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CONTENT OF HEAVY METALS IN RIGOSOLS FROM THE AREA OF VELES

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Abstract
The scope of the investigations was to determine the quantity of total forms (Cu, Mn and Zn) and available forms of heavy metals (Cu, Fe, Mn and Zn) in rigosols from the area of Veles. Digestion of soil samples was performed with concentrated HCl and HNO_3 in a 3:1 ratio. The available forms of heavy metals were extracted with the DTPA method. Determination of the content was performed on atomic absorption spectrophotometer Agilent 55. The results of the investigation showed that the total zinc contents in all soil samples were lower than the reference value. Total copper content in 3 soil samples is lower than the reference values, while in 5 soil samples had higher contents than reference value, but much lower than intervention value. Total manganese content is lower than the maximum allowed concentration for agricultural soils. The quantities of available copper are in the ranges of low to very high, of iron and zinc is between very low to medium, while of manganese between low to high.

Keywords: soils, zinc, copper, iron, manganese.

Introduction
This paper presents data on the mechanical composition, some chemical properties and the content of the total (Cu, Mn and Zn) and available forms of copper, iron, manganese and zinc in rigosols from the Veles region. The rigosols are formed by with deep plowing (80-100 cm) of chromic luvisol on saprolite. The investigated site is located about 5 km southeast of Veles in the vicinity of the village Karaslari. Data on the content of total and available forms of copper, iron, manganese and zinc in the chromic luvisol on saprolite and other soils from the Veles region are encountered in the works of Стојковска and Спировски (1963), Јекиќ and Савиќ (1972), Џекова et al. (1988), Андреевски et al. (2006), Stafilov et al. (2008) и Mitkova and Markoski (2008). For the content of total and available forms of these heavy metals in the chromic luvisol on saprolite from other parts of the Republic, we find data in the works of Стојковска and Спировски (1963), Spirovski and Georgiev (1971), Јекиќ and Савиќ (1972), Митрикески (1995), Митрикески et al. (1997), Митрикески and Миткова (2000), Петковски et al. (2001) и Petkovski and Melovski (2006). According to the proposed classification of the soils of the Republic of Macedonia (Филиповски, 2006), we classified the surveyed profiles in the large group of soils Anthroposols, soil type rigosol, subtype chromocambsolic, variety nonterraced. Based on this, it can be concluded that the soils are formed by deep plowing of the chromic luvisol on saprolite. Out of the field research we conclude that the plowing was performed to a great depth (somewhere and deeper than 1 m), so that part of the carbonate lake sediment was also involved and mixed in the soil profile. The examined area was a fallow, which perversely was a vineyard uprooted more than ten years before our investigations. In fact, on the examined parcel, the vineyard was grown over a long period of time. The parent material is Neogene lake sediment. The examined site is located at an altitude of about 160-190 m. The relief is wavy with a slope of 3-8% and is characterized by good external drainage. In the profiles there were no signs of gleyic processes (oxidation-reduction processes) which means that the drainage is good. The aim of this paper is to investigate the content of the total (Cu, Mn and Zn) and available forms of copper, iron, manganese and zinc in rigosols from Veles area, which will

contribute to gaining a better understanding of the content of these heavy metals in the soils of the Republic of Macedonia. One of the goals of this paper is to examine the influence of soil properties and agrochemicals on the distribution of heavy metals in the profile.

Material and methods

Field examinations have been performed according to accepted methods in Former Yugoslavia (Filipovski ed. 1967). The laboratory analyses have been done according to the standard adopted methods in Former Yugoslavia and Republic of Macedonia, as follows: Mechanical composition of soil has been determined by the pipet method (Resulović ed. 1971); the dispersion of the particles has been done with 0,1M Na-pyrophosphate. The separation of the mechanical elements in fractions has been done by the international classification. pH (reaction) of the soil solution has been determined with glass electrode in water suspension and in NKCI suspension (Bogdanović ed. 1966). Easy available forms of P_2O_5 and K_2O were determinate by Al method (Džamić et al. 1996). Content of calcium-carbonate was determined using Scheibler's calcimeter (Bogdanović ed. 1966). Active lime has been determinate by the method of Galet (Bogdanović ed. 1966). The content of humus has been determinate at the base of total carbon by the method of Tjurin modified by Simakov (Орлов and Гришина 1981).Dissolution of soil samples was performed by concentrated. HCl and HNO_3 in a ratio 3:1 (Džamić et al. 1996). The available forms of heavy metals are extracted with the DTPA method (Page ed. 1982).Determination of the content is perfumed with AA spectrophotometer Agilent 55 and Agilent graphite furnace 240 Z.

