Regression model for prediction availability of essential heavy metals in soils

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Abstract
The aim of paper was to compare relationshipsof total and plant available essential heavy metals in soils considering soil acidity and humus impacts. Regression models should provide additional data (EDTA-extractable fraction) from available data (heavy metal total content, soil pH). The 60 soil samples were analysed for pH, humus, phosphorus, potassium, and additionally for essential heavy metals (Fe, Mn, Zn, Cu, Ni) by extraction by aqua regia and by ethylenediaminetetraacetic acid (EDTA). The heavy metal with highest total content was iron, then manganese, zinc, nickel, and copper regardless of soil pH. The order of EDTA-extracted elements changed with copper jumping from last to third place, but the percentage of total content extracted by EDTA was quite opposite: Cu, Ni, Zn, Mn, and Fe. Soil pH impacted on EDTA-extractable fraction and the regression models can predict the EDTA-extractable fraction of Zn, Cu and Ni with acceptable average errors, but not for Fe and Mn. The obligate input data for models are total soil content of certain heavy metal and pH. Model errors decreased using humus content as additional input data. The lowest model errors were for copper in acid soils and nickel in calcareous soils.

Key Words
Aqua regia, EDTA, iron, manganese, zinc, copper, nickel.

Introduction

Heavy metals importance for plants differs since there are essential micronutrients heavy metals (Fe, Mn, Zn, Cu, Ni, Mo), and also beneficial (Co) or nonbeneficial toxic heavy metals (Cd, Cr, Pb, Hg). The concentration of heavy metals in soils is influenced by activities such as agricultural practices and industrial activities and is associated with biological and chemical cycles. Intensification of agriculture production pointed out the role of micronutrients. Increase of fertilization may cause some negative effects because of changes in essential heavy metal availability (Györi 2006). For Most micronutrients availability is impacted by soil pH. Boron and molybdenum become toxic in high alkaline soils, and iron and manganese become toxic in highly acidic soils. Osztoics *et al.* (2005), also reported that a high Mn concentration was found in extremely acidic soils. Soil extraction techniques to measure the status of available micronutrients for plants are important in the diagnosis of deficiency or toxicity (Garcia *at al.* 1997). The aqua regia microwave acid digestion techniques produced the fastest, safest and accurate analytical results with precision better than 5% for determination of microelements in soil (Melaken *et al.* 2005) and this analysis is obligate in Croatia for determination of soil quality in term of organic agriculture and protection of agricultural soils. However, aqua regia digestion does not identify the plant available fraction of soil heavy metals. Hence, this method is not appropriate for determination of soil heavy metal impact on environment or on plant nutrition. On the other hand, soil extraction with EDTA is the most common method in Croatia regarding the determination of soluble or plant available fraction of essential heavy metals. EDTA or similar methods are not obligate in Croatia, either considering organic agriculture or conventional fertilization recommendations. Furthermore, the relation of total and soluble content of heavy metals in Croatian soils is not adequately investigated, although some results were published and the difference of fraction extracted by different methods was pointed out (Lončarić *et al.* 2008). The aim of this paper was to compare relationships of total and plant available essential heavy metals in soils considering possible soil acidity and humus content impacts on total and available essential heavy metals fractions. Also, the aim of regression models was to provide additional data (EDTA-extractable fraction) from other available data (total heavy metal content and soil pH).

Methods

The 60 soil samples were collected from arable soils from the depth 0-30 cm in continental part of Croatia. All the samples were analysed for basic chemical properties such as soil pH_{H2O} and pH_{KCl} (ISO 10390), soil organic matter by sulfochromic oxidation (ISO 14235) and plant available P and K extracted by ammonium-lactate (Egner *et al*. 1960). In addition to basic analyses, the essential heavy metals (Fe, Mn, Zn, Cu and Ni) were extracted by aqua regia (ISO 11466), and by ethylenediaminetetraacetic acid (EDTA).The fraction

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extracted by aqua regia was considered as soil total content, and the EDTA-extractable fraction as plant available content. The concentrations of extracted heavy metals were measured by the AA flame method and by ICP-OES. The statistical analyses and regression models were done using PC applications Microsoft Excel and SAS.

Results

The pH_{H2O} of analysed soils varied from 4.45 to 8.83 and pH_{KCl} values were 3.61 to 7.88. The average difference between pH_{H2O} and pH_{KCl} was 1.05 pH units (6.63 vs. 5.58). The pH_{KCl} of 56 % samples was lower than 6 and hydrolytic acidity of these samples varied from 1.7 to 6.8 cmol/kg. The carbonate content in the rest of the samples for, 44% samples with pH_{KCl} higher than 6, was 0.84 to 40.9 % $CaCO_3$. The humus content of analysed soils was in a wide range 0.61 to 4.60 % with an average 1.75 %

Total essential heavy metals extracted by aqua regia

The total essential heavy metal concentrations in soils extracted by aqua regia were in expected order (Table 1): Fe was extracted in highest concentration, followed by Mn, Zn, Ni and Cu. Jurković *et al.* (2006) reported for acid Croatian soils highest level of available Fe and Mn and significantly lower Zn and Cu.

