CONTAMINATION WITH HEAVY METALS AND PAH's IN SOIL IN THE CANTON SARAJEVO IN PERIOD 2009-2015

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ABSTRACT

In accordance with the role and importance of which in the world and in our country is attached to soil as a bio production factor, the need to examine and protect soil from contamination is imposed. Heavy metals are very common contaminants of soils. Highly toxic and carcinogenic PAHs are natural components of raw petro chemical compounds. Due to their negative influence on plants and animal world as well as on human population, it is necessary to evaluate and determine heavy metals and PAHs content in soils, especially in ones intended for agricultural production.

In this work, we have examined agricultural and urban soils in the Canton Sarajevo, for content of heavy metals and polycyclic aromatic hydrocarbons. Analyzed samples were in scattered state, taken from a depth of 0-30 cm. The total number of determined soil samples was one hundred and twenty (120), in the period of 2009-2015.

According to determined general chemical characteristics, soils are from slightly acetous to slightly alkaline. According to mechanical texture composition, examined soils have showed the following texture marks by Ehwald: clay and sandy loam.

Using flame/electrothermal atomic absorption spectrometry and gas chromatography with FID detection we have established the content of seven heavy metals and polycyclic aromatic hydrocarbons. In determining the content of heavy metals following methods were used: BAS ISO 11466:2000 and BAS ISO 11047:2000, and for PAHs the method was BAS ISO 18287:2008. Results were compared with the limit values from "Regulation on determining the allowable amounts of harmful and dangerous substances in soils and methods of their examination" specified in Official Gazette of the Federation of B&H, No. 72/09.

Keywords: *contamination, heavy metals, PAHs, AAS method, GC-FID*

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INTRODUCTION

It is a well-known fact that the land is a natural wealth, but unlike other resources such as mineral resources, forests, flora and fauna, his reserves, along with reserves of water and air, were considered to be inexhaustible. However, with the increase in urbanization, we have witnessed a disturbing degree of threat and soil contamination in all spheres of the environment. So, the land did not receive any necessary attention, although symposiums of pedologists have warned the public about the land care, as one of the most important parts of the ecosystem (plant - animal - man - water - air). A modern system of land management as a multifunctional medium, underlines that, in addition to the primary production of biomass, it has a set of other functions/roles, that are the foundation of establishing a balanced system and sustainability. All soil functions are inherent and equally important, and they include: ecological-regulation functions of the soil (receiver, collector and exchanger of various defects), such as: climate-regulation, spatial function, carrier of infrastructure, water purifier, source of genetic resources and biodiversity, landscape design, and the role of soil as a historical media-the development of civilization.

MATERIAL AND METHODS

Our research included the field and laboratory examination and data processing. Researches were carried out in 2009, 2010, 2012, 2013, 2014/15 year. 120 soil samples, from a depth of 0-30 cm, were taken from agricultural and urban land. The main task of the research was to determine the level of contamination of agricultural and urban land with inorganic pollutants: lead (Pb), cadmium (Cd), zinc (Zn), nickel (Ni), chromium (Cr), cobalt (Co) and copper (Cu), and with (PAHs) polycyclic aromatic hydrocarbons as organic pollutants. The limit values were determined in accordance with the Regulation on determining the allowable amounts of harmful and dangerous substances in soils and methods of their examination (Official Gazette of the Federation of B&H, No. 72/09).

