Preliminary geochemical investigation of agricultural soil from Eastern Serbia (Sokobanja Basin)

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Abstract: The origin of heavy metals in living environment is different and rough division can be made into geogenic and anthropogenic. On and in soil heavy metals arrive through acid rain, dust, and carbon black. Into the layer of soil that has been used for agriculture, so called plough land, heavy metals come through plants that suck them in from deeper layers, and thus deposit them in more shallow layers. The most significant anthropogenic sources of soil pollution with heavy metals are motor vehicles, metal industry, mines and metal smelter, organic and mineral fertilizers. The aim of this study is to determine the content of heavy metals in agricultural land Sokobanja basin. The analysis results show that dissolubility of the tested samples goes from 19.1% to 31.8% for the samples from the soil surface, and from 17.8% to 30.4% for the samples from 30 cm depth. FTIR analysis determines lower contents of the carbonate minerals in comparison to the silicate minerals, and that is confirmed with stereomicroscopy. Based on the results gained from ICP analysis it can be concluded that most of the soil from the tested area is safe for agriculture usage.

Keywords: soil, heavy metals, Sokobanja, fractionation, ICP analysis.

1. Introduction

Sedimentary rocks are being created by deposition of solid material in water environment, where organic and/or non-organic substance existed in the form of suspension or dissolution, under the moderate temperature and pressure. The process of sediments creation lasts for a very long time and it is being carried out through more or less separate processes: decomposition of

the primal rocks, transfer and deposition of the material created in that manner, transformation of the sediments into the firm rocks or deposition and post deposition processes (physical/chemical changes on the sediment).

The initial material for sediments creation comes from igneous and metamorphic rocks, after their erosion and denudation (Nesse, 2000). The process of igneous and metamorphic rocks creation is very long and comprises the following: erosion of the igneous and metamorphic rocks caused by water, ice, wind, climate and temperature changes; transportation of the material in solid or liquid state or in the form of resolution; settling (sedimentation, deposition) that occurs when the energy of the transport environment is too low to allow transportation process, and digenesis that includes all processes of sediments conversion into the solid rocks.

Based on predominant type of physical, chemical, biochemical and geological processes sediment rocks are being divided into: Exogenous (classical, detrital) rocks created by physical and chemical deterioration, especially through other rocks physical degradation, and during that period created particles are physically deposited after longer or shorter transport, and Endogenous rocks that are created by amorphous or crystal sedimentation from resolution as well as by biochemical processes. However, greatest part of the sediments is of the polygenetic origin, which makes their qualification difficult.

Sediment rocks contain very important information about Earth history, where differences between neighboring layers indicate changes of the sedimentation environment as well as atmosphere, hydrosphere and tectonic changes that happened over time. They also contain fossils; since contrary to the igneous and metamorphic rocks, they are being created at the temperature and pressure that does not destroy fossil remain.

The importance of these rocks comes from the fact that roughly, 85 - 90 % of all mineral raw materials are derived from sediment rocks, and only 10 - 15 % is derived from igneous and metamorphic rocks (Goldschmidt, 1937). Basic characteristics of sediment rocks are layering, porosity, and transmission. These very characteristics are responsible for frequent occurrence of the sediment rocks as a reservoir of the natural gas, oil, and mineral water. The most present sediment

rocks are sandstones, limestone, and bituminous shale. They comprise roughly 95 % of all sediments (Pettijohn, 1983).

The origin of heavy metals in living environment is different and rough division can be made into geogenic and anthropogenic. In the form of fine dust particles, heavy metals can get to the atmosphere where they continue to deposit in water (carbonates that are difficult for solution, sulphates or sulphides that are being deposited at the bottom) and in soil. On and in soil heavy metals arrive through acid rain, dust, and carbon black (Efe, 2010). Into the layer of soil that has been used for agriculture, so called plough land, heavy metals come through plants that suck them in from deeper layers, and thus deposit them in more shallow layers. The most significant anthropogenic sources of soil pollution with heavy metals are motor vehicles, metal industry, mines and metal smelter, organic and mineral fertilizers.

