TOTAL AND PLANT AVAILABLE TOXIC TRACE ELEMENTS (Cd, Cr, Co AND Pb) AT FARMS OF EASTERN CROATIA

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Original scientific paper UDK 631.453(497.5)

ABSTRACT

It is well known that soil properties, metal speciation and plant species, especially soil-plant interactions, determine the availability of metals in soils. Therefore, various one-step extraction methods such as EDTA and DTPA have been used to represent the available fraction. In present study we observed the total (*aqua regia*) and available fraction (EDTA and DTPA) of toxic trace elements (Co, Cd, Cr and Pb) from soil on two farms (Berak and Vinogradci) in eastern Croatia that have different soil properties. The study included 106 soil samples from soil depth 0-30 cm that were collected during 2013-2014. Samples were analyzed for standard soil properties (pH, organic matter, AL-P, AL-K) as well as for total and available fractions of toxic trace elements. Analyses of main soil properties show vide variety of soils. Soil pH (in H_2O) was in range 4.4-8.6 (avg: 6.5), thus sampling sites included range from very acid to alkaline soils. Farm in Berak (average pH was 7.2) had more alkaline soils while farm in Vinogradci was acidic (average pH was 5.9). Organic matter varied from 1.1-2.8% (avg: 1.9), average phosphorous was 17.4 mg/100g and potassium 20.9 mg/100g. Total concentration of trace elements extracted by *aqua regia* show satisfactory results as not one sample had elevated levels of toxic trace elements (Co, Cd, Cr and Pb). In that regard all sites satisfy Croatian regulation on pollutants in agricultural fields. However, EDTA and DTPA extractions show higher availability of Cr, Co and Pb for both extractions (EDTA and DTPA) at farm in Vinogradci where soils are more acidic compared to farm Berak. Only available Cd was shown to be higher in Berak than in Vinogradci.

Keywords: *availability, aqua regia, DTPA, EDTA, trace elements*

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INTRODUCTION

In most legislation maximum permissible concentrations (MPC) of trace elements are defined by total concentrations in soil. However, large number of studies has shown that plant uptake and potential toxicity are not so dependent on total concentrations as much as on available fractions. Soil properties, metal speciation and plant species, especially soil-plant interactions, determine the availability of metals in soils (Ehlken and Kirchner, 2002). Therefore, numerous one-step extraction methods such as EDTA, DTPA, $CaCl_2$, $NaNO_3$, water extraction etc. have been used to represent available fraction. The most widely used extraction methods are EDTA and DTPA extractions. Both of these methods have been used due to their ability to form very stable, water-soluble and well-defined complexes with metal cations (Norvell, 1984; Brun *et al*., 2001; Hammer and Keller, 2002; Chaignon *et al*., 2003; Feng *et al*., 2005). Previous studies of trace elements in this area have shown that there is a significant correlation between available factions (EDTA) and total concentrations (HCl extraction) (Lončarić *et al*., 2008). In addition, soil pH have shown to have a significant impact on available fraction of trace elements (Ivezić *et al*., 2012; Lončarić *et al*., 2008) therefore in present study we have observed relationship between total concentration, extracted by *aqua regia*, and available fractions, represented by EDTA and DTPA extraction methods, on two farms with different soil properties (acid and alkaline soils). The aim of our study was to investigate two extraction methods of available fractions under different soil pH conditions.

MATERIALS AND METHODS

The study was conducted on two farms (Berak and Vinogradci) in Danube basin of eastern Croatia where 106 samples from soil depth 0-30 cm were collected during 2013-2014. Sampling locations had different soil properties so both, acid and calcareous soils, were represented in the study. Soil samples were analyzed for standard soil properties (pH, organic matter, ammonium lactate phosphorous (AL P_2O_5), ammonium lactate potassium (AL K_2O)) as well as for total (*aqua regia*), EDTA and DTPA extractable toxic trace elements (Co, Cd, Cr and Pb). In addition to soil samples, 18 plant samples of wheat and corn grain were collected as well. Statistical analysis was done in Minitab statistical software and Microsoft Excel.

