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CONTENT OF TOTAL AND AVAILABLE COPPER AND ZINC IN THE PSEUDOGLEY SOIL IN KRALJEVO AND KRUSEVAC BASIN

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Abstract

Notorious acidity of pseudogley, and negative properties caused by it, consequently complicate plant nutrition on this soil type. One ought to pay a special attention to potentially high concentrations of some nutritive elements' available forms. Thus, nutritive elements content higher than allowable limits disqualifies their necessity, making them harmful for crops, and putting pseudogley among soil types that do not give appropriate conditions for soil nutrition. The objective of the paper was to compare content of copper and zinc, with a maximum permissible concentrations (MPC) in the Kraljevo and Krusevac area, on the soil type pseudogley. The district in which researches have been done is a part of pseudogley area situated in the Zapadna Morava valley, at the Kraljevo region, and Krusevac region. Content of total and available copper has been determined up to 60 cm of soil depth. By these researches it has been detected that content of total Cu (20.6-24.2 mg · kg^{-1}) and Zn (43.6-49.2 mg · kg^{-1}) is bellow the maximum allowed concentrations, which excludes their toxicity for crops. Results of the study offer possibility for defining dynamics of available forms of copper and zinc in pseudogley profile.

Key words: *pseudogley, copper, zinc, total, available*

Introduction

Zapadna Morava valey, in which are situated regions of Kraljevo and Krusevac, represents important and well developed agriculture region in Serbia, in which pseudogley is significantly represented. General physico-chemical properties of the pseudogley at the region, particularily expressed acidity (Boskovic-Rakocevic and Bokan, 2005; Dugalić et al., 2002) and unfavorable texture (Dugalić et al., 2004) are limiting intensive crop production.

Acidity of the soil is global limiting factor of crop production (Sumner and Noble, 2003). No matter on the acidity origin (natural or anthropogenic) various specific factors and their interraction can inhibit plant growth, starting from direct harmful influence of high concentrations of H^{+}, Al^{3+} and some organic acids, to the different solubility which leads to the different availabilities of the elements. Particularly sensitive question is mobilization and acquisition of heavy metals, among which some of them, as copper and zinc is, essential in plant nutrition, and which overdoses are toxic for plants (Arsova, 1996; Mery et al., 1986).

Chemism of copper and zinc, and their behavior in soil (as well as of other metals), depends on pH and Eh, but of soil texture and it's properties, i.e. content of soil filosilicates, organic matter, hidratized oxides etc. (Adriano, 2001; Charlatchka and Cambier, 2000; Lair et al. 2007). Their natural source is parent soil material. However, today'human is becoming more influent factor on content of heavy metal changes, very often increasing their content up to the toxic level. The highest anthropogenic origin contaminations are in the vicinities of industrial centers (primary polutants), but nowadays are more and more actual secondary polutants, who are in a long term also very very dangerous polutants. So, on the copper concentration in soils human is more and more influent, by applying numerous pesticides and fertilizers, which has taken to the increase its content, particulary in the topsoil (Facchinelli et al., 2001; Topalović et al., 2011).

Numerous sources of zinc in the soil have anthropogenic character as well. Mobility of antghropogenic origin zinc is much higher than of natural released from the parent soil substrate (Chlopecka et al., 1996).

Material and the methods

Investigation of Cu i Zn at the pseudogley area in the Zapadna Morava river has been done in two regions: Kraljevo and Krusevac. Localities for sampling for the Kraljevo region (I) were Gračac - Ia and Vrnjacka banja - Ib (15 and 23 km south from Kraljevo), and for Krusevac region (II) Čitluk - IIa and Globoder - IIb (5 and 12 km north from Kruševac). Total number of analyzed samples was 154 (48 samples for depth 0-20 cm, 48 samples for depth 20 - 40 cm and 48 samples for depth 40 - 60 cm).

Soil pH has been determined by glass electrode in soil-water slurry and suspension with 1M KCl (1:2,5). Humus has been determined by Kotzman method. Available P_2O_5 and K_2O by AL-method acording to Egner-Riehm, after extraction in 0.1M ammonium-lactate. Available K has been detected directly from the soil extract, by emission spectrophotometry, on flame photometer. Available phosphorous has been detected on spectrophotometer, after a coloring of extract with ammonium-molibdate and $SnCl_2$.

Copper and zinc have been determined by atomic absorption spectrophotometry (AAS), total content after the soil digestion with concentrated HNO_3, and available after the extraction in DTPA (Soltanpour et al., 1996).

Statistical analysis has been done by variance analysis, using PC applications, Microsoft Excel and Statistics.