Heavy metals connect to the adsorption complex in the soil or can be found in the form of ions within the soil resolution, and in both forms they are available for plants. The sorption ability of a heavy metal ion depends more from the form in which occurs in the soil than its quantity (Kabata-Pendias *et al.* 2001, Pierzynski *et al.* 2000).

Heavy metals naturally exist in the soil mostly in complexes with other minerals (Kabata-Pendias *et al.* 2001, Pierzynski *et al.* 2000). Cation metals (in the soil they exist in the form of a positively electrified cation for ex. Pb^{2+}) as well as mercury, cadmium, lead, nickel, copper, zinc, chrome, and manganese mostly cause the problems. Most common anion chemical compound (in combination with oxygen, for example negatively electrified MoO_4^{2-}) are arsenic, molybdenum, selenium and boron (Alloway 2013, Hu, 2013).

Sokobanja (SB) basin is situated about 60 km north from Niš (Figure 1) and its surface is 250 km^2. Sokobanja basin is a tectonic depression placed in the direction north-south, 29 km long and 16 km wide. The basin is filled with 1500m thick layer of limestone sediment, deposited in the time interval from lower Paleogene until upper Miocene, and thus a typologically very versatile soil was created in the Sokobanja area (Radivojević, 2008).

2. Materials and methods

20 samples have been tested from the Sokobanja basin. (Figure 1). This samples have been collected along the Moravica river flow and marked: A (1-

10) samples from the soil surface and B (1-10) samples taken at the depth approximately 30 cm.

Table 1. Soil type in SB basin

| Soil type	Surface (ha)	%
Smonitsa	6800	12.9
Eroded smonitsa	1200	2.8
Smonitsa in limiting	4700	8.9
Smonitsa loessivized	1400	2.7
Smonitsa alluvial-meadow soil	400	0.8
Rendzina on limestone	1600	3.0
Brownised rendzina and brown soil on limestone	15437	29.3
Brown soil on limestone	2200	4.2
Brown loessivized soil	600	1.2
Red land in Permian sandstone	1300	2.5
Brown skeletal soil on phyllites	5000	9.5
Brown skeletal soil on phyllites with quartzite	500	0.9
Brown shallow skeletal soil on sandstone	2400	4.6
Brown soil on andesite	600	1.2
Parapodzol	400	0.8
Alluvium loamy	1200	2.8
Delluvium	1100	2.1
Skeletal soil on limestone	5200	9.8
Skelet- rocky ground	600	1.2
Total	52 637	100

Figure 1. Geographical location of the SB samples

Moist soil samples have been shaken on plastic plates and recorded in the soil samples book, where a laboratory number was given to each. The samples have been finger crunched until pieces 1 – 3 cm big were made and left to be air-dried. After drying, the samples were grinded in a soil mixer that works on a principle of two sliding plates, sifted and placed in boxes with a laboratory number.

1.   *Fractionation procedure.* Before treatment with mineral acids, the samples were grinded in a vibrating mill to particle size of 100 μm. The fractionation procedure was similar to that used by Premović *et al.* 2000. The flow chart in Figure 2 outlines the major steps in preparing the two fractions of samples from SB basin.

2.   *Dilution in hydrochloric acid*. The insoluble residue was demineralized further by repeated treatment with cold 6 M HCl. This acid solution removed mostly metal oxides. After rinsing and drying, the remainder was measured and determined by the fractions soluble in cold HCl. The soluble material constitutes the fraction of metal oxides and hardly soluble carbonates.
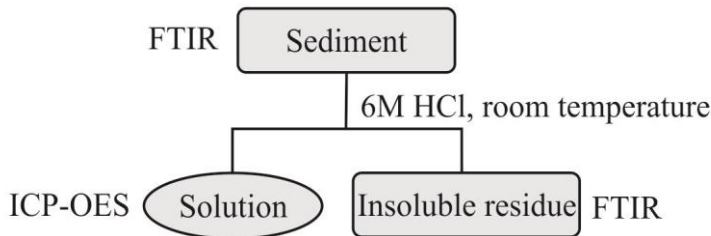
3.