Results and discussion

Mechanical composition and chemical properties

Data on the mechanical composition and some chemical properties of the tested soils are presented in Tables 1 and 2.

Table 1. Mechanical composition of rigosols from the area of Veles

			In % of fine earth					
Profile No	Horizon and depth cm	Skeleton > 2mm	Coarse sand 0.2 - 2mm	Fine sand 0.02 - 0.2mm	Coarse + fine sand 0.02 - 2mm	Silt 0.002 - 0.02mm	Clay <0.002mm	Silt + clay <0.02mm
1	P 0-30	4,6	10,0	50,9	60,9	15,4	23,7	39,1
1	P 30-51	5,6	11,5	46,9	58,4	11,4	30,2	41,6
1	P 51-73	15,2	10,0	52,5	62,5	10,1	27,4	37,5
1	C 73-105	12,1	5,5	44,7	50,2	21,4	28,4	49,8
2	P 0-31	10,2	12,7	56,9	69,6	9,3	21,1	30,4
2	P 31-69	5,2	11,0	58,9	69,9	8,0	22,1	30,1
2	P 69-105	4,2	12,9	61,9	74,8	7,9	17,3	25,2
2	C 105-140	18,2	20,0	50,6	70,6	16,4	13,0	29,4

Table 2. Chemical properties of rigosols from the area of Veles

Profile No.	Horizon and depth in cm	$CaCO_3$ %	Active $CaCO_3$ %	Humus %	pH		Easyavailable mg/100g soil	
					H_2O	nKCl	P_2O_5	K_2O
1	P 0-30	3,71		2,00	8,30	7,00	12,22	21,30
1	P 30-51	2,89		1,88	7,50	6,40	10,90	14,80
1	P 51-73	1,65		1,74	7,50	6,40	0,56	11,91
1	C 73-105	45,40	19,00	1,50	8,50	7,20	7,89	5,42
2	P 0-31	2,09		1,85	7,90	6,60	6,95	16,25
2	P 31-69	2,51		1,14	7,70	6,50	1,50	11,55
2	P 69-105	2,92		1,01	7,90	6,40	0,75	8,30
2	C 105-140	25,47	9,00	0,81	8,50	7,60	9,77	3,61

Content of total forms heavy metals Cu, Mn and Zn

In Table 3 are shown the data related to the content of total forms of Zn, Mn and Cu in examined soils. For comparison of the results the Dutch reference standards will be used (Ministerie van Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer 2010).

Table 3. Content of total forms heavy metals in rigosols from the area of Veles

Profile No.	Horizon and depth in cm	Total content in $mg \cdot kg^{-1}$		
		Cu	Mn	Zn
1	P 0-30	80,52	693,76	111,21
1	P 30-51	55,41	806,43	78,74
1	P 51-73	36,82	565,93	66,85
1	C 73-105	18,27	139,92	30,11
2	P 0-31	51,40	661,14	83,11
2	P 31-69	54,65	649,23	69,85
2	P 69-105	30,04	509,81	58,38
2	C 105-140	16,86	241,30	35,55
Referent value		36		140
Intervent value		190		720