Results and the discussion

Average values of the investigated basic parameters of soil fertility are given in the table 1. Results of analyzes indicates on similar chemical and physical properties, and accordingly on equalization of pseudogley soils at the area.

Table 1. Basic properties of the pseudogley

Location	Depth (cm)	pH		Humus (%)	Available (mg · $100g^{-1}$)		Particles
		H_2O	KCl		P_2O_5	K_2O	< 0,02 mm
Ia Gračac	0 - 20	5.48	4.35	2.47	4.57	14.9	61.5
	20 - 40	5.33	4.18	1.17	3.97	12.6	58.9
	40 - 60	5.32	4.45	0.21	1.43	13.8	62.1
Ib V. Banja	0 - 20	5.85	4.72	2.18	7.7	15.0	62.7
	20 - 40	5.72	4.53	1.02	0.9	8.6	64.4
	40 - 60	5.28	4.80	0.39	0.7	8.2	72.3
IIa Čitluk	0 - 20	5.57	4,41	2.63	8.9	17.3	62.4
	20 - 40	5.64	4.57	1.84	6.2	13.8	65.6
	40 - 60	5.86	4.52	0.77	3.4	13.4	67.8
IIb Globoder	0 - 20	5.78	4.43	2.38	7.2	14.1	57.8
	20 - 40	5.51	4.51	1.53	5.3	12.8	58.4
	40 - 60	5.69	4.68	0.62	1.8	13.2	59.7

As it has been expected, very high acidity has been determined, low content of available phosphorous, medium content of humus and available potassium, as well as high content of physical clay. So unfavorable agrichemical and agriphysical properties of pseudogley, are limitating it's suitability for succesful plant production, and are forcing obligatory applying pedo-meliorative measures, which confirm numerous cases in the region. (Bošković-Rakočević and Bokan, 2005; Dugalić et al., 2002; Jelić et, al., 2011).

Total Cu content in the investigated areas ranged from 20.6 - 24.2 mg kg^{-1}, which is significantly less than the maximum permissible concentration - MPC (Table 2). Bu this it has eliminated any doubt that high concentrations of this element could potentially be a limiting factor of crop production at the soil type pseudogley. Reviewing of the results, it can be noticed a clear difference between the copper content between the regions, but no difference between the localities within the region. In the region of Krusevac pseudogley has higher content of total Cu in comparison to the region of Kraljevo. Also, it should be noted that in all the localities, the surface layer (0 - 20 cm) is characterized by a higher content of total Cu compared to the other two analyzed depths. Approximately the same total Cu content in pseudogley has been determined near Sabac - Varna (Cakmak et all., 2010) and around Lajkovac (Pivić et all., 2011). And more precise, in these areas the value of total copper were slightly lower compared to those determined in the region of Krusevac and Kraljevo.

Table 2. Content of total and available Cu (mg kg^{-1})

Locality (B)	Depth (cm)	Total Cu (mg · kg^{-1})	Available Cu (mg · kg^{-1})			
			x (A)	SD	CV	Range
Ia Gračac	0 - 20	22.5	4,70	0.77	16.32	3.5 - 5.7
	20 - 40	21.7	3.48	0.75	21.64	2.1 - 4.5
	40 - 60	21.2	3.08	0.37	11.98	2.5 - 3.7
Ib Vrnjačka banja	0 - 20	22.3	5.98	1.02	17.02	4.5 - 7.7
	20 - 40	21.8	4.66	0.88	18.80	3.1 - 6.1
	40 - 60	20.6	4.28	0.39	9.18	3.7 - 5.0
IIa Čitluk	0 - 20	23.8	8.74	1.65	18.85	6.7 - 12.2
	20 - 40	22.4	5.56	0.85	15.22	4.1 - 6.6
	40 - 60	22.6	5.40	0.54	9.93	4.5 - 6.1
IIb Globoder	0 - 20	24.2	7.02	1.25	17.86	4.9 - 8.6
	20 - 40	22.1	4.64	1.16	24.93	2.6 - 6.2
	40 - 60	21.9	4.68	0.84	17.93	3.5 - 6.4
** MPC Cu (total) 100 mg · kg^{-1}			LSD	A	B	
			0.05	0.86	0.72	
			0.01	1.17	0.98	

**MPC - maximum permissible concentration according to Guidelines on Permissible Amounts of Dangerous and Harmful Substances in Soil and Irrigation Water and Methods of testing Them

Differences between the regions and between the investigated depths are especially evident when it comes to the content of available forms of copper. There is clearly a higher content of available copper at the localities in the vicinity of Krusevac than in the region near the Kraljevo, and the noticed differences were statistically significant. In all cases, very high content appears in pseudogley, similar to other areas. Thus, in pseudogley of the headwaters Western Morava river (Boskovic-Rakocevic and Bokan, 2005; Dugalić, et all., 2002), as well as pseudogley near Sabac - Varna (Cakmak et all., 2010) and Lajkovac (Pivić et all. , 2011) have been determined very high values of available Cu.