Figure 2. *Flow chart of fractionation procedure*

4.   *Fourier Transform Infrared (FTIR) Spectrometry*. FTIR spectra were recorded, in absorbance mode, with a BOMEM Michelson Series MB FTIR spectrometer set to give undeformed spectra. The resolution was 4 cm^{-1} in the 400-4000 cm^{-1} analyzed range. Spectra were obtained at room temperature from KBr pressed pellets prepared by mixing 1.5 mg of a clay sample with 150 mg of KBr.

5.   *Inductively coupled argon plasma (ICP).* The concentrations of metal ions dissolved from the rest (Todorović, 1997, Kerovec, 2010) are determined ICP-Optical Emission Spectrometer iCAP 6000 Series, Thermo Scientific, Cambridge, United Kingdom. Analysis was used Multi Standard -Ultra Scientific Analytical Solutions, USA.

3. Results and discussion

pH. pH values for all samples were also determined and they vary, as it can be seen in the Table 2, from 5.12 to 7.30, for the surface samples A and from 5.17 up to 7.47 for the samples taken from the depth B.

Table 2. Results of measuring pH of the soil from SB basin

Sample	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	A-9	A-10
pH	6.14	6.91	7.21	7.30	7.26	7.26	6.67	6.74	5.12	7.13
Sample	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	B-9	B-10
pH	6.74	7.04	7.33	7.30	7.26	7.47	6.61	6.74	5.17	5.89

Stereomicroscopy. Stereo-micro photos (taken with stereomicroscope "Krüss" and taken with "Nikon 4500" camera) of the fine grinned raw (Figure 3A) and sample treated with hydrochloric acid (Figure 3B) show that the material is homogenous. Stereo images confirm the results of the FTIR analysis – indicate lesser presence of the carbonate in comparison to the silicate material, as well as the absence of the organic substance.
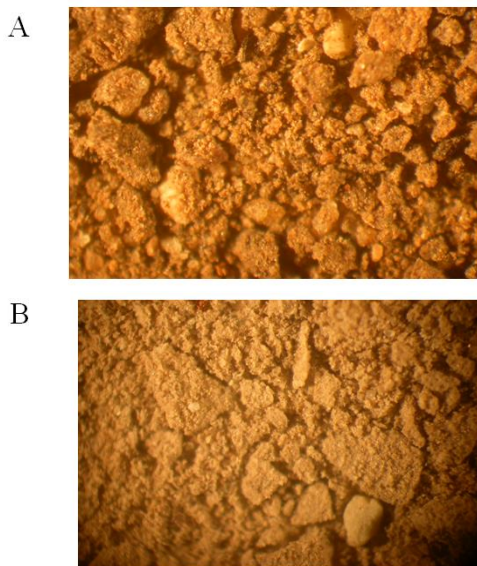
A

B

Figure 3. *Stereo microphotography (180 × magnification:) A) untreated sample and B) sample of SB treated with hydrochloric acid*

Fractionation procedure. Dissolubility of the soil samples was tested. Dissolubility values (Table 3) go from 19.1% to 31.8% for the samples from the soil surface (samples A) and from 17.8% to 30.4% for the samples taken at the depth out of 30 cm (samples B).

