THE TOTAL AND AVAILABLE CONCENTRATIONS OF ESSENTIAL TRACE ELEMENTS IN AGRICULTURAL SOILS OF EASTERN CROATIA

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ABSTRACT

The research objective was to determine the influence of basic soil chemical properties on total concentration and available fractions of essential trace elements in the soil. Agrochemical soil analysis were conducted at two localities of different soil properties Berak and Vinogradci in eastern Croatia. The soil at the site Berak was eutric cambisol of neutral reaction (pH average (H_2O) 7.20), while the soil in Vinogradci was luvisol of slightly acid reaction (average pH (H_2O) 5.87). Both soils were poor in organic matter and well supplied with phosphorus and potassium. As expected, at both analyzed sites the highest average concentrations were determined for total Fe, Mn and Zn followed, and the lowest concentrations were for total Cu. Higher total concentrations of analyzed microelements were recorded at the Berak site. The total concentrations of Zn and Cu in all analyzed soil samples were below the maximum permissible concentrations. The highest average concentration of available microelements fraction by EDTA Extraction, were at the Berak site determined for Mn (50.52 mg/kg), then Fe (21.77 mg/kg), Cu (4.78 mg/kg), and the lowest for Zn (1.47 mg/kg). At the Vinogradci site average concentrations of available fraction of microelements determined by EDTA extraction were the highest for Fe (77.09 mg/kg), then Mn (30.75 mg/kg), Cu (4.36 mg/kg), and the lowest for Zn (1.76 mg/kg). Identical order of average concentrations at both sites was also recorded for extraction with DTPA solution. Comparing available fraction of microelements by localities, higher average concentrations of Mn and Cu were found at the site Berak, while on site Vinogradci higher average concentrations were of Fe and Zn. At both sites the DTPA method extracted more of Fe and Mn, an average of 51.06% and 6.39% more than the EDTA method, but the method EDTA extracted more Zn and Cu, an average of 127.10% and 100.40% than DTPA method. The smallest share of the available fraction of the total concentration was recorded for Fe (0.06% by EDTA -

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0.09% by DTPA), followed by Zn (1.20% by DTPA - 2.74% by EDTA) and Mn (5.93% by EDTA – 6.31% by DTPA), while the largest share was observed for Cu (10.92% by DTPA and 21.84% by EDTA).

Keywords: *microelements, total concentrations, available fractions*

INTRODUCTION

Soil reaction affects the soil chemical properties in wide range, especially soil nutrients mobility and plant availability. Furthermore, soil acidity and elemental toxicities or deficiencies associated with it, affects crops growth and restricts yields through the world (Rengel *et al*., 2003). The increase in cultivation intensity with the increasing demand for higher yields with better quality has resulted in increasing demand for microelements.

Microelements such as Fe, Mn Zn and Cu play an essential role in the assimilation and dissimilation processes of plants in terms of activators and inhibitors of metabolic processes. Availability of micronutrients in agricultural soils is defined with pH as main factor. Changes of soil reaction impacts to the Fe, Mn, Zn and Cu soil status turnover. Increase of fertilization may cause some negative effects because of changes in micronutrient availability (Györi, 2006). Zn and Fe deficiency are currently listed as major risk factors for human health globally (Cakmak, 2008). Micronutrient deficiency in general can noticeably reduce the performance and profitablity of agroecosystem (Fisher, 2008).

Soil extraction techniques to measure the status of available micronutrients for plants are important in the diagnosis of deficiency or toxicity (Garcia at all, 1997). Threfore, the aim of this paper was to was to determine the influence of basic soil chemical properties on total concentration (aqua regia) and available fractions (EDTA and DTPA) of essential trace elements (Fe, Mn, Zn Cu) on acid and neutral soils of continental part of Croatia.

MATERIAL AND METHODS

Soil samples for conducted research were collected from arable soils (0-30 cm depth) on location Vinogradci, from luvisol soil in type Osijek-baranja county and location Berak, eutric cambisol soil in Vukovar-srijem county. Both locations are situated in eastern part of continental Croatia. A total of 106 soil samples of arable soils were taken on both localities for agrochemical analysis. The basic methods of soil analysis included determination of soil pH in a suspension of soil and water as well as soil and KCl solution, humus content, content of available forms of phosphorus and potassium, hydrolytic acidity and $CaCO_3$ content.