From Table 3 it can be seen that the total copper content in the tested soil samples is higher than the reference values (except for hor. P 69-105 cm and hor.C of prof. 1 and 2), but lower than the intervention values, which means that there is no danger of contamination of the soil and plants with this metal. An increased content at the top of the profile is notable. Bearing in mind that the surface area has been under vineyards for many years, it can be assumed that the increased content originates from the use of chemicals (pesticides) containing copper. Increased content of total copper in the upper part of the profile in rigosols under vineyards was noted by Андреевски et al. (2011). Андреевски et al. (2012) found an increased content of total copper in the soils from Kochani, on which rice was grown for many years and copper containing chemicals were used. In the chromic luvisol on saprolite from various parts of the Republic, Јекиќ and Савиќ (1972) found a total copper content of 12.0 to 30.4 mg kg^{-1} soil. Митрикески and Миткова (2000) reports data for 11.16 to 36.03 mg kg^{-1} of total copper content in chromic luvisol on saprolite from the Prilep and Kumanovo regions. The content of total copper of 12.3 mg kg^{-1} soil in chromic luvisol on saprolite from Kamnik-Skopje (0-20 cm) was confirmed by Петковски et al. (2001). Petkovski and Melovski (2006) reported data of 7.4 and 9.4 mg kg^{-1} soil for two surface soil samples of the chromic luvisol on saprolite from the Skopje region (Morani). The total copper content of Veles and its surroundings based on 201 surface soil samples (0-5 cm) ranges from 11 to 1700 mg kg^{-1} (Stafilov et al. 2008). It should be noted that the high values are in the immediate vicinity of the lead and zinc smelter. Stafilov and Šajn (2016) conducted soil analysis (0-30 cm) for 60 heavy metals from 1025 locations in Republic of Macedonia. According to these authors the content of total copper ranges from 1.6-270 mg kg^{-1} soil, mean value 27 mg kg^{-1} soil and median 28 mg kg^{-1} soil. The total manganese content in the examined soils ranges from 139.92 to 806.43 mg kg^{-1}. According to Pendias-Kabata and Pendias (2001), the global soils average is 437 mg kg^{-1}. Maximum allowed concentrations for Mn in agricultural soils are 1500 mg kg^{-1} (Pendias-Kabata and Pendias 2001). The examined soils contain significantly less total manganese and no danger of toxicity. Стојковска and Спировски (1963) concluded that the total Mn content in chromic luvisol on saprolite from Republic of Macedonia is 540-1200 mg kg^{-1}. Јекиќ and Савиќ (1972) reported data of 340-900 mg kg^{-1} for the chromic luvisol on saprolite of the R of Macedonia. The content of total manganese of 322.2 mg kg^{-1} soil in chromic luvisol on saprolite from Kamnik-Skopje (0-20 cm) was confirmed by Петковски et al. (2001), and for two surface soil samples of chromic luvisol on saprolite from the Skopje region (Morani), Petkovski and Melovski (2006) reported data of 235.9 and 286,5 mg kg^{-1} soil. The total manganese content of Veles and its surroundings of 159 surface soil samples (0-5 cm) ranges from 160 to 8300 mg kg^{-1} (Stafilov et al. 2008). According to Stafilov and Šajn (2016), the content of total manganese in surface soil samples from the Republic of Macedonia (0-30 cm depth, 1025 locations) ranges from 17 -> 10 000 mg kg^{-1}, mean value 880 mg kg^{-1} and median 900 mg kg^{-1}. The content of total zinc varies within the range of 30.11 to 111.21 mg kg^{-1} soil and is lower than the reference values. This means that there is no danger of contamination of the soil and plants with zinc. According to Lindsay 1982 in: Kastori ed. (1997) the total zinc content of the soil ranges between 10 and 300 mg kg^{-1}, an average of 50 mg kg^{-1}. Chromic luvisol on saprolite from different parts of the Republic (0-20 and 20-40 cm) contains from 10.8 to 56.0 mg kg^{-1} soil total zinc (Јекиќ and Савиќ 1972). For the chromic luvisol on saprolite from the Prilep and Kumanovo regions Митрикески and Миткова (2000), report data from 12,21-52,04 mg kg^{-1} soil. The content of total zinc (two soil samples of chromic luvisol on saprolite from 0-20 and 20-40 cm from the site of village Izvor, Veles) of 74.64 and 98.76 mg kg^{-1} are reported by Андреевски et al. (2006). One surface soil sample of chromic luvisol on saprolite from Kamnik-Skopje location had a content of 75.6 mg kg^{-1} soil (Петковски et al. 2001), and two soil samples from the cultivated surface layer of chromic luvisol on saprolite from the location of Morani-Skopje had a content of 40.17 and 41.99 mg kg^{-1} soil (Petkovski and Melovski 2006). The total zinc content of Veles and its surroundings in 201 surface soil samples (0-5 cm) ranges from 22 to 27 000 mg kg^{-1} (Stafilov et al. 2008). High values were detected in the immediate vicinity of the lead and zinc smelter. According to Stafilov and Šajn (2016), the content of total zinc from 1025 sites from the Republic (surface soil samples from 0-30 cm depth) ranges from 8 to> 10 000 mg kg^{-1} soil, the average value is 82 mg kg^{-1} soil and median 83 mg kg^{-1} soil.

Content of available forms heavy metals Cu, Fe, Mn and Zn

Table 4 shows the content of available forms of heavy metals Cu, Fe, Mn and Zn in the studied soils. These heavy metals are essential trace elements in plant nutrition and their deficiency can cause growth failure while the greater scarcity can cause extinction of plants. On the other hand, if these trace elements are present in high concentrations can lead to phytotocsicity. From the data in the table it can be concluded that the tested soils have low (2), medium (1), high (1) and very high (4) content of available copper. This raised values in the upper part of the profiles are probably as a result of the use of copper containing chemicals over many years, which are used to protect the vineyards. Out of the 12 soil samples from the chromic luvisol on saprolite from different parts of the country (0-20 and 20-40 cm) 10 are with rich and 2 with very high content (Јекиќ and Савиќ 1972). Chromic luvisol on saprolite from the Prilep and Kumanovo regions have poor, medium to rich content of available copper (Митрикески et al. 1997). Spirovski and Georgiev (1971) reported data from 15 soil profiles (76 soil samples) on the chromic luvisol on saprolite from various parts of the country. They concluded that all soil samples have good content, except two that have poor and one with insufficient content. From the obtained results, they conclude that the appearance of carbonates leads to a reduction in the available copper. In our research, we also found that soil samples with the highest content of carbonates (hor. C in prof. 1 and 2) contains least available copper.