Table 3. Results solubility of soil samples from SB basin

ample	-1	-2	-3	-4	-5	-6	-7	-8	-9	-10
olubility (%)	1.8	9.2	0.2	4.8	8.2	0.0	9.2	6.0	9.1	2.2
ample	-1	-2	-3	-4	-5	-6	-7	-8	-9	-10
olubility (%)	0.3	7.8	2.8	0.4	3.0	0.2	3.0	3.1	1.5	9.7

FTIR. Analysis by sequential demineralization shows that the samples taken from the Sokobanja basin are partially dissoluble in cold/hot water HCl (up to 31.8 %) which indicates absence of carbonate minerals as well as organic matters, implying the presence of the silicate minerals.

FTIR spectrum of the untreated samples 1, 2 i 3 are presented on Figure 4. Spectrum of all samples is very similar so the mentioned ones were the only presented.
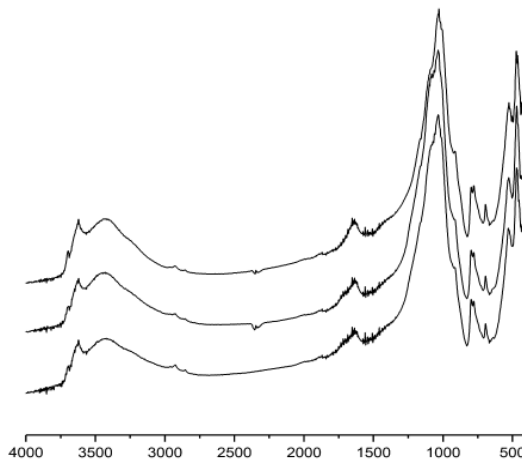

Figure 4. *FTIR spectra of untreated SB samples*

Presented spectrum shows domination of the inorganic fraction stripes in comparison to the organic.

FTIR samples spectrum dominating inorganic fraction tapes are those at about 1615, 875 and 712 cm^{-1}, they are characteristic for carbonate minerals, especially calcite with admixture of aragonite as well as at 3623, 1095, 1030, 920, 789, 777, 527, 470 and 417 cm^{-1} characteristically for silicate matters (Madejova, 2003).

Tape at 1031 cm^{-1} (coming from Si and Si-Al mineral) is the most dominant in the spectrum and based on relative intensity of that tape we could say that Si and Si-Al minerals are the most common ones. This corresponds to the fraction analysis data of the inorganic fractions where carbonate fraction (remaining after the cold/hot water treatment HCl) is present in this sample 30 %, and silicate up to 70%, as well as with data that agricultural soil in this part of Serbia is mostly sandy soil type.

Because of the insufficient division of these tapes, it is almost impossible to determine minerals responsible for this tapes occurrence. However, it can be said that these tapes surely generate from the Si/ Si-Al minerals and according to that, it is possible to give short list of the most probable ones, which are:

- montmorillonite
- illite
- secundary aluminous chlorite
- interstratified montmorillonite/illite
- interstratified montmorillonite/chlorite
- cristobalite
- quartz.

From the mentioned Si/Si-Al minerals the most present are secondary aluminous chlorite, interstratified montmorillonite/illite, and interstratified montmorillonite/chlorite. Quartz in these samples can be found in traces. Of course, more detail mineral examinations are necessary in order to gain contents confirmation for the above-mentioned minerals (Frost *et al.* 2002).

ICP-OES. Dissolving the samples by fractionation, the resulting solutions were prepared for ICP-OES analysis to determine the concentrations of certain heavy metals in the SB basin soil.

Vanadium (V). In the Figure 5. values of the vanadium concentrations in samples are presented (ppm), and a histogram of this values comparative with maximum allowable concentration (MAC) values for this metal (Premović *et al.* 2001, Premović *et al.* 2002, Đorđević, 2009).

