CADMIUM (Cd) DISTRIBUTION IN TUZLA TOPSOIL

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The paper presents the results of geoecological-pedological researches of cadmium (Cd) concentrations in the topsoil of Tuzla. The main goal of the research was to determine the extent to which the area of the city of Tuzla is contaminated with cadmium and to determine the origin of pollutants. The terrain investigations were based on collecting 264 soil samples, covering an area of 303 km^2. The cadmium concentrations in soil samples was determined by mass spectrometry (ICP-MS) with a detection range of 0.02 – 4,000ppm. Exceedance of the maximum permitted concentrations of cadmium, defined by the Ordinance of the determination of permitted amounts of harmful and dangerous substances in soil and methods of their testing, was recorded in soil samples number: 66, 87, 106, 109, 115, 116, 120, 121, 179, 220 and 252a .

The range of exceeded cadmium concentrations is <0.02 - 4.62 ppm, and the average value is 0.515ppm. The highest concentration of cadmium was recorded in sample 116 (4.62 ppm), which was collected in the immediate vicinity of the city landfill. Higher concentrations of cadmium were recorded near the slag and municipal waste landfill, main roads, open mine pit "Dubrave" and on certain areas used for agricultural purposes, which shows that the sources of contamination with these element are a result of human activity in the researched area.

Key words: cadmium (Cd), pollution, soil, 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 Dinaric mountain system and is generally mildly tilted towards the Upper Spreča valley. There are about 111,000 inhabitants living in 66 settlements in the researched area (Stjepić Srkalović, 2015., Popis stanovništva, 2013.).

The geological base of the soil implies the surface of the rock from which the soil is created and developed under the influence of several factors. Soil material can be produced by any rock, provided that it is on the surface and is thus subject to physical, chemical and biological influences that lead to the disintegration of its surface layer (Ćirić, 1991.).

For a longer period, the area of the city and the wider surroundings of Tuzla has been marked by processes of urbanization and deruralization, industrialization and deagrarization, which has largely contributed to soil pollution, degradation and devastation (Stjepić Srkalović, et al, 2016.).

The main goal of the research was to determine the extent to which the area of the urban part of Tuzla is contaminated with heavy metals, primarily cadmium (Cd). Cadmium enters the environment through waste, decomposition of paints and preservatives (Halamić, 2009), phosphate fertilizers, incineration of fossil fuels, traffic, municipal waste and sludge, cement production, etc. and is considered one of the most toxic heavy metals (Brevik, Burges, 2013).

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.

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) (Čičić, et al, 1988.).

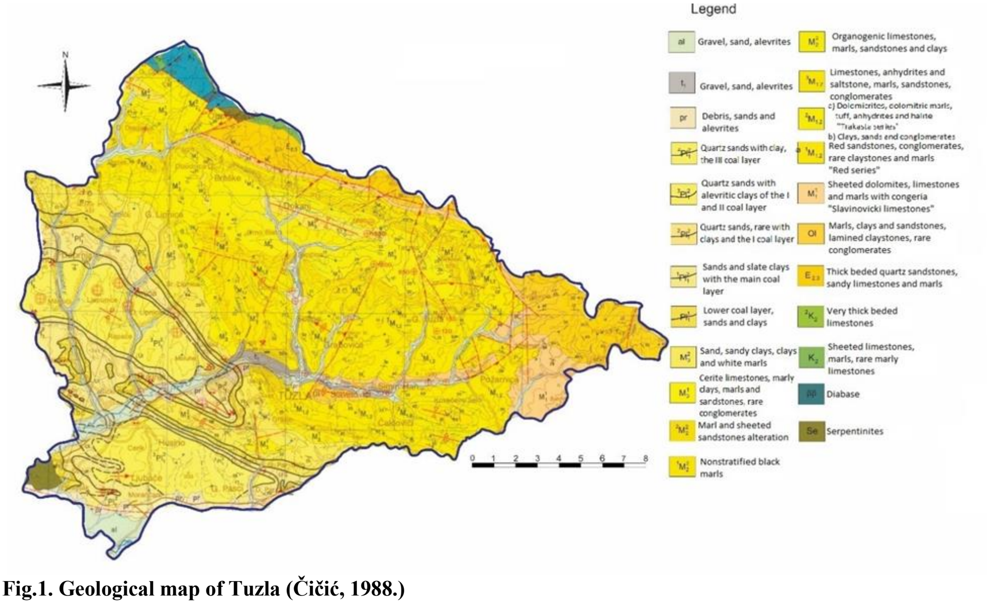

Fig.1. Geological map of Tuzla (Čičić, 1988.)