RESULTS AND DISCUSSION

Standard soil properties show significant differences ($p<0.001$) of main soil properties between two farms for pH, organic matter and available potassium (Table 1). Soil pH (in H_2O) was in range 4.4-8.6 (avg: 6.5), thus sampling sites included range from very acid to alkaline soils. Berak site had more alkaline soils while Vinogradci site had more acidic soils (Table 1). Organic matter (OM) varied from 1.1-2.8% (avg: 1.9), again Berak site had significantly ($p<0.001$) higher concentrations. Average available phosphorous was 17.4 mg/100g and available potassium 20.9 mg/100g, Berak had higher concentrations of both elements (P and K) although only concentrations of available K were significantly higher ($p<0.001$).

Table 1. Main soil properties of sampling sites

	Location	n	Mean	StDev	Min.	Max.
pH (H_2O)	Berak	51	7.2[a]	0.999	5.3	8.6
	Vinogradci	55	5.9[b]	0.847	4.4	8.4
pH (KCl)	Berak	51	6.4[a]	1.082	4.5	7.7
	Vinogradci	55	5.0[b]	0.907	3.9	7.7
OM	Berak	51	2.1[a]	0.2506	1.6	2.8
%	Vinogradci	55	1.7[b]	0.3383	1.1	2.7
AL P_2O_5	Berak	51	21.0[a]	24.7	5.6	100.0
mg/100g	Vinogradci	55	14.1[a]	15.05	3.5	95.2
AL K_2O	Berak	51	24.3[a]	4.573	15.7	35.6
mg/100g	Vinogradci	55	17.8[b]	6.81	9.9	44.1

[a,b] indicate significant differences at $p<0.001$, OM-organic matter, AL P_2O_5 - available P, AL K_2O – available K

In addition to mineral fertilizers, farm in Berak was also using organic fertilizers while farm in Vinogradci was only using mineral fertilizers, which is probably the reason for slightly better soil quality at Berak site. Organic fertilizers can improve soil fertility in a long term, primarily organic matter content but also the bioavailability of phosphorus and potassium as well (Lončarić *et al*., 2005).

Total concentration of trace elements extracted by *aqua regia* show significantly ($p<0.001$) higher concentrations for all four investigated toxic elements at Berak site (table 2.), however the concentrations were below the MPC for all analysed samples. In that regard all sites satisfy Croatian regulation on pollutants in agricultural fields (Official Gazette, 2010).

Available fractions of trace elements show higher availability of Cr, Co and Pb (although only Cr (EDTA) was significantly higher) for both extractions (EDTA and DTPA) at farm in Vinogradci where soils are more acidic than at farm Berak, while available Cd was shown to be significantly higher at Berak site compared to Vinogradci. This can be explained by higher total concentrations of Cd at Berak site as well as by Cd dependence on pH at Berak site in contrast to Vinogradci site where there was no such correlation (Table 3). Vinogradci had lower soil pH but the total Cd concentration was also significantly lower than at Berak site so we can argue that the pool from which the EDTA and DTPA were extracting Cd was much smaller at Vinogradci site. Soil pH influences the availability which is confirmed by correlation analysis of available fraction of trace elements (EDTA and DTPA) with pH (Table 3) from which we can see that most of the available fractions are highly correlated with pH.

Table 2. Trace element concentrations (*aqua regia*, EDTA and DTPA)