Taking into account MAC value, which is far above found concentrations, we could say that, as far as vanadium is concerned, the examined soil is safe for agriculture (Rehder, 1991).
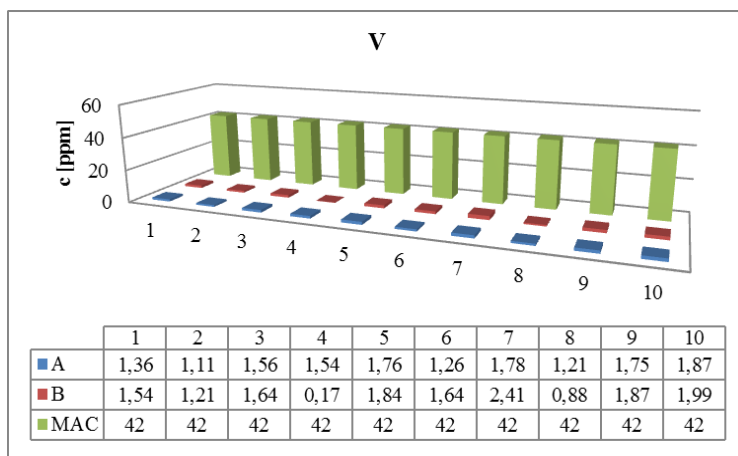

	1	2	3	4	5	6	7	8	9	10
■A	1,36	1,11	1,56	1,54	1,76	1,26	1,78	1,21	1,75	1,87
■B	1,54	1,21	1,64	0,17	1,84	1,64	2,41	0,88	1,87	1,99
■MAC	42	42	42	42	42	42	42	42	42	42

Figure 5. Vanadium concentrations in the examined samples and MAC

Chromium (Cr). Chromium concentrations in the samples are represented in the Figure 6. On this figure a histogram of this values in comparison to the MAC values (Kabata-Pendias *et al.* 2001) is presented for this metal.

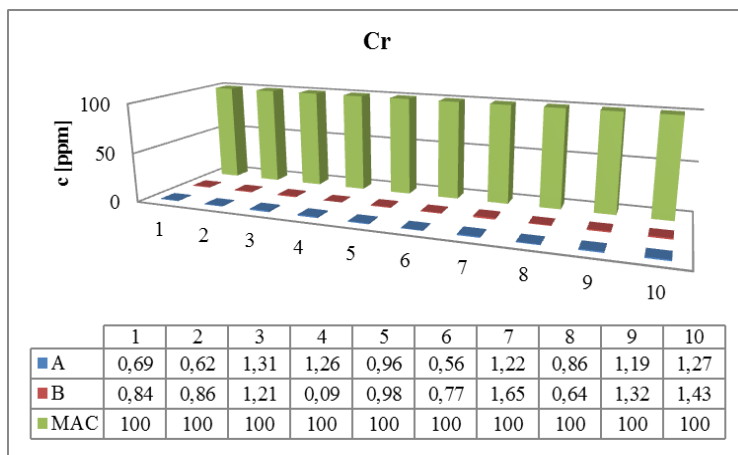|	1	2	3	4	5	6	7	8	9	10
■A	0,69	0,62	1,31	1,26	0,96	0,56	1,22	0,86	1,19	1,27
■B	0,84	0,86	1,21	0,09	0,98	0,77	1,65	0,64	1,32	1,43
■MAC	100	100	100	100	100	100	100	100	100	100

Figure 6. Chromium concentrations in the examined samples and MAC

Based on the results represented in the Fig. 6 it can be concluded that soil from the tested area is, as far as the chromium is concerned, safe for agriculture.

Cobalt (Co). In the Figure 7. values of the cobalt concentration in the samples are presented, and histogram of this values and MAC value for cobalt.