Pedogeographic characteristics

On the pedological map (R=1:50000) of the Tuzla's urban area, there are 25 (automorphic and hydromorphic) soil types (Stjepić Srkalović, 2015.) (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.

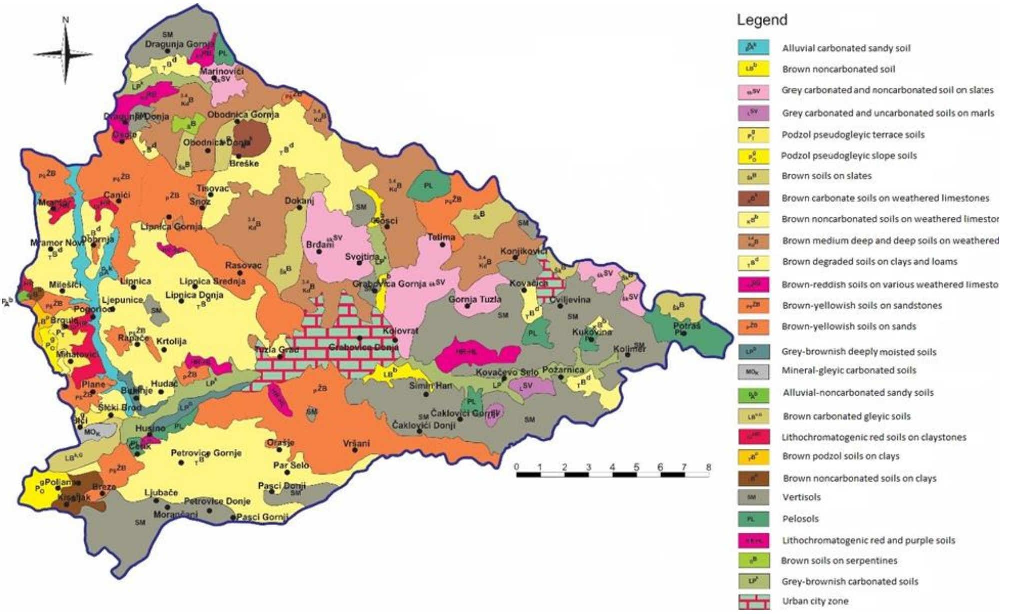

Fig.2. Pedological map of Tuzla

Cadmium is present in the soil as its natural ingredient, where its content is usually 0.1-1.0ppm (Goletić, 2005), with an average content of this element of 0.5ppm (Halamić, 2009). The tolerable level of cadmium content in the soil is 2ppm. Its content in soils is low, but it has a high tendency to accumulate in surface horizons (Goletić, 2005). Soils with a concentration of this element greater than 5ppm result in lower yields (Halamić, 2009).

According to the *"Ordinance on determining the permitted amounts of harmful and dangerous substances in the soil and methods of their testing"*, the maximum permitted concentrations of cadmium in sandy soils are 0.5ppm, in powdery-loam soils 1ppm, while in clay soils the maximum permissible concentrations are 1.5ppm.

METHODS OF RESEARCH

During the research for the paper, various methods were used, such as analysis of the results of previous researches, defining the concept of work and the order of research, terrain researches, preparation of samples for laboratory tests and making thematic maps and tables etc.

Table 1: Limited values for Cd depending on soil texture for FB&H *(according to Ordinance).*

Teški metal	Pjeskovito tlo	Praškasto-ilovasto tlo	Glinovito tlo
Kadmij (Cd) u ppm	0,5	1	1,5

Field work included the collection of soil samples (240 samples) from 303 km^2 (within the city borders of Tuzla). The sampling network in the urban part is 1km x 1km, and in the rural part 1.5km x 1.5km. Samples in the far eastern part of the study area were not collected because the area was mined. Samples marked with "a" after the ordinal number (246a-264a) are control samples collected near schools in the urban part of the city 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)) (Ottesen, et al 2008.).