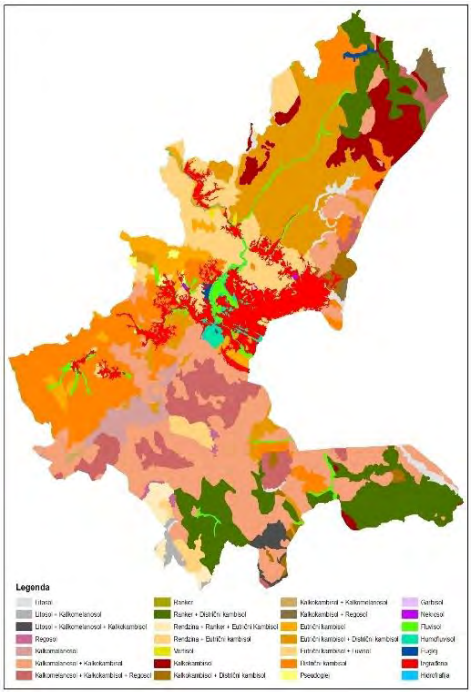


Figure 1. Pedological map of Canton Sarajevo
Source: Čustović et al., 2011

Sarajevo Canton occupies area of 126,994.59 ha, of which agricultural land is 48,118.97 ha, forest is 10,287.38 ha and unfertile land is 10,287.38 ha. The most represented with 90% are the automorphic soils (lithosols, regosols, rendzinas, rankers, mould, calcocambisols, distric cambisols and eutric cambisols). Hydromorphic soils are represented with 10% (fluvisol, pseudogley, semigley and eugley) A study of the use value of the land of the Canton Sarajevo are presented in Figure 1. The climate is continental, semi-humid with an annual average temperature of 9,5^{o}C, and annual average precipitation of 961 mm (according to Lange's rain factor).

RESULTS

Some agricultural and urban soils in the Canton Sarajevo were examined for the content of heavy metals and PAHs. 120 soil samples, taken from a depth of 0-30 cm, were analysed in scattered state. We have shown the average values of the results of the heavy metals content in the soil, analysed by atomic absorption spectrometry (flame/graphite furnace), and the results of the PAHs determination, analyzed by gas chromatography with FID detection. BAS ISO11466:2000 and BAS ISO11047:2000 were used for heavy metals while BAS and ISO18287:2008 for the PAHs determination Values of the results are presented in Tables 1-7 and Graphs 1-5.

Table 1. The textural composition of the soil

Year	The percentage content of soil particles with diameter in mm				Texture mark by Ehwald
	Rough sand 2-0.2	Fine sand 0.2-0.02	Fine Silt 0.02-0.002	Clay < 0.002	
2009	0.38	62.30	23.89	13.42	Sandy loam
2013	13.21	59.82	10.69	9.22	Loamy sand soil
2014/15	8.20	65.71	13.19	12.70	Loamy sand soil

According to the above test results, textural composition of the soil shows no major differences per year, and Loamy sand soil mainly prevails.

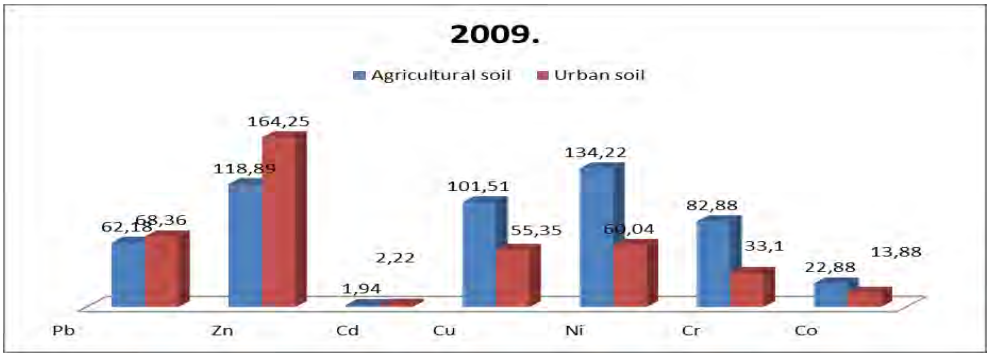
Table 2. General chemical properties of the soil

Year	Type of soil	pH values in		Humus content	$CaCO_3$ content
		H_2O	KCl	in %	in %
2009	Agricultural and urban	6.62	5.66	3.27	0.93
2010	Agricultural and urban	6.40	5.60	2.90	0.45
2012	Agricultural and urban	6.97	5.75	2.78	0.82
2013	Agricultural and urban	6.80	5.67	3.21	0.57
2014/15	Agricultural and urban	8.45	6.87	2.35	0.98

The pH value in H_2O is in the range from 6.40 to 8.45, while in 1MKCl ranges from 5.60 to 6.87. According to Schefter-Schatschabela limit values, soil is mildly acidic to mildly alkaline. The humus content ranges from 2.27% to 3.21%, and according to Gračanin the soil has low to medium humus content. The content of calcium carbonate is from 0.45% to 0.98% and it is a poorly calcareous soil.

