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Distribution and forms of iron in the vertisols of Serbia

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Abstract: Soil of arable land and meadows from the Ap horizon, taken from ten different localities, were investigated for different forms of Fe, including total (HF), pseudo-total (HNO₃), 0.1 M HCl extractable and DTPA (diethylenetriaminepentaacetic acid)-extractable. A sequential fractional procedure was employed to separate the Fe into fractions: water soluble and exchangeable Fe (I), Fe specifically adsorbed with carbonates (II), reducibly releasable Fe in oxides (III), Fe bonded with organic matter (IV) and Fe structurally bonded in silicates (residual fraction) (V). The soil pH, cation exchange capacity, and size fractions (clay and silt) had a strongest influence on the distribution of the different forms of Fe. The different extraction methods showed similar patterns of the Fe content in arable and meadow soils. However, the DTPA iron did not correspond with the total iron, which confirms the widespread incidence of iron-deficiency in vertisols is independent of the total iron in soils. The amount of exchangeable (fraction I) and specifically adsorbed (II) iron showed no dependence on its content in the other fractions, indicating low mobility of iron in vertisols. The strong positive correlation ($r = 0.812$ and 0.956) between the content of iron in HNO₃ and HF and its contents in the primary and secondary minerals (fraction – V) indicate a low content of plant accessible iron in the vertisol. The sequential fractional procedure was confirmed as suitable for accessing the content and availability of iron in the vertisols of Serbia.

Keywords: soil; iron solubility; plant availability; adsorption; distribution of iron.

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INTRODUCTION

Vertisols are the predominant soils in Central and western Serbia and cover 780 000 ha, which is 8.93 % of the total land area in Serbia.¹ These soils, developed through degradation of lake sediment, are suitable for vegetable, fruit and vine crops production. However, the unfavourable characteristics induced by high clay contents, poor structure (a prismatic polyedric structure with the frequent occurrence of angled aggregates) and generally high acidity could limit their productivity potential.

The distribution and availability of heavy metals in soils is important when assessing the environmental quality of an area, since increased concentrations in soil, water and plants pose a serious threat to human and animal health. The origin of heavy metals in the soil is mainly geochemical (originating from the parent substrate) and partly anthropogenic (various sources of pollution). The soil solution contains considerably small amounts of the microelements, thus heavy metals occur in soil in water-soluble, exchangeable forms, bound to specific sites of the organic and inorganic soil components and in the structure of primary and secondary minerals.²⁻⁵

The bioavailability, mobility and chemical reactivity of heavy metals in soils are often associated with their distribution among certain soil fractions and the dynamic equilibrium among them.^{6,7}

Iron is an important micronutrient which availability could be significantly affected by the soil properties. Generally, the total iron increases with increasing cation exchange capacity (CEC) and the clay and silt content.⁸ Complexation of iron by soil organic matter may result in increased plant availability, and microbial exudates can supply additional iron to plant routes.² Likewise, exchangeable iron adsorbed onto inorganic sites and diethylenetriaminepentaacetic acid (DTPA) extractable iron increase with increasing soil organic matter but decrease with higher soil pH and calcium carbonate content.^{4,28}

The determination of the mobile and potentially mobile iron forms is the key issue in the estimation of iron availability to plants. However, the simple selection of methods for their extraction is not sufficient for conceptualisation of their availability, sources or interconnection with a phase of a soil. Accordingly, iron distribution among the different fraction is essential an understanding of their chemistry in soils. Many authors suggested the employment of a sequential extraction procedure for investigation of heavy metals in the environment, sediment of natural origin or in substrates secondarily enriched with heavy metals (*e.g.*, agriculture, industry, road traffic).^{7,9-12} These method eliminate the disadvantages of individual extraction procedures and provide information on the total and available content of selected heavy metals in soils, the strength of the bonding and their relationship with specific compounds in the solid phase of soil.¹⁰ Hitherto in Serbia, many single or sequential extraction procedures, mainly based

on the Tessier procedure or different versions thereof, have been applied to soils and sediments to fractionate metals by using different extractants or reagents to obtain more useful information about the bioavailability and mobility of metals.^{1,14–16}

The aim of this study was to assess the distribution and forms of iron in the environmental conditions of vertisols soils in Serbia by utilizing different extraction methods and a sequential extraction procedure.

EXPERIMENTAL

The investigations were conducted on vertisols (smonitza) type of soils taken from the Ap horizon at ten different localities in Serbia (Fig. 1): (1) Milutovac, (2) Priština, (3) Trnava, (4) Rekovac, (5) Vranje (Neradovac), (6) Zaječar, (7) Bela Crkva, (8) Blace, (9) Salaš and (10) Kragujevac. The sub-samples were taken from field and meadow ecosystems at a depth of 0 to 20 cm, after which they were air-dried, crushed in a porcelain mortar and sieved through stainless steel screens. Particles 2 mm in size were used for soil characterization and Fe-fraction analyses.