In the sample with mark B-10 a value was measured where cobalt contents was above MAC value (Kabata-Pendias *et al.* 2001), and it can be concluded that the tested soil is not safe for agriculture as far as cobalt is concerned, and this requires cleaning measures.
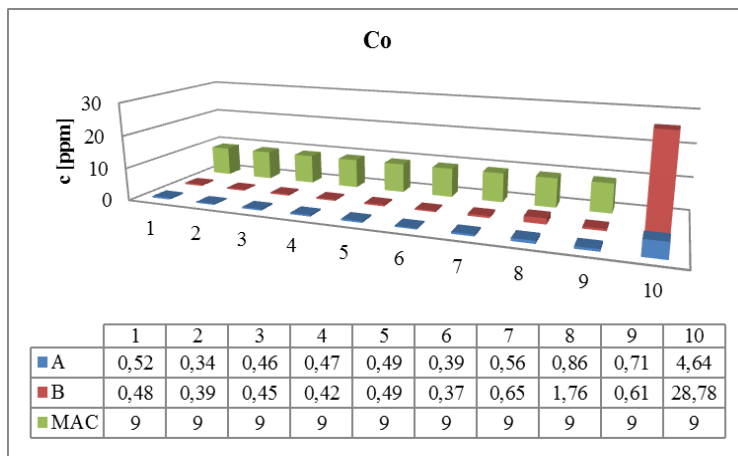

	1	2	3	4	5	6	7	8	9	10
■ A	0,52	0,34	0,46	0,47	0,49	0,39	0,56	0,86	0,71	4,64
■ B	0,48	0,39	0,45	0,42	0,49	0,37	0,65	1,76	0,61	28,78
■ MAC	9	9	9	9	9	9	9	9	9	9

Figure 7. Cobalt concentrations in the examined samples and MAC

Nickel (Ni). Values of the vanadium concentration (ppm) found in samples are presented in Figure 8 and a histogram of this values is presented comparative with MAC values for this metal.

As it can be seen from the Fig.8 found values of the nickel concentration are under MAC values (Kabata-Pendias *et al.* 2001), and it can be concluded that as far as nickel is concerned, examined soil is safe for agriculture.
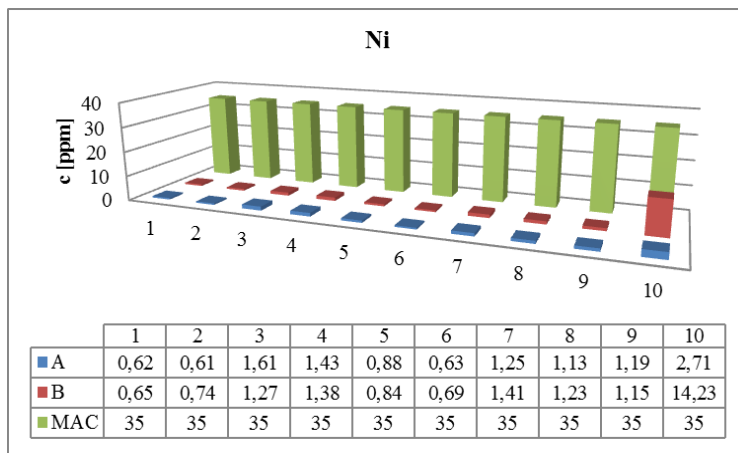
Figure 8. Nickel concentrations in the examined samples and MAC

	1	2	3	4	5	6	7	8	9	10
■ A	0,62	0,61	1,61	1,43	0,88	0,63	1,25	1,13	1,19	2,71
■ B	0,65	0,74	1,27	1,38	0,84	0,69	1,41	1,23	1,15	14,23
■ MAC	35	35	35	35	35	35	35	35	35	35

Copper (Cu). In the Figure 9. copper concentrations, found in samples, were presented, and a histogram of this values is presented as well as MAC for this metal (Kabata-Pendias *et al.* 2001).