Table 3. Average results (in mg/kg) of heavy metals and PAHs in 2009

year	Soil type	Pb	Zn	Cd	Cu	Ni	Cr	Co	PAH
2009	agricultural	62.18	118.9	1.94	101.5	134.2	82.88	22.88	n.d.
	urban	68.36	164.3	2.22	55.35	60.04	33.10	13.88	n.d.
	Limit values	***<150***	***< 300***	***< 1***	***< 100***	***< 60***	***<100***	***< 50***	***< 2***



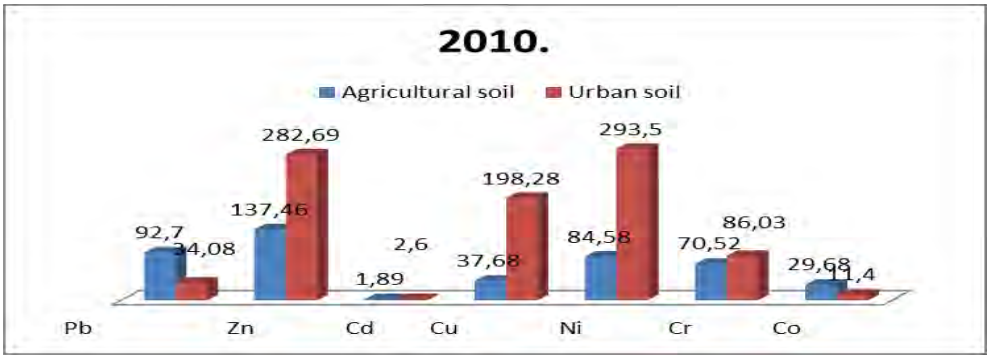
Graph 1. Average results of heavy metals for 2009

- Cadmium content is above the limit value, ranging from 1.94 mg/kg on agricultural soils, and 2.22 mg/kg in urban soils.
- Copper content is above the limit value, ranging from 101.51 mg/kg on agricultural soils, and 55.35 mg/kg in urban soils.
- Nickel content is above the limit value, ranging from 134.22 mg/kg on agricultural soils, and 60.04 mg/kg in urban soils.

The content of other heavy metals: lead, zinc, chromium and cobalt, and PAHs are below the limit values.

Table 4. Average results (in mg/kg) of heavy metals and PAHs in 2010

year	Soil type	Pb	Zn	Cd	Cu	Ni	Cr	Co	PAH
2010	agricultural	92.70	137.5	1.89	37.68	84.58	70.52	29.68	0.19
	urban	34.08	282.7	2.60	198.3	293.5	86.03	11.40	0.34
	Limit values	***<150***	***< 300***	***< 1***	***< 100***	***< 60***	***<100***	***< 50***	***< 2***

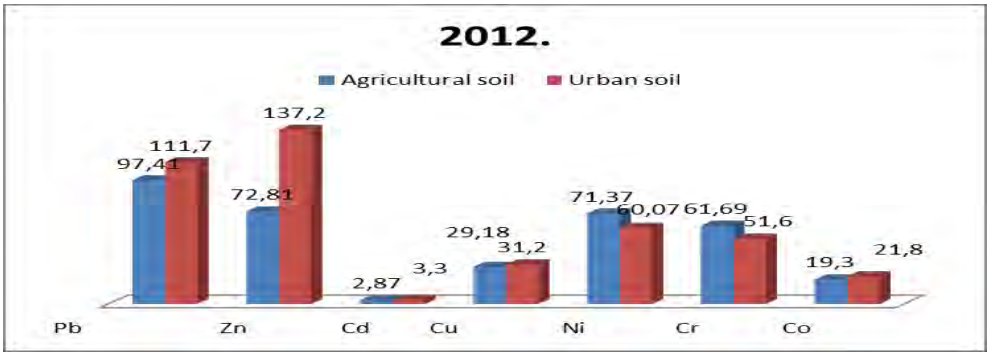


Graph 2. Average results of heavy metals for 2010

- Cadmium content is above the limit value, ranging from 1.89 mg/kg on agricultural soils, and 2.60 mg/kg in urban soils.
- Copper content is above the limit value, ranging from 198.28 mg/kg on agricultural soils, while is below the limit value in urban soils.
- Nickel content is above the limit value, ranging from 84.58 mg/kg on agricultural soils, and 293.5 mg/kg in urban soils. PAHs are below the limit values.