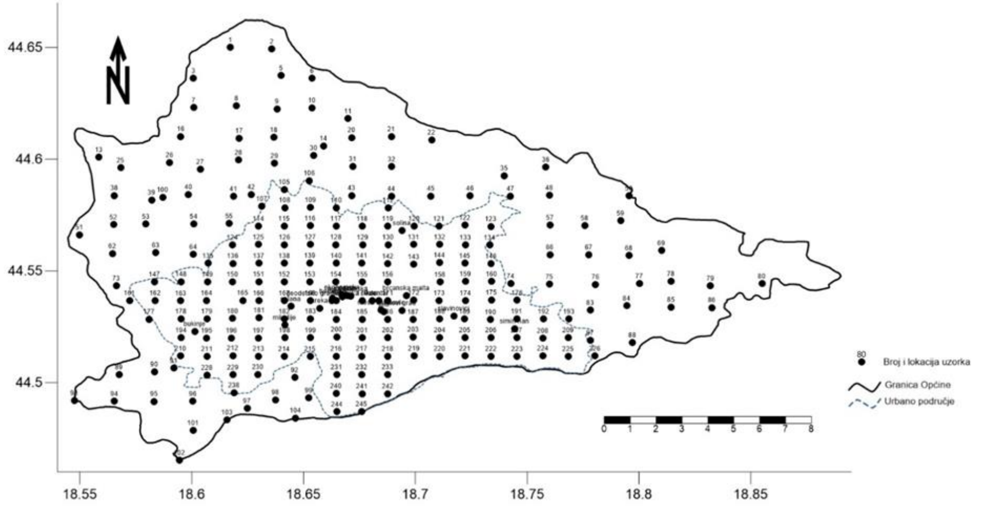

Fig. 3. Sample locations

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 cadmium is 0.02 ppm – 4,000 ppm. The graphical processing of the results was made in the Golden Software Surfer 16 software package.

RESEARCH RESULTS

Cadmium concentrations were analyzed in 240 soil samples collected in the Tuzla city area and are shown in Table 2. A graphical representation of Cd concentrations in the soil of the Tuzla city area are shown in Figure 4.

Table 2: Cadmium concentrations in soil of Tuzla

No.	Cd ppm	No.	Cd ppm	No.	Cd ppm	No.	Cd ppm	No.	Cd ppm	No.	Cd ppm
1	0,09	53	0,34	106	1,79	152	0,09	198	0,4	250a	0,66
2	0,05	54	0,21	107	0,27	153	0,62	199	0,55	251a	0,71
3	1,09	55	0,47	105	1,08	154	0,32	200	0,48	252a	1,6
5	0,76	57	0,67	108	0,71	155	0,7	201	0,24	253a	0,82
6	0,09	58	0,61	109	2,07	156	0,41	202	1,64	254a	0,58
7	0,25	59	0,36	110	0,32	158	0,42	203	0,52	255a	0,61
8	0,14	62	0,48	112	0,83	159	0,41	204	0,27	256a	0,85
9	0,47	63	0,12	114	0,09	160	0,35	205	0,3	257a	0,63
10	0,68	64	0,46	115	2,37	161	0,21	206	0,44	258a	0,59
11	0,22	66	2,89	116	4,62	162	0,19	207	0,31	259a	0,67
13	0,12	67	0,68	117	0,47	163	0,38	208	1,1	260a	0,38
14	0,22	68	0,37	118	0,19	164	0,41	209	0,54	261a	0,39
15	0,15	69	0,59	119	0,42	165	0,06	210	0,37	262a	0,51
16	0,35	71	0,29	120	2,37	166	0,32	211	0,27	263a	0,18
17	0,94	72	0,19	121	2,27	167	0,33	212	0,24	264a	0,12
18	0,32	73	0,44	122	0,17	168	0,18	213	0,22	Avg	0,515
19	0,51	74	0,39	123	0,15	169	0,28	214	0,18		
19a	0,39	75	0,48	124	<0,02	170	0,71	215	0,41		
20	0,36	76	0,15	125	0,11	171	1,04	216	0,2		
21	0,26	77	0,14	126	1,31	172	1,42	217	0,22		
22	0,11	78	0,09	127	1,22	173	0,41	218	0,13		
25	0,04	79	0,33	128	0,56	174	0,54	219	1,24		
26	0,16	80	0,26	129	0,34	175	0,33	220	2,41		
27	0,56	83	0,34	130	0,38	176	0,41	221	0,56		
28	1,36	84	0,16	131	0,37	177	0,08	222	1,11		
29	0,11	85	0,25	132	0,26	178	0,34	223	0,31		
30	0,09	86	0,35	133	0,31	179	2,74	224	0,13		
31	1,14	87	1,86	134	0,24	180	0,26	225	0,19		
32	0,39	88	1,27	135	0,14	181	0,56	226	0,4		
35	0,7	89	0,36	136	0,09	182	0,55	228	0,21		
36	0,16	90	0,11	137	0,03	183	0,38	229	0,17		
38	0,08	91	0,25	138	0,24	184	0,38	230	0,31		
39	0,13	92	0,47	139	0,48	185	1,03	231	0,23		
40	0,11	93	0,07	140	0,95	186	0,72	232	0,13		
41	0,38	94	0,05	141	0,41	187	0,81	233	0,09		
42	0,96	95	0,15	142	0,56	188	0,51	238	0,24		
43	0,6	96	0,32	143	0,38	189	0,26	240	0,05		
44	0,12	97	0,83	144	0,38	190	0,35	241	0,2		
45	0,22	98	0,12	145	0,41	191	0,4	242	0,34		
46	0,27	99	0,12	146	0,39	192	0,25	244	0,92		
47	0,22	100	0,19	147	0,82	193	0,49	245	0,23		
48	1,33	101	0,28	148	0,3	194	0,63	246a	0,46		
50	0,25	102	0,29	149	0,46	195	1,14	247a	1,12		
51	0,27	103	0,26	150	0,12	196	0,48	248a	0,6		