From the presented results of the analysis, it can be concluded that, as far as copper concentration is concerned, the examined soil is safe for agriculture.
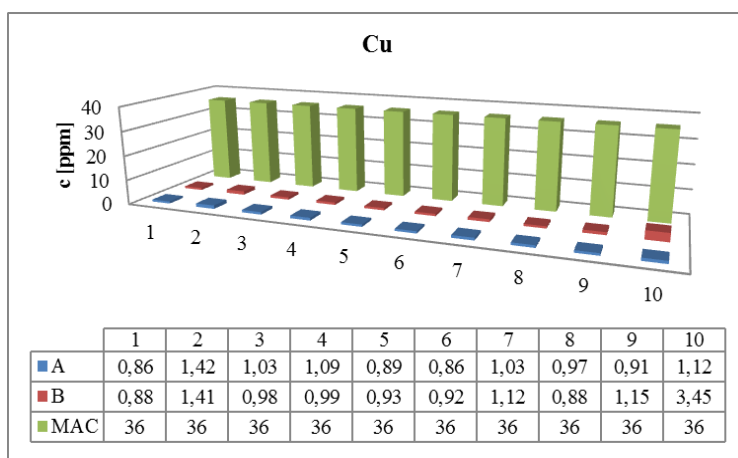

	1	2	3	4	5	6	7	8	9	10
■ A	0,86	1,42	1,03	1,09	0,89	0,86	1,03	0,97	0,91	1,12
■ B	0,88	1,41	0,98	0,99	0,93	0,92	1,12	0,88	1,15	3,45
■ MAC	36	36	36	36	36	36	36	36	36	36

Figure 9. Copper concentrations in the examined samples and MAC

Zinc (Zn). In the Fig. 10 zinc concentrations are given found in the samples. Histogram was presented of the found concentrations and compared with MAC values for zinc (Kabata-Pendias *et al.* 2001).

By examining zinc concentrations in the soil samples from SB basin values of the concentration, which is under MAC level for zinc, and it can be concluded that as far as the zinc concentration is concerned the soil is safe for agriculture.
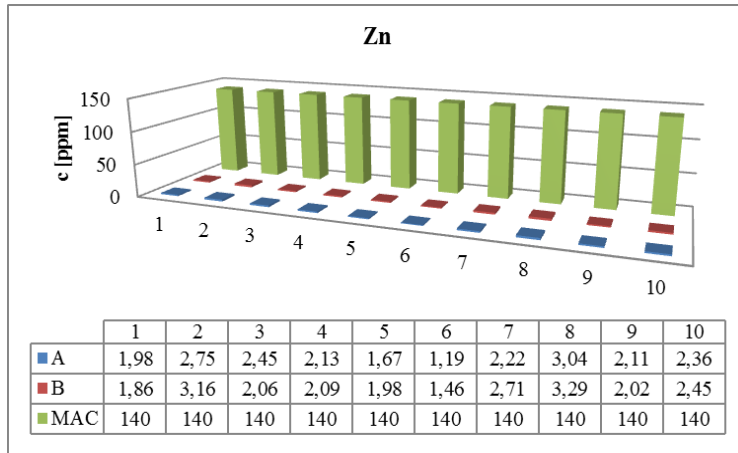
Zn

	1	2	3	4	5	6	7	8	9	10
A	1,98	2,75	2,45	2,13	1,67	1,19	2,22	3,04	2,11	2,36
B	1,86	3,16	2,06	2,09	1,98	1,46	2,71	3,29	2,02	2,45
MAC	140	140	140	140	140	140	140	140	140	140

Figure 10. Zinc concentrations in the examined samples and MAC

4. Conclusion

The analysis results show that dissolubility of the tested samples goes from 19.1% to 31.8% for the samples from the soil surface, and from 17.8% to 30.4% for the samples from 30 cm depth.

FTIR analysis determines lower contents of the carbonate minerals in comparison to the silicate minerals, and that is confirmed with stereomicroscopy.

Based on the results gained from ICP analysis it can be concluded that soil from the tested area is safe for agriculture usage, except the soil from the area where sample with mark B-10 was taken and where Co concentration was found to be bigger than allowed for this metal. Measures of soil purification are recommended in this area in the aim of Co concentration reduction for the values above MAC.

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