The total concentration of mineral elements in the soil, including the analyzed microelements are determined by various methods of partial or complete digestion of

the soil (hydrofluoric acid, nitric acid, aqua regia). Soil samples for this investigation were digested in aqua regia according to method ISO, 1995b using freshly prepared mixture of 1/3 HNO_3 + 2/3 HCl.

For determination of plant available Fe, Mn, Zn and Cu concentrations in soil the different extraction solutions (EDTA, DTPA, AA-EDTA, HCl and water) are used, and for this study extraction methods with a solution of EDTA (ethylenediaminetetraacetic acid) and DTPA solution (dietientiaminpentaoctena acid) were used. The extraction method with EDTA (Trierweiler and Lindsay, 1969) is commonly used in the Republic of Croatia.

RESULTS AND DISCUSSION

Basic agrochemical soil properties as soil pH, humus content, plant available phosphorus and potassium and carbonate content were analyzed in all soil samples (Table 1). The soils at the site Berak were in average neutral (pH average (H_2O) 7.20), moderately supplied with organic matter and well supplied with phosphorus and potassium, moderately calcareous and according to hydrolytic acidity liming was not required. The soils in Vinogradci were in average moderately acid (average pH (H_2O) 5.87), poor in organic matter and also poorly supplied with phosphorus and potassium, moderately calcareous and liming was not obligate but it could be beneficial.

Table 1. Basic soil properties

	pH_{H_2O}	pH_{KCl}	AL-P_2O_5 mg/100 g	AL-K_2O mg/100 g	humus (%)
Berak	7.20a	6.38a	20.99a	24.31a	2.08a
Vinogradci	5.87b	4.95b	14.09a	17.79b	1.66b
Mean	6.51	5.64	17.41	20.92	1.86
St. dev.	1.13	1.22	20.47	6.67	0.36

As expected, at both analyzed sites the highest average concentrations of total concetrations of essential trace elements were determined for total Fe, Mn and Zn followed, and the lowest concentrations were for total Cu (Table 2).

Table 2. Total concentrations of microelements in soil (mg/kg)

	Fe	Mn	Zn	Cu
Berak	30.134a	839.5a	62.82a	21.75a
Vinogradci	26.469b	659.9b	53.92b	15.94b
Mean	28.233	746.3	58.21	18.73
St. dev.	3.051	163.3	7.59	3.78

Higher total concentrations of all analyzed microelements were recorded at the Berak site compared to Vinogradci site. It is important to point out that total concentrations of Zn and Cu in all analyzed soil samples (Berak and Vinogradci) were below the maximum permissible concentrations, which are for Zn 150.00 mg/kg and for Cu 90 mg/kg.

The highest average concentration of available microelements fraction by EDTA extraction (Table 3) were at the Berak site determined for Mn (50.52 mg/kg), then Fe (21.77 mg/kg), Cu (4.78 mg/kg), and the lowest for Zn (1.47 mg/kg). At the Vinogradci site average concentrations of available fraction of microelements determined by EDTA extraction were the highest for Fe (104.62 mg/kg), then Mn (38.60 mg/kg), Cu (3.46 mg/kg), and the lowest for Zn (1.69 mg/kg).

Table 3. Available concentrations of microelements in soil by EDTA extraction

	Fe	Mn	Zn	Cu
Berak	21.77b	50.52a	1.47a	4.78a
Vinogradci	104.62a	38.60b	1.69a	3.46b
Mean	64.76	46.95	1.58	4.10
St.dev.	67.42	21.40	0.94	1.10

Identical order of average available concentrations at Berak site (Mn>Fe>Cu>Zn) and at Vinogradci site (Fe>Mn>Cu>Zn) was recorded for extraction with DTPA solution (Table 4).

