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DYNAMICS OF THE HEAVY METALS CONTENT IN THE SOIL OF THE STEELPLANT SURROUNDINGS IN ZENICA

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ABSTRACT: *The Steelplant surroundings in Zenica has been loaded by heavy metals for almost 120 years, sulfur dioxide and other pollutants emitted from metallurgical and thermal power plants [1]. Anthropogenic emissions were influencing on the redistribution of heavy metals in the soil in wider surroundings of the steelplant. Because of that the soil and the plants were considerably contaminated with heavy metals and the production of many crop plants was risky due to heavy metals involvement in animal and humane food chain [2]. Primary metallurgical plants were not working in the period from 1992 to 2008, and the thermal power plants were working with 20% - 45%. By the middle of 2008 a revitalized integral production line was put in operation, with all key primary metallurgical plants and with the production volume of around 600 000 to 700 000 t/g of steel and 680 000 t/g of coke. Because of that the contamination of the soil and other environmental elements with heavy metals, sulfur and other pollutants was significantly reduced [3]. The monitoring of heavy metals and sulfur in the soil of the Steelplant in Zenica surroundings has a goal of determining the contamination of the agricultural land and the suitability of its use for agricultural production, as well as tracking the effects of measures implementation for reducing emissions from the Steelplant technological processes. In this paper the research results of the dynamics of the heavy metals and sulfur content in the surroundings of Steelplant in Zenica in the period from 1989 to 2011 are presented.*
KEYWORDS: *heavy metals, soil, Steelplant, contamination*

INTRODUCTION - MATERIAL AND WORK METHODS

Research of the heavy metals and sulfur content in soil are realized in nine localities in the Steelplant in Zenica surroundings, which have been used in the perennial monitoring. The localities are placed by the system of concentric circles at diffrent distances from the Steelplant on the three most frequent and ecologicaly most valuable types of soil (rendzina, eutric and dystric cambisol).

Experimental polygons are set on agricultural land. The soil samples are taken from depth of 0 to 25 cm (arable layer), on exemplary pedologicaly homogeneus surfaces. At the every location average samples of soil (about 2kg) are taken and prepared for analysis by the standard procedure. The dissolution of the samples is done in HNO_3 and $HClO_4$. Determination of the total content of heavy metals (Pb, Cd, Zn, Co, Cu, Cr, Ni, Mn and Fe) is done by atomic absorption spectrometry procedure. Sulfur is determined by Gravimetric method.

For the result interpretation in this paper criteria and limiting values are used which are assinged by the book of regulations determining the allowed amount of harmful and dangerous matters in soil and its methods of examination, as well as literature data. All laboratory tests are done by the ISO 11466 and ISO 11047 standards.

RESULTS AND DISCUSION

A soil as a specific and dynamic natural system is connected with other environmental components, primarily through matter exchange. Heavy metals and sulfur have a normal biogeochemical cycle like other matters and they get into the soil where they can stay for short or long time depending on their physico – chemical properties. They are very slowly removed by washing out the soil and by crops removal. Because of that they can accumulate in the soil in waste amounts and than they can violate the natural physico – chemical properties, fertility and the filtration capacity of the soil. That is why knowing the factors influencing the heavy metals behavior in the soil and their accessibility to living organisms is of great ecological importance. Average values of heavy metals and sulfur content in the soil of the Steelplant in Zenica surroundings are shown in the table 1.

Periodic studies have shown that the heavy metals content in the Steelplant in Zenica surroundings soil has a dynamics of decline, what is a result of a 16 years of an primary metallurgical plants inactivity, partially changed technology, reduced volume of production and preparation of technical and technological measures for reduction of air emissions, and their continuous removal from the soil by crops and water washout.