Table 5. Average results (in mg/kg) of heavy metals and PAHs in 2012

year	Soil type	Pb	Zn	Cd	Cu	Ni	Cr	Co	PAH
2012	agricultural	97.41	72.81	2.87	28.18	71.37	61.69	19.3	0.13
	urban	111.7	137.2	3.3	31.2	60.07	51.6	31.8	0.46
	Limit values	***< 150***	***< 300***	***< 1***	***<100***	***< 60***	***<100***	***< 50***	***< 2***



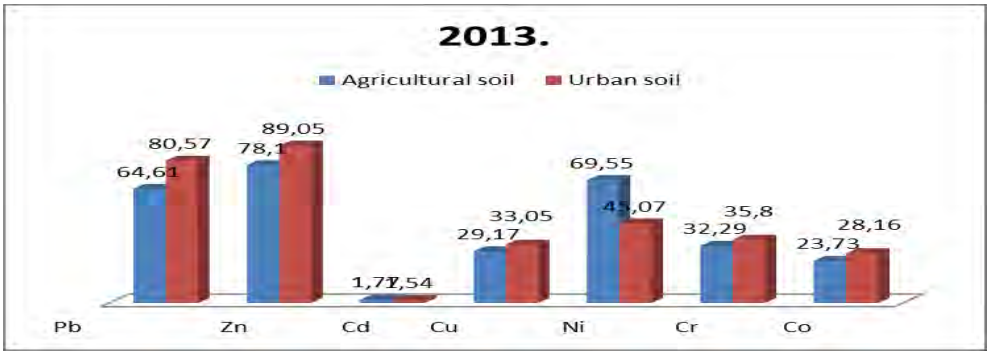
Graph 3. Average results of heavy metals for 2012

- Cadmium content is above the limit value, ranging from 2.87 mg/kg on agricultural soils, and 3.3 mg/kg in urban soils.
- Nickel content is above the limit value, ranging from 71.37 mg/kg on agricultural soils, and 60.07 mg/kg in urban soils.

The content of other heavy metals: lead, zinc, copper, chromium and cobalt, and PAHs are below the limit values.

Table 6. Average results (in mg/kg) of heavy metals and PAHs in 2013

year	Soil type	Pb	Zn	Cd	Cu	Ni	Cr	Co	PAH
2013	agricultural	64.61	78.1	1.77	29.17	69.55	32.29	23.73	0.12
	urban	80.57	89.05	1.54	33.05	45.07	35.8	28.16	0.45
	Limit values	***< 150***	***<300***	***< 1***	***< 100***	***< 60***	***<100***	***< 50***	***< 2***



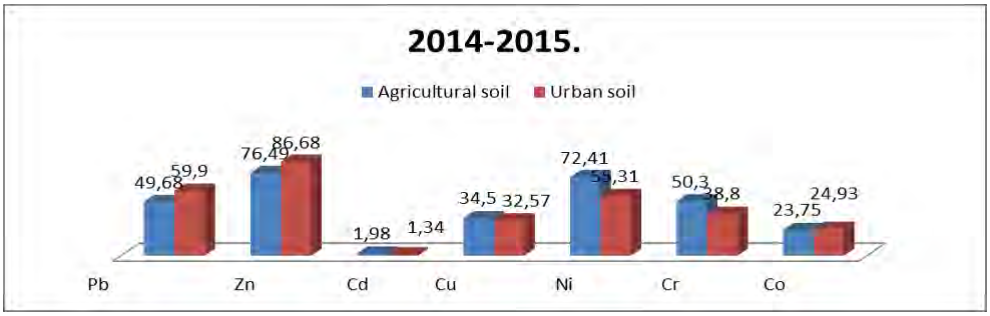
Graph 4. Average results of heavy metals for 2013

- Cadmium content is above the limit value, ranging from 1.77 mg/kg on agricultural soils, and 1.54 mg/kg in urban soils.
- Nickel content is above the limit value, ranging from 60.55 mg/kg on agricultural soils, while 45.07 mg/kg in urban soils is below the limit value.

The content of other heavy metals: lead, zinc, copper, chromium and cobalt, and PAHs are below the limit values.

Table 7. Average results (in mg/kg) of heavy metals and PAHs in 2014/15

year	Soil type	Pb	Zn	Cd	Cu	Ni	Cr	Co	PAH
2014-2015	agricultural	49.68	76.49	1.98	34.0	72.41	50.3	23.75	0.21
	urban	59.9	86.68	1.34	32.57	55.31	38.8	24.93	0.31
	Limit values	***< 150***	***< 300***	***< 1***	***100***	***< 60***	***<100***	***< 50***	***< 2***



Graph 5. Average results of heavy metals for 2014/15

- Cadmium content is above the limit value, ranging from 1.98 mg/kg on agricultural soils, and 1.34 mg/kg in urban soils.
- Nickel content is above the limit value, ranging from 72.41 mg/kg on agricultural soils, while 55.31 mg/kg in urban soils is below the limit value.