Particular attention has appeared due to the fact that at the surface layer has been determined significantly higher content of physiologically active form of copper, compared to deeper horizons. The differences were statistically significant and were characteristic at all four localities. For explaining the differences among the horizons, it should be noted that an unequal conditions are present, especially water-air regime for transition of inaccessible Cu to the easily available forms for plants vice versa. However, besides the favorable water-air conditions for the mobilization of Cu, as well as factors that have significantly contributed to its visible accumulation at surface layer such as are organic matter and texture. The organic matter shows a high sorption affinity towards copper (Fernandez - Calvia et all., 2009), building active complexes with it, especially with humic and fulvic acids. On the other hand, copper has property of exchangable adsorption for colloidal fraction, limiting its transfer to the deeper layers. Since at all the localities, very high content of the clay total (Table 1) has been recorded, as well as organic matter, its rinsing has ben prevented. However, taking into consideration the more odten oppinions about very significant impact of human (anthropogenic factors) on the dynamics of copper in the soil, especially in its accumulation in the surface layer (Facchineli et all., 2001; Topalović et all., 2011), we can complete the picture about the causes of larger concentrations of this element. Thus, to the natural reserves of available Cu in surface horizons potentially can be added and annual quantities added with protective means, and fertilizers enriched with microelements, including Cu as well.

Total zinc content of the treated localities of Kraljevo and Krusevac in all the cases was below the maximum permited limits (Table 3). The average values of total reserves of zinc, depending on location and depth at which it was measured, ranged from 43.6-49.2 mg $\cdot kg^{-1}$, which is about the content of the same soil type in Lajkovac (Pivić et all., 2011). Generally, for level of zinc can be concluded that it is not a danger to the crops.

Table 3. Content of total and available Zn (mg kg^{-1})

Locality	Depth (cm)	Total Zn (mg · kg^{-1})	Available Zn (mg · kg^{-1}) x	SD	CV	Range
Ia Gračac	0 - 20	45.3	2.10	0.51	24.15	1.7 - 3.4
	20 - 40	47.2	1.12	0.29	25.57	0.6 - 1.7
	40 - 60	45.9	1.12	0.47	41.72	0.4 - 2.1
Ib Vrnjačka banja	0 - 20	46.8	2.66	0.74	27.89	1.4 - 3.7
	20 - 40	46.1	1.20	0.48	39.72	0.6 - 2.3
	40 - 60	43.6	1.04	0.42	40.28	0.5 - 1.9
IIa Čitluk	0 - 20	47.1	2.60	0.54	20.75	2.1 - 3.7
	20 - 40	49.2	1.28	0.39	30.32	0.9 - 2.1
	40 - 60	47.7	1.18	0.54	45.83	0.5 - 2.4
IIb Globoder	0 - 20	48.5	2.56	1.07	41.84	1.2 - 4.6
	20 - 40	46.8	1.20	0.56	46.70	0.6 - 2.4
	40 - 60	47.9	1.14	0.35	30.72	0.8 - 2.1
** MPC Zn (total) 300 mg · kg^{-1}			LSD	A	B	
			0.05	0.37	0.29	
			0.01	0.50	0.39	

**MPC - maximum permissible concentration according to Guidelines on Permissible Amounts of Dangerous and Harmful Substances in Soil and Irrigation Water and Methods of testing Them

Similar to available copper, it has been noticed it's higher concentration in the topsoil, and differences compared to the content in the subsoil were statisticaly very signifficant. Between the investigated localities there were not signifficant differences, and the detremined values are mainly similar to the other authors (Bosković-Rakocevic i Bokan, 2005; Cakmak et al., 2010; Dugalić et al., 2002; Pivić et. al., 2011).

Assumption that anthropogenic factor could be the cause of appeared difference of content of available zinc by the layers, in this case is without the ground. Distribution of zinc, by depth without clearly visible leyers in which it has been accumulated like total, as well as like available, indicate that specifficaly status of this element in the investigated soil is result of it's chemism.

Conclusion

Content of total copper and zinc in the investigated region was considerable under the maximum permissible concentrations, and these elements do not represent potential threat for the cultivated plants. The content and distribution of Cu within the depths, and its accumulation in the surface layer are primarily result of unequal conditions for mobilization through the horizons, and partialy the result of human activities related to the application of pesticides. Types of available zinc within the depths is the result of natural resources of this element in pseudogley, and the conditions for its mobilization and immobilization.

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