Table 1. The heavy metals content in the rendzina on marlstone and marlstone clay soil (mg/kg of soil)

Phisico-chemical soil properties	Localities															Limiting values
	Tetovo			Pehare			Gradište			Mutnica			Arnauti			
	1989	1999	2011	1989	1999	2011	1989	1999	2011	1989	1999	2011	1989	1999	2011	
pH of H_2O	7.32	7.55	7.98	6.58	6.72	8.06	7.41	7.63	7.99	6.96	6.97	7.59	7.38	7.42	7.79	
pH of KCl	6.86	7.02	7.16	6.03	6.07	7.02	6.72	7.27	7.40	6.02	6.05	6.85	6.33	6.70	6.81	
Content of $CaCO_3$ (%)	2.49	4.82	1.80	1.05	4.61	4.12	3.53	17.34	15.23	-	3.16	-	2.63	12.10	1.32	
Content of humus (%)	5.54	6.80	5.88	9.02	8.10	8.13	4.78	6.19	6.78	3.86	4.20	6.75	5.62	5.71	6.88	
Elements in the soil																
Lead (Pb)	263	197	174.6	128	115	116	129	108	117	80	68	51	49	56	33.0	80
Cadmium (Cd)	7.50	2.12	0.74	8.50	2.34	0.28	7.80	2.37	0.25	8.50	1.45	0.24	8.60	1.49	0.05	1
Zink (Zn)	215	303	205	157	151	190	168	170	176	123	130	107	84	95	96.5	150
Copper (Cu)	65	64	67	58	56	51.6	48	59	58.4	52	42	38	64	50	44.3	65
Nickel (Ni)	245	-	156	182	-	127	175	-	116	236	-	135	456	-	298	40
Chrome (Cr)	329	-	81	274	-	65.5	244	-	42.1	347	-	71.3	647	-	183.7	80
Cobalt (Co)	51	-	33.7	45	-	30.5	40	-	28.3	43	-	24.5	54	-	47.8	45
Manganese (Mn)	1676	-	1186	1197	-	2172	887	-	873	1693	-	618	890	-	968	-
Iron (Fe)	68500	50445	40900	46733	38478	34733	40700	37956	27933	50367	34822	26866	62933	36867	30333	-
Sulfur (S)	600	769	2600	1300	571	4200	733	725	4600	267	227	2500	333	320	2200	400

Table 2. The heavy metals content in the eutric cambisol on flysch soil (mg/kg of soil)

Phisico-chemical soil properties	Localities						Limiting values
	Stranjani			Janjićki Vrh			
	1989	1999	2011	1989	1999	2011	
pH of H_2O	6.23	6.25	6.67	4.81	5.18	6.73	
pH of KCl	5.48	5.51	5.36	4.43	4.55	5.67	
Content of $CaCO_3$ (%)	-	3.83	-	-	3.15	-	
Content of humus (%)	5.91	5.42	5.10	3.63	4.77	4.01	
Elements in the soil							
Lead (Pb)	75	56	51	70	55	48	80
Cadmium (Cd)	6.8	2.00	0.30	5.5	1.47	0.17	1
Zink (Zn)	106	112	98	107	96	115	150
Copper (Cu)	39	40	45	38	38	37	65
Nickel (Ni)	120	-	47.5	92	-	41	40
Chrome (Cr)	241	-	46.4	164	-	32.5	80
Cobalt (Co)	40	-	29.1	32	-	20.1	45
Manganese (Mn)	151	-	1315	993	-	884	-
Iron (Fe)	46733	34578	28200	42067	30667	26800	-
Sulfur (S)	267	274	2500	167	203	3000	400

Table 3. The heavy metals content in the dystric cambisol on cherts soil (mg/kg of soil)

Phisico-chemical soil properties	Lokaliteti						Limiting values
	Orahovica			Šerići			
	1989	1999	2011	1989	1999	2011	
pH of H_2O	4.52	5.08	5.45	4.89	5.40	5.49	
pH of KCl	4.14	4.36	4.08	4.21	4.63	4.07	
Contetnt of $CaCO_3$ (%)	-	4.89	-	-	2.42	-	
Content of humus (%)	4.71	5.42	4.47	4.81	6.81	4.99	
Elements in the soil							
Lead (Pb)	57	45	34	67	48	39	80
Cadmium (Cd)	6.8	1.37	0.16	6.0	1.44	0.20	1
Zink (Zn)	93	91	81	135	121	70	150
Copper (Cu)	85	81	74	65	42	38	65
Nickel (Ni)	78	-	32	83	-	18	40
Chrome (Cr)	119	-	20.5	146	-	24	80
Cobalt (Co)	47	-	24.9	47	-	27.9	45
Manganese (Mn)	2273	-	1772	2203	-	2265	-
Iron (Fe)	32367	27845	17300	36100	27189	15550	-
Sulfur (S)	300	249	2500	433	374	2400	400