Table 1. Minimum, maximum and average concentrations (mg/kg) extracted by aqua regia.

	Fe	Mn	Zn	Ni	Cu
Minimum	17058	997	38	12	4.0
Maximum	45123	9757	99	58	41
Average	27217	6254	70	31	21

Maximum concentrations of zinc, copper and nickel as potentially toxic essential heavy metals were not higher than thresholds allowed for agricultural soils in Croatia (300, 100, 60 mg/kg, respectively).
The correlations between extracted total concentrations of analysed elements were very significant with manganese as an exception (Table 2) regardless of soil acidity and nickel in calcareous soils. However, soil acidity did not impact significantly on Fe, Mn and Zn total concentrations, but total concentration of copper was 15% and nickel 20% higher in calcareous than in acid soils (on average).

Table 2. Correlation coefficients for extracted elements in all soils, and acid and calcareous soils separately.

	All soils				Acid soils				Calcareous soils			
	Fe	Mn	Zn	Ni	Fe	Mn	Zn	Ni	Fe	Mn	Zn	Ni
Mn	ns				ns				ns			
Zn	0.81	ns			0.82	ns			0.83	ns		
Ni	0.50	ns	0.50		0.92	ns	0.85		ns	ns	ns	
Cu	0.68	ns	0.66	0.58	0.73	ns	0.58	0.78	0.83	ns	0.85	ns

Available essential heavy metals extracted by EDTA

Heavy metals extracted by EDTA should be the fraction available for plants. Hence, these amounts of heavy metals are significantly lower than total amounts in soils (Table 3), and percentage of total amounts extracted by EDTA differ among elements: copper was extracted in the highest relative amount (19%), than nickel (4.5%), zinc (3.5%) manganese (0.6%) and iron (0.3%). However, iron was extracted in highest absolute amounts, followed by manganese, than copper, zinc and nickel in lowest amounts. Similar results were published earlier (Lončarić *et al.* 2008) with the same relationships for iron, copper and zinc, rather lower for nickel, and significantly higher for extractable Mn.

Table 3. Minimum, maximum and average concentrations (mg/kg) extracted by EDTA

	Fe	Mn	Zn	Ni	Cu
Minimum	6.9	5.2	0.6	0.3	1.6
Maximum	453.8	112.5	7.7	3.8	10.1
Average	80.6	40.9	2.4	1.4	4.1
% of total amount	0.3%	0.6%	3.5%	4.5%	19.3%

Only few correlations among elements extracted by EDTA are significant, more for calcareous soils (Fe-Cu, Mn-Cu, Ni-Cu) than acid soils (Ni-Cu) and these relationships are not strong enough for prediction of analysed elements concentrations using regression models. However, it is well known that soil pH has a significant impact on heavy metal availability which is decreased by raising soil pH. For the analysed soils

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considering Fe, Mn and Ni were extracted in lower propotions of total content from calcareous soils than from acid soils (75% lower, 46% and 14%, respectively). The extracted fractions of Zn and Cu were in slightly lower percentages of total amounts for acid soils than for calcareous soils (6 and 12%, respectively).

Regression model

The very significant impact of soil pH on the extractable fraction of heavy metals was used to generate regression models for prediction of EDTA-extractable amount of analysed heavy metals. Two regression models are described in this paper (Table 4):

1. TA model for prediction EDTA-extractable fraction of heavy metal, where total (T) heavy metal content extracted by aqua regia (in mg/kg) and soil pH_{KCl} (A) were used as input data,
2. TAH model - using all the data as TA model, plus humus (H) content (in %) as additional input data.

Table 4. Regression parameters in relation Y (= EDTA-extractable metal) = $TX_1 + AX_2 + HX_3$ (in mg/kg).

	Acid soils				Calcareous soils			
Model	Total metal (T)	pH_{KCl} (A)	humus (H)	r	Total metal (T)	pH_{KCl} (A)	humus (H)	r
TA (Zn)	0.015	0.259	-	0.82	0.054	-0.178	-	0.89
TA (Cu)	0,040	0,604	-	0,97	0,125	0,268	-	0.93
TA (Ni)	0.044	0.026	-	0.92	0.041	-0.0004	-	0.90
TAH (Zn)	0.017	-0.178	1.041	0.84	0.060	-0.163	-0.297	0.89
TAH (Cu)	0.068	0.095	1.003	0.96	0.106	0.036	1.171	0.95
TAH (Ni)	0.053	-0.252	0.580	0.94	0.029	-0.061	0.498	0.93

Although soil pH impacted significantly on the fraction of extracted Fe and Mn, the regression models TA and TAH were not good enough for prediction of EDTA-extractable Fe or Mn using total Fe or Mn content, soil pH_{KCl} and humus content as input data. The reason could be that extremely low fraction of Fe (0,3%) and Mn (0,6%) extracted by EDTA and variations of input data were too high. On the other hand, the impact of soil pH on the extractable fraction of Zn, Cu and Ni was rather low, but the fractions were higher (3,5; 19,3 and 4,5%, respectively) and very significant correlation enabled quite useful regression models.