The content of other heavy metals: lead, zinc, copper, chromium and cobalt, and PAHs are below the limit values.

DISCUSSION

Investigations were carried out in the period from 2009 to 2015, on agricultural and urban soils in Canton Sarajevo. Analysis of the soil contamination in the studied period is presented in tables and graphs. Based on the comparison of the obtained average values of heavy metals and PAHs with a limit values, it can be established that the soil of the Canton Sarajevo is slightly exposed to contamination with heavy metals cadmium, nickel and partly with copper. The average concentration of other heavy metals and PAHs do not exceed the permissible limits.

Research conducted in 2009 and 2010 had determined the contamination of urban soil with nickel, copper and cadmium, while in agricultural soils higher contents of cadmium and nickel were found. The data obtained of cadmium content indicate slight contamination in agricultural and urban soils, while data from urban localities indicate intensive contamination with pollutants nickel and copper, whose average values are twice the permissible. The average copper content in urban soils ranged in value of 198.28 mg/kg, and the average nickel content was 293.5 mg/kg.

In the period from 2012 to 2015 the land of Canton Sarajevo was subjected to mild contamination with cadmium and nickel. In agricultural soils the average concentration value was 1.98 mg/kg for cadmium and 72.41 mg/kg for nickel.

On investigated localities of the Canton Sarajevo, contamination with other heavy metals was not established. The lead content ranged from 34.08 to 97.41 mg/kg, zinc content from 72.1 to 282.69 mg/kg, chromium content from 32.29 to 86.03 mg/kg and the content of cobalt ranged from 11.4 to 29.68 mg/kg.

Based on the results of the polycyclic aromatic hydrocarbons content, a slight increase in values in the period from 2010 to 2015 can be observed. The higher content of PAHs was found in urban localities, and lower content on agricultural soils, which seems to be a result of industrialization. The values of the PAHs content in urban soils ranged from 0.314 to 0.461 mg/kg, and for agricultural soils from 0.119 to 0.216 mg/kg. Taking into account that the examined samples are slightly acid to slightly alkaline, this is supported by the fact that in this range of pH values, heavy metals are less accessible to plants.

CONCLUSIONS

Field and laboratory studies were conducted from 2009 to 2015, on agricultural and urban soils in Canton Sarajevo for the presence of heavy metals: lead (Pb), cadmium (Cd), zinc (Zn), nickel (Ni), chromium (Cr), cobalt (Co) and copper (Cu), and the content of PAHs in soil.

In 2009 there was an increased content of cadmium 1.94 mg/kg in agricultural soils and 2.22 mg/kg in urban soils, copper 101.51 mg/kg in agricultural soils and 55.35 mg/kg in urban soils and nickel 134.22 mg/kg in agricultural soils, and 60.04 mg/kg in urban soils.

In 2010 there was an increased content of cadmium 1.89 mg/kg in agricultural soils and 2.60 mg/kg in urban soils, copper 198.28 mg/kg in urban soils and nickel 84.58 mg/kg in agricultural soils and 293.50 mg/kg in urban soils.

In 2012 there was an increased content of cadmium 2.87 mg/kg in agricultural soils and 3.3 mg/kg in urban soils and nickel 71.37 mg/kg in agricultural soils and 60.07 mg/kg in urban soils.

In 2013 there was an increased content of cadmium 1.77 mg/kg in agricultural soils and 1.54 mg/kg in urban soils and nickel 69.55 mg/kg in agricultural soils and in urban soils the content was below the limit value.

In 2014/15 there was elevated cadmium content of 1.98 mg/kg in agricultural soils and 1.34 mg/kg in urban soils and nickel of 72.41 mg/kg in agricultural soils, while in urban soils the content was below the limit value.

We can observe in 2013, 2014 and 2015 a slight decrease in the content of cadmium and nickel. Elevated concentrations of the se metals in agricultural soils are most likely of the lithological origin; while in urban soils are both lithological and anthropogenic origins.

The concentrations of lead, zinc, nickel, chromium and cobalt are below the limit values. The same can be applied for PAHs compounds. Higher content of PAHs was found in urban localities, while lower was present on agricultural sites as a result of most likely anthropogenic impact.

Since increased concentrations of cadmium, nickel, and copper have a toxic affect on plants, and through them on the animals and humans, it is necessary to conduct more detailed researches of elevated concentrations of cadmium, nickel and copper in Canton Sarajevo.

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