Research results are showing that the heavy metals content in the soil on localities closer to the Steelplant are slightly higher then allowed limiting values. Equally, research results are showing that the heavy metals content in the soil is still greater then natural state, as a result of their anthropogenic redistribution. Lead content in the soil is on average of 0.1 – 20 mg/kg. Cadmium 0.1 – 1 mg/kg, zinc 3 – 5mg/kg, copper 35 – 40 mg/kg, cobalt 10 – 15 mg/kg, iron 3.2%, etc. The sulfur content in the soil has a growth trend and values of the last series of measurements are significantly higher then limiting values, what is probably a result of increased anthropogenic influence [6].

The heavy metals content in the Steelplant surroundings soil has varied depending on the locality position, their distance from the emission source, soil type, metal kind and other environmental conditions. The highest heavy metals content has been registered in the soil on localities closer to the Steelplant. These localities had the highest heavy metals pollution, especially with Pb, Ni, Cr and Zn. The soil type on these localities is rendzina on marlstone and marlstone clay, which has a neutral to slightly alkaline pH value and it is a good absorption complex. That contributes to the heavy metals immobilization, which complicates their absorption by the plants. Free metal carbonates, larger organic matter content in the soil and higher pH value of the soil increase the soil's protective ability.

At the brinks of Zenica basin eutric cambisol on flysch is most represented, it has a weakly acidic or acidic pH value and a lower absorption complex. In this type of soil there are slightly lower values of the heavy metals content then in rendzina and a lowest content of total sulfur. Weakly acidic soil reaction has probably benefited the higher absorption of sulfur and its removal from the soil by plants [6].

The lowest values of the heavy metals content were registered on the furthest localities from the dominating emission sources. Dystric cambisol on charts is represented on these localities. This soil has a lowest imission of heavy metals emitted from the anthropogenic sources. Dystric cambisol, due to its low absorption complex and low pH values improves the heavy metals mobility and their higher absorption and accumulation in plants. The plants feel the worst on acidic soils, because in those conditions they most intensively absorb and accumulate heavy metals, which cause different toxic effects [7]. Acidic soils in industrial regions should be carefully used in agricultural production to protect people's health. With these soils it is recommended to use protective measures to fix the absorption complex, as calcification, humification and etc.

Studies have shown that the soil capacity of Zenica region is still limited for imission and harmless binding of heavy metals and sulfur. Obtained values show that there is a real possibility for heavy metals inclusion into the geobiochemical cycle, especially on acidic soils. Because of those measures for controlled use and soil protection should be taken to increase their protective abilities. It is very important to take all necessary measures that the soil contamination does not happen to preserve it's fertility and suitability for agricultural production. Those measures have an ecological and economical importance. Quality and fertile soil is a basis for the production of biologicaly safe food, which is a condition for healty nutrition.

CONCLUSIONS

- *With the monitoring of heavy metals in the Steelplant in Zenica surroundings soil it is concluded that the heavy metals content in the soil has a dynamics of decline, what is a result of a 16 years of an primary metallurgical plants inactivity, partialy changed technology, reduced volume of* *production and preparation of technical and technological measures for reduction of air emissions, and their continuous removal from the soil by crops and water washout. The sulfur content in the soil has a growth trend, what is probably a result of increased anthropogenic influence [6].*

- *Research results show that the heavy metals content in the soil is increased in regard to natural state, what is a consequence of anthropogenic emissions and their redistribution. Obtained values most often do not cross the border standards.*
- *Because of increased presence of heavy metals and sulfur in the soil there is a real possibility of their inclusion into the animal and humane food chain, especially on acidic soils. Because of that it is necessary to provide the monitoring of heavy metals in podosphere and plants, take measures for controlled use of soil for agricultural production and the implementation of the soil protective measures (liming, humification, soil phytoremediation etc.) to protect the population's health.*

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