52	0,47	104	0,12	151	0,37	197	0,15	249a	1,2		

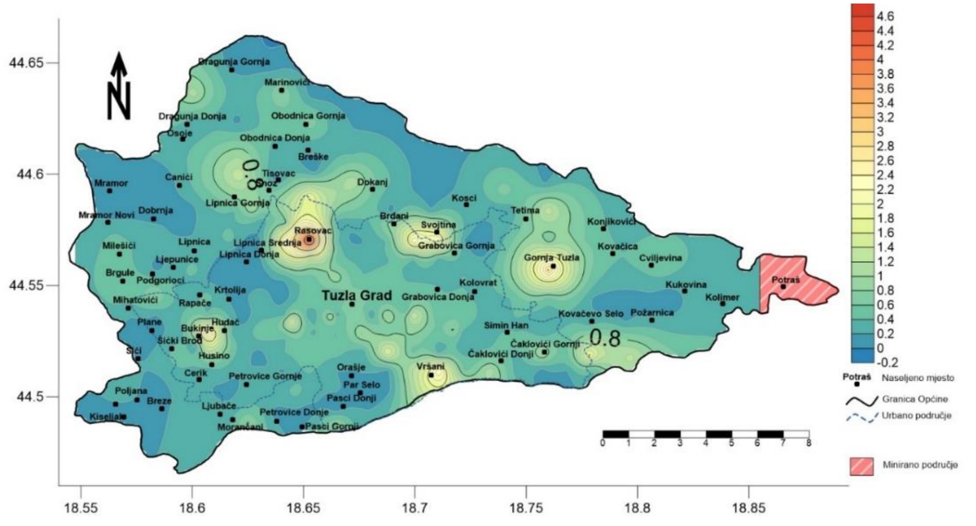

Fig.4. Cadmium (Cd) concentrations in soil of Tuzla

DISCUSSION

Of all the non-essential heavy metals, cadmium is probably the metal that has attracted the most attention in pedological researches because of its potential toxicity to humans. Since the 1960s, scientists have warned of the dangers of cadmium accumulation in the food chain through pollutants i.e. fertilizers. Interest has been further intensified following the contamination of agricultural land in Japan with cadmium-contaminated wastewater, leading to serious human health problems (itai-itai disease) (Mohajer, et al, 2013).

Cadmium (Cd) is a rare chalcophilic element and is ranked 65th in frequency in the Earth's crust. The average cadmium content in igneous rocks is from 0.05 to 0.19 ppm. In shales it is 0.3ppm, in sandstones 0.02 ppm, in carbonates 0.035 ppm and in clays 0.42 ppm. The mean content of this element in soils is 0.5 ppm. The mobility of cadmium is very low and highly dependent on environmental pH values. It is resistant to atmospheric influences. Cadmium is enriched in waste sludge, which is often used as fertilizer in agriculture (Halamić, 2009).

Cadmium does not have any essential biological function, but it is still found in more than 1,000 species of terrestrial and aquatic flora and fauna. It is absolutely the most dangerous heavy metal in the soil and the environment in general. The natural source of cadmium is the parent substrate and it most often appears in the composition of the minerals sphalerite and galena, i.e. as an impurity in sulfide ores of zinc and lead and is obtained as a by-product in their production (Goletić, 2005).

It enters the environment through volcanic emissions, forest fires, as well as anthropogenic emissions from the industry for processing raw materials, traffic, municipal waste and sludge, burning fossil fuels, cement production and used batteries that are disposed of in waste. In developed countries, phosphate fertilizers are the largest anthropogenic sources of cadmium (Halamić, 2009; Brevik, 2013; Goletić, 2005).