The tested soils have very low (1), low (5) and (2) intermediate content of available iron. Due to the presence of $CaCO_3$, the content of available iron is unsatisfactory, with a risk of appearance of iron chlorosis in some crops. Unsatisfactory content of available iron is found in the carbonate rigosols from Kavadarci region (Андреевски et al. 2008). The condition with available manganese is satisfactory. The tested soil samples have low (2), medium (1) and high (5) content of available manganese. It is especially important that soil samples in the upper part of the profile have high content. Reduction of the available manganese for different soil types (including the chromic luvisol on saprolite) in depth of the profile was determined in the work of Стојковска and Спировски (1963). Same conclusion can be find in the work of Spirovski and Georgiev (1971) for the chromic luvisol on saprolite from various parts of the country. Furthermore, same authors pointed out that these soils, with rare exceptions, are well supplied with active manganese. All 12 soil samples of chromic luvisol on saprolite from various parts of the country (0-20 and 20-40 cm) are very richly supplied with available manganese (Јекиќ and Савиќ 1972). The most unfavorable condition is with the content of available zinc. The investigated soils have very low (4), low (1) and intermediate (3) content of available zinc (Table 4), due to the high pH values and the content of $CaCO_3$. The solubility of zinc is especially low in soils with high pH value, as well as in the presence of $CaCO_3$ (Kastori, 1990). According to Јекиќ and Савиќ (1972), the chromic luvisol on saprolite from various parts of the country (0-20 and 20-40 cm) have very poor, poor to medium content of available zinc. For two soil samples of chromic luvisol on saprolite from the location of Izvor-Veles, high content of available zinc was detected (Андреевски et al. 2006). Chromic luvisol on saprolite from the Prilep and Kumanovo regions have very poor, poor, medium to rich content of available zinc (Митрикески et al. 1997). As a general conclusion, it can be said that the content of available micronutrient forms is larger in the upper part of the profile and is a result of the long-term use of agrochemicals that accumulates mainly in the upper part of the profile and the favorable conditions for their mobilization. The lowest is the availability in the parent material (the highest pH values and the highest content of $CaCO_3$).

Tab. 4 Content of available forms heavy metals in rigosols from the area of Veles

Profile No.	Horizon and depth in cm	Available forms in $mg \cdot kg^{-1}$			
		Cu	Fe	Mn	Zn
1	P 0-30	10,30	9,88	21,68	2,93
1	P 30-51	3,39	14,00	23,16	1,14
1	P 51-73	1,47	7,68	16,98	0,41
1	C 73-105	0,71	5,62	4,05	0,23
2	P 0-31	6,21	12,22	29,24	2,59
2	P 31-69	2,93	10,16	22,04	0,96
2	P 69-105	1,03	6,74	10,71	0,27
2	C 105-140	0,44	2,64	4,34	0,16
very low		<0,3	0-5	0-4	<0.5
low		0.3-0.8	5-10	4-8	0.5-1.0
medium		0.9-1,2	11-16	9-12	1.1-3.0
high		1.3-2,5	17-25	13-30	3.1-6.0
very high		>2,5	>25	>30	>6.0

Conclusions

Based on the conducted research the following conclusions can be drawn:
Total zinc contents in all soil samples are lower than the reference value. Total copper content in 3 soil samples is lower than the reference values, while in 5 soil samples had higher contents than reference value, but much lower than intervention value. The increase content of total coper in the upper part of the soil profile originates out of the prolonged use of agrochemicals containing coper in vineyards. Total manganese content is lower than the maximum allowed concentration for agricultural soils. Out of the obtained results we can conclude that there is no danger of contamination of the soil and plants with these heavy metals. The content of available copper and manganese is satisfactory, while the content of available zinc and iron unsatisfactory.The availability of micronutrients is higher in the upper part of the soil profile and is a result of long-term use of agrochemicals that accumulate mainly in the upper part of the profile and the more favorable conditions for their mobilization.

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