Table 4. Available concentrations of microelements in soil by DTPA extraction

	Fe	Mn	Zn	Cu
Berak	43.44b	51.13a	0.68a	2.28a
Vinogradci	107.31a	43.07b	0.71a	1.81b
Mean	76.58	44.40	0.69	2.03
St.dev.	53.11	21.15	0.44	0.51

Analysed neutral and acid soils significantly differed in soil pH, soil organic matter content and plant available potassium. Average total concentrations of microelements for all soils significantly differed in decreasing order Fe (28233 mg/kg) > Mn (746.3) > Zn (58.21 mg/kg) > Cu (18.73 mg/kg) according to all samples mean. Significant difference between neutral (Berak) and acid soils (Vinogradci) in total concentrations of microelements was recorded for all analysed essential trace elements where significantly higher total concentrations were observed in neutral soils (Berak site).

Comparing available fractions of microelements by localities, plant available fractions of Fe and Zn extracted with EDTA or DTPA were significantly higher in acid soils (Vinogradci site), while on neutral soils (Berak site) significantly higher average concentrations in the same extractants were observed for Mn and Cu (Table 5). At both sites the DTPA method extracted more of Fe and Mn, an average of 51.06% and 6.39% more than the EDTA method, but the method EDTA extracted more Zn and Cu, an average of 127.10% and 100.40% than DTPA method.

Table 5. Total and available microelements content in neutral and acid soils

	Neutral soils (Berak)					Acid soils (Vinogradci)				
	Total mg/kg	**EDTA mg/kg**	**EDTA % of T**	**DTPA mg/kg**	**DTPA % of T**	**Total mg/kg**	**EDTA mg/kg**	**EDTA % of T**	**DTPA mg/kg**	**DTPA % of T**
Fe	30134	21.77	0.07	43.44	0.14	26469	104.62	0.39	107.31	0.40
Mn	839.5	50.52	6.02	51.13	6.09	659.9	38.60	5.85	43.07	6.53
Zn	62.82	1.47	2.34	0.68	1.08	53.92	1.69	3.13	0.71	1.32
Cu	21.75	4.78	21.98	2.28	10.48	15.94	3.46	21.71	1.81	11.35

In all analysed soils and in both extraction solutions the lowest share of available fraction in total content were determined for Fe, follows Zn, then Mn and Cu had the highest share of the available fraction in total content. According to all samples mean, share of the available fraction of the total concentration was for Fe 0.06% by EDTA and 0.09% by DTPA extraction, for Zn 2.74% by EDTA and 1.20% by DTPA solution, for Mn 5.93% by EDTA and 6.31% by DTPA extraction, and for Cu 21.84% by EDTA and 10.92% by DTPA method.

Although acid soils had lower total concentrations of all analyzed microelements compared to neutral soils, the share of available fractions of the total concentrations were higher in acid soils than in neutral soils for all analyzed microelements.

Significant correlations between total concentrations of microelements and amounts extracted by EDTA or DTPA were not observed. On the other hand, very significant correlations were determined for plant available Fe, Mn, Zn and Cu between EDTA and DTPA (Table 6).

Table 6. Correlation coefficients between EDTA and DTPA solution for analysed microelements

	all soils	neutral soils	acid soils
Fe	0,832	0,877	0,741
Mn	0,848	0,808	0,919
Zn	0,957	0,855	0,974
Cu	0,748	0,351	0,829

Three extracted microelements by EDTA and by DTPA extraction solution were the most comparable in acid soils (Mn r=0,92, Zn r=0,97, Cu r=0,83; n=55). The highest correlation among EDTA and DTPA method for Fe was obtained in neutral soils (r=0,88; n=51). There was no significant correlation between EDTA and DTPA extracted Cu in neutral soils.

CONCLUSIONS

It can be concluded that EDTA solution extracted higher plant available concentrations of Zn and Cu than DTPA solution regardless of soil pH. Lončarić *et al*. (2008) reported for soils in Croatia that the ratio of available and total concentrations of micronutrients was strongly impacted by soil pH and all analysed elements had higher plant available concentrations in acid soils compared to calcareous soils. At the same time, DTPA solution resulted with higher concentrations of plant available Fe and Mn compared to EDTA method. Higher portion of available fractions of the total concentrations were observed in acid soils than in neutral soils for analyzed microelements. The highest ratio of available fraction of total content was recorded for Cu and the lowest for Fe in neutral and acid soils. Very significant correlations were determined between EDTA and DTPA method, and available Mn, Zn and Cu showed the highest correlation in acid soils, while Fe showed the highest correlations in neutral soils.

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