In the United Kingdom, cadmium soil contamination through phosphate fertilizers is 4.3 g/ha per year (Johanneson, 2002). The cadmium content in the soil is very low, but has a high tendency to accumulate, especially in surface horizons. The content of cadmium in plants depends on the type of plant, and it is known that it can be translocated from underground to aboveground parts of plants (Goletić, 2005).

Cadmium has been classified as a human carcinogen by several regulatory agencies, as well as by „*The International Agency for Research on Cancer*" (IARC). About 25% of all cancer-related deaths are related to gastrointestinal cancers. Heavy metals such as cadmium pose a risk to human health, as they are non-degradable substances with a wide range of effects. Cd tends to accumulate in the body, most commonly in the kidneys, liver, pancreas, thyroid gland and bones.

Chronic exposure to lower concentrations of cadmium manifests itself in the form of anemia and liver dysfunction. It also affects the nervous and digestive systems and has carcinogenic consequences, especially in children (Mohajer, 2013).

Table 3: Limited values of Cd (in ppm) in soils of developed countries

Države	Kanada	Danska	Finska	Češka	Holandija	Švicarska	Irska	Ist. Europa
Granične vrijednosti za Cd (ppm)	0,5	0,3	0,3	0,4	0,8	0,8	1,0	0,2

Source: http://pubs.sciepub.com/wjac/4/2/3/

Cadmium concentrations in the soil of the city of Tuzla vary from <0.02ppm (sample 124 in the settlement of Lipnica) to 4.62ppm (sample 116), which is the maximum value recorded in the study area.

Cadmium concentrations at several locations exceed the concentrations allowed by the *Ordinance on determining the permitted amounts of harmful and dangerous substances in the soil* (Table 2, Figure 4). The highest measured concentrations of cadmium in the soil were recorded in the area of the settlement Rasovac (samples number: 106, 109, 115 and 116), then in the area of the settlement Svojtina (samples number 120 and 121), in the area of the settlement Bukinje - Hudeč (sample 179), in the settlement Vršani (sample 220) and in Gornja Tuzla (samples 66 and 87).

The samples taken in the direction of the settlement Rasovac - Moluška rijeka, include a sample collected in the immediate vicinity of the city landfill "Desetine", while the sample 179 is located near the landfill slag and ash Divkovići I and II. It should be emphasized that the samples were taken in and around the settlement of Vršani in the immediate vicinity of open pit mine Dubrave. These locations undoubtedly indicate the sources of soil pollution with this element. Other sites with elevated concentrations of Cd are spread throughout the city (urban and rural part), and the causes of pollution can be different, from excessive use of phosphate fertilizers to burning fossil fuels, traffic, etc. All these samples exceed 1.5ppm, which is the upper limit for heavy soils (according to the Ordinance) in Bosnia and Herzegovina. However, if Cd limit values were adhered to in the soils of developed countries

(Table 3), it is clear that a much larger number of samples would exceed the limit values, which is more than worrying given the consequences of long-term exposure to this element.

CONCLUSION

Cadmium concentrations were analyzed on 264 soil samples collected in the city of Tuzla. Samples were collected according to the correct network (1x1km in the urban part and 1.5x1.5km in the rural part of the city), on an area of 303km2. Laboratory analysis was performed at Bureau Veritas Commodities Canada Ltd. laboratory in Vancouver - Canada, by the method of ICP-MS (Inductively Coupled Plasma - Mass Spectrometry), code MA 250. The detection limit of this method for cadmium is 0.02 ppm – 4,000 ppm. The results of the analysis were processed in the Golden software Surfer 16 package and presented by cartographic contouring method. The mentioned map shows that the concentrations of cadmium in the study area are elevated and vary from <0.02ppm - 4.62ppm.

Elevated cadmium concentrations were recorded at a dozen of sites (according to the Ordinance). The highest concentrations were recorded in samples number: 66, 87, 106, 109, 115, 116, 120, 121, 179, 220 and 252a. The highest concentration of cadmium was recorded in sample 116 (4.62ppm), collected in the immediate vicinity of the city landfill and exceeding the permitted value three times.

The number of samples exceeding the allowed values would be drastically higher if they were guided by the instructions of developed countries.

Analyzing the spatial distribution of samples, we can conclude that elevated concentrations of cadmium were recorded near slag and municipal waste landfills, road infrastructure, open pit mine "Dubrave" and in certain areas used for agricultural purposes, which indicates that the sources of pollution by this element are due to human activities in the research area.

Since it is a carcinogenic element, which tends to accumulate in the body, even more detailed research should be conducted on the concentration of cadmium in soil, water, plants and air, in order to reduce carcinogenic diseases in Tuzla.

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