmful in higher doses by causing gastrointestinal distress, damage to liver, the immune system, neurological system and reproductive ability [12].

Copper is strongly adsorbed to soil particles and therefore has very little mobility relative to other trace metals [13]. As a result of this limited mobility, applied copper tends to accumulate in soil [14]. Soil types have finite holding capacities for copper ions, and leaching can occur when the copper levels applied exceed this capacity [15].

Accumulation of copper in soils is mainly due to anthropogenic origin, such as mining or industrial activities. Agricultural use of products containing copper is also common, especially in pesticides applied in vineyards and orchards. This might be a reason, why soil samples with high Cu concentrations can be found in the countries of the Mediterranean, where these land uses are common. Although most crops take up and accumulate Cu in small quantities only, continuous exposure to Cu in food may cause negative health effects in humans [6].

Copper has a broad application both in industry and other economy branches. It is used for production of water-pipe and hydronic tubes, copper wires, electromagnets, roof plates, statues, coins, etc. besides, copper is widely used in agriculture (mineral fertilizers and pesticides) and as food supplement for poultry and cattle.

Its impact on environment comes trough the processes of melting, trough industrial dust, waste, and application of chemicals (for instance, fungicides in agriculture). The sources of atmospheric pollution by copper are foundries, metal and non-metal ores, combustion of fossil fuels, cast houses, cement factories and waste mud [11].

Elevated concentrations of copper in Tuzla's topsoil are recorded in 64 samples. The copper concentrations in these samples ranges from 50 ppm to 156,1 ppm. Highly exceeded concentrations are recorded in samples No: 64, 66, 163, 170, 171, 182, 187, 195, 214 and 249a, located mostly in the western part of Tuzla. The highest registered concentration of copper is 156,1 ppm (sample 195) located near the thermal power plant, and it is two times higher then allowed.

By inspecting the spatial position of the analyzed samples, it can be specified that the elevated copper concentrations are recorded close to the roads, urban infrastructure, slag and waste depot and the thermal power plant, implying that a source of pollution is mostly anthropogenic.

On all other samples, copper concentrations are ranged from 5,3 ppm to 50 ppm, which is in the range of the limited values for this element. Considering that the geological substrate is mostly made of limestones and sandstones, that are poor in Cu (Table 3), it's evident that copper in Tuzla's topsoil came elsewhere. It's interesting that there is no big difference regarding the soil type, because the copper content in the investigated area varies in sandy and loamy soils as well, which also implies on anthropogenic activities as a source of pollution.

CONCLUSION

The copper concentrations were analyzed in 240 soil samples collected in the city of Tuzla. Samples were taken in a proper network (1x1 km in the urban part, and 1,5x1,5 km in the rural part of the town), on the area of about 303 km^2. The results of the soil analysis are processed in the Golden software Surfer 13 package and are displayed as a contour map. On the aforementioned map it is apparent that the range of Cu concentration in the investigated area ranges from 5,3 ppm to 156,1 ppm, with an average of 43,52 ppm.

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