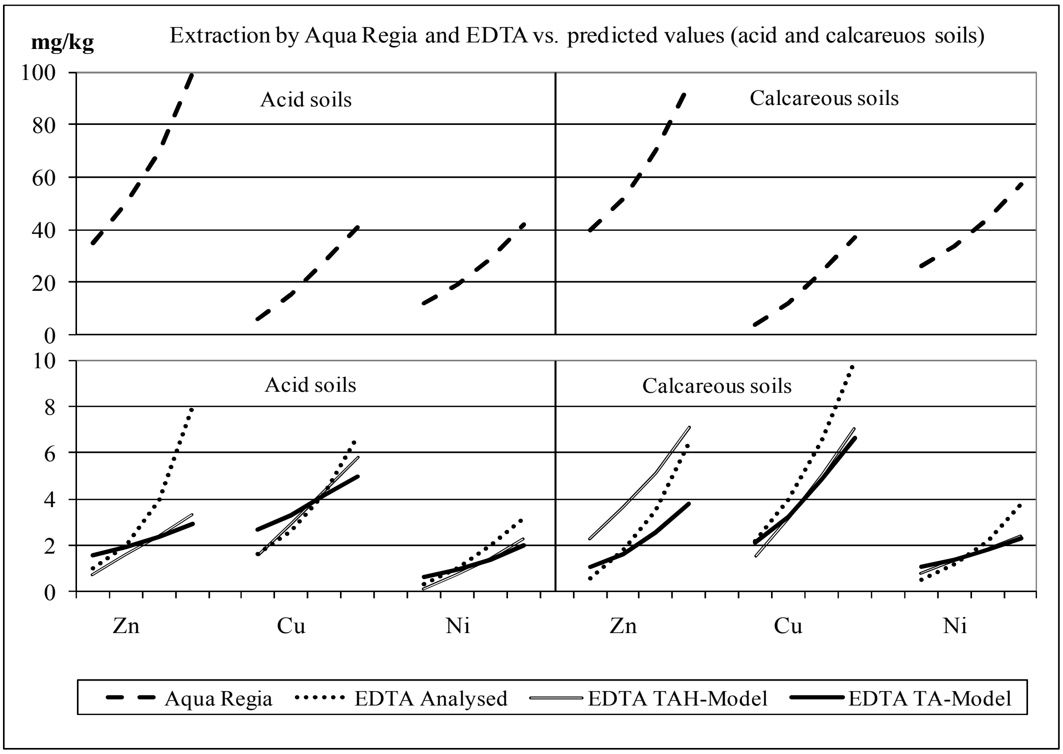

Figure 1. The comparison of total soil heavy metal contents, EDTA-extractable analytical values from acid and calcareous soils, and EDTA-extractable values predicted by TA and TAH models.

The model with highest error (28 and 34% for TAH and TA models) was the zinc prediction model for acid soils, and model error increased with increasing total soil Zn content, pH and humus content. For zinc, there is significant difference between TA and TAH models for calcareous soils with almost equal errors (around

30%), but the TA model predicts lower and TAH model higher values than actually measured (Figure 1). Also, the TA model is better for lower total soil zinc contents, and TAH model for highest contents. The most precise model was TAH copper model for acid soils with average error only 4.3% and 12.6% for calcareous soils. TA model had average error for acid soils 5,1%, but copper prediction is too high at low total copper contents and too low at higher total copper contents. The basic properties of all nickel models are average model errors in the range 17-29%, low difference between TA and TAH models, slightly lower error of the TAH model, and higher model accuracy at lower total soil nickel contents.

Conclusion

The heavy metal with highest total content in analysed agricultural soils was iron, followed by manganese, zinc, nickel and copper regardless to soil pH. The total contents correlated significantly with exception of manganese. The order of EDTA-extracted elements was almost the same with copper jumping from last to third place, but, the percentage of total content extracted by EDTA was quite opposite in order Cu, Ni, Zn, Mn and Fe. Soil pH impacted significantly on EDTA-extractable fractions and regression models for prediction of EDTA-extractable fraction in soil can be used for Zn, Cu and Ni with acceptable average errors (up to 34; 12,6 and 29%, respectively), but not for Fe and Mn. The obligate input data for models are total soil content of heavy metal and soil pH_{KCl} value, and model errors are rather lower using humus content as additional input data. The lowest model errors were for copper in acid soils and nickel in calcareous soils. Regression model can be successfully used for prediction extractable fraction of Zn, Cu and Ni (analyses is not obligate by bylaws in Croatia) using total soil contents of Zn, Cu and Ni (analyses obligated by bylaws in Croatia).

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