	Location	n	Mean	StDev	Min.	Max.
Co(AR)	Berak	51	14.5[a]	1.068	11.4	16.4
	Vinogradci	55	12.6[b]	1.548	9.2	16.2
Cr(AR)	Berak	51	45.9[a]	3.517	35.15	54.11
	Vinogradci	55	36.3[b]	3.601	28.53	44.01
Cd(AR)	Berak	51	0.34[a]	0.06464	0.21	0.47
	Vinogradci	55	0.27[b]	0.06577	0.11	0.41
Pb(AR)	Berak	51	15.7[a]	1.625	9.9	17.6
	Vinogradci	55	13.3[b]	1.425	9.5	16.1
Co(EDTA)	Berak	51	0.16 [a]	0.0714	0.05	0.33
	Vinogradci	55	0.18 [a]	0.0692	0.07	0.46
Cr(EDTA)	Berak	51	0.10 [b]	0.03288	0.04	0.21
	Vinogradci	55	0.18 [a]	0.07382	0.06	0.34
Cd(EDTA)	Berak	51	0.11 [a]	0.01456	0.07	0.15
	Vinogradci	55	0.08 [b]	0.02615	0.05	0.19
Pb(EDTA)	Berak	51	2.36 [a]	0.4157	1.65	3.45
	Vinogradci	55	2.54 [a]	0.845	1.45	7.45
Co(DPTA)	Berak	51	0.16 [a]	0.06675	0.061	0.293
	Vinogradci	55	0.18 [a]	0.06697	0.052	0.388
Cr(DPTA)	Berak	51	0.015 [a]	0.006981	0.005	0.028
	Vinogradci	55	0.017 [a]	0.006006	0.003	0.027
Cd(DPTA)	Berak	51	0.069 [b]	0.01124	0.036	0.098
	Vinogradci	55	0.043 [a]	0.01633	0.014	0.115
Pb(DPTA)	Berak	51	1.14 [a]	0.2906	0.70	2.30
	Vinogradci	55	1.19 [a]	0.316	0.59	2.07

[***] indicates significant differences at $p<0.001$

Table 3. Correlation matrix

	Vinogradci pH(H_2O)	Berak pH(H_2O)
Co(EDTA)	-0.514***	-0.616***
	0.001	0.001
Cr(EDTA)	-0.74***	-0.754***
	0.001	0.001
Cd(EDTA)	-0.221	-0.323*
	0.105	0.021
Pb(EDTA)	-0.369**	0.041
	0.006	0.775
Co(DPTA)	-0.749***	-0.888***
	0.001	0.001
Cr(DPTA)	-0.777***	-0.875***
	0.001	0.001
Cd(DPTA)	-0.178	-0.71***
	0.194	0.001
Pb(DPTA)	-0.636***	-0.331*
	0.001	0.018

*** indicates significant correlation

Relationship between extraction methods representing available fractions show that EDTA and DTPA were highly correlated (Table 4), but EDTA shows significantly higher values for Cr, Cd and Pb. However, since both extraction methods were highly correlated we can easily predict values of one method by using the values of the other. Correlation between available fractions with total concentrations of investigated trace elements was reported only for some elements (Table 4). On the other hand, correlation of EDTA and DTPA with soil pH was present for most of the elements (Table 3). Therefore, we can argue that pH was influencing the mobility and availability of investigated toxic trace elements in a greater extent than the total concentrations did on both sites, Berak (alkaline site) and Vinogradci (acidic site).

Table 4. Correlations between extraction methods (*aqua regia*, EDTA and DTPA)

Berak	EDTA with *aqua regia* for: Co ($p<0.001$) and Cr ($p<0.05$)
	DTPA with *aqua regia* for: Co ($p<0.001$), Cr ($p<0.01$) and Pb ($p<0.001$)
	EDTA with DTPA for: Co, Cr, Cd and Pb ($p<0.001$)
Vinogradci	EDTA with *aqua regia* for: Cd ($p<0.001$)
	DTPA with *aqua regia* for: Co ($p<0.01$), Cd ($p<0.001$) and Pb ($p<0.001$)
	EDTA with DTPA for: Co, Cr, Cd and Pb($p<0.001$)

CONCLUSIONS

Total concentrations of all four investigated toxic trace elements (Cd, Co, Cr and Pb) were bellow maximum permissible concentrations prescribed by Croatian legislation. Two extraction methods, EDTA and DTPA, are most commonly used for determination of available trace elements. In our study they were correlated between each other for all investigated trace elements, regardless of the investigating site (Berak or Vinogradci), which indicates that if we have the results from one method we can still predict the values of the other one. The difference in soil pH between the sites did not affect this relationship, EDTA showed higher values for Cd, Cr and Pb at both sites. Further analysis of plant material is necessary to investigate the relationship of plant uptake and EDTA and DTPA extraction methods on such sites with different pH levels.

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