Fig. 1. Geographical locations of the investigated soil samples in the Republic of Serbia.

Determination of the soil characteristics

Soil pH was determined in a suspension in water and 1 M KCl at the ratio of soil:solution ratio of 1:2.5 after a 0.5 h equilibration period; the organic content was determined using the humus method of Kotzmann²⁷ and the available P₂O₅ and K₂O content was determined using the Egner-Riehm Al method.^{13,14} The CEC was determined using the method with 1 M NH₄OAc, pH 7, and the particle size distribution was determined by a pipette method. The total iron was determined by atomic adsorption spectrophotometry (AAS, Model Carl Zeiss Jena AAS 1N). A cold extraction method was used for the determination of the total and pseudo-total iron in which 0.5±0.001 g of sample was transferred into a centrifuge tube and then 10 mL of 0.5 M HCl was added. The solution was shaken, subjected to vortex for a short time and placed on a shaking-table for agitation for 1 h. After agitation, the solution was centrifuged at 3000 rpm (1,900×g) for 15 min, and then filtered through a 0.45-µm syringe filter to remove particulates.

The total iron was determined by AAS after digestion of the soil sample (0.5 g), which had previously been heated in Pt dishes for 2 h at 450 °C with a mixture of acids (HF, HNO₃ and HClO₄). The pseudo-total content of iron was determined by AAS spectrometry after the finely grounded soil sample (2 g) had been digested for 2 h with 20 ml conc. HNO₃ and then treated with 3 ml 30 % H₂O₂ and heated for 15 min.¹³

Sequential fractional procedures

Iron (Fe) in different soil fractions was extracted using the procedure proposed by Tessier *et al.*¹⁰ The methods followed for the fractionation procedures are outlined below:

1. Water soluble and exchangeable metals were determined by extraction with 0.1 M CaCl₂ (pH 7.0). 10 g of soil was agitated in plastic pots with 100 cm³ of solution for 20 min, and then filtered.

2. Specifically adsorbed metals and metals bound to carbonates were determined by extraction with 1.0 M NaOAc (pH 5.0). Again, 10 g of soil was added to 100 cm³ of solution, agitated for 5 h at room temperature and then filtered. In this case, the sum of 1) and 2) was obtained and by subtraction, fraction 2 was obtained.

3. Reductant releasable Fe occluded in oxides of Fe and Mn was determined in the following manner. 2.5 mg of soil was placed in a centrifuge tube and, after extraction of fractions 1 and 2, 50 cm³ of 0.04 M hydroxylamine hydrochloride in 25 % of HOAc, pH 3, was added. The tubes were then kept in a water bath for 6 h at 85 °C and stirred. Subsequently, the total volume was set to 50 cm³ by addition of distilled water, closed and then agitated for 10 min, and centrifuged for 10 min at 3000 rpm. The clear solution was removed into reagent bottles, while the remaining soil was washed with 20 cm³ of distilled water.

4. Metals bound to the organic matter were determined in the following way. 7.5 cm³ of 0.02 M HNO₃ and 12.5 ml of H₂O₂ pH 2.0 were added to the test tubes with the soil remaining from the previous three extractions. The tubes were kept in a water bath at 86 °C for 2 h, under stirring. After cooling, 7.5 cm³ of 30 % H₂O₂ was added and the mixture was again kept at 86 °C for 3 h. After cooling, 12.5 cm³ of 3.2 M NH₄OAc in 20 % HNO₃ was added. The final volume was set by adding distilled water and then the tubes were closed. They were then shaken for 30 min and centrifuged for 10 min at 3000 rpm. The clear solution was transferred into reagent bottles.

5. Metals structurally bound in silicates (residual fraction) were determined by calculation as the difference between the total content determined with HNO₃-HF-HClO₄ and the sum of the first four fractions.

The distribution of iron in the chemical fractions 1–4 was determined by flame AAS (atomic absorption spectrometry).

Statistical analysis

The results obtained for the different contents of iron (total, accessible and different chemical fractions) in the vertisols were statistically evaluated by the Student's *t*-test and the Pearson correlation coefficients.¹⁸

RESULTS AND DISCUSSION

Basic characteristics of examined Serbian vertisols are given in Table I.

TABLE I. Examined physico-chemical characteristics of vertisols in Serbia (mean, range and standard deviation); *t*-test field: meadow; NS – application of the Student *t*-test showed that there is no statistical significance between the examined characteristics of field and meadow soils

Soil characteristic	Field			Meadow		
	Mean	Range	Standard deviation	Mean	Range	Standard deviation
pH (H ₂ O)	7.1	5.8–8.1	0.9	6.9	5.6–8.1	0.9
pH (KCl)	6.0	4.6–6.9	0.9	5.8	4.7–7.0	0.9
Humus content, %	3.3	2.5–4.0	0.5	3.5	2.0–5.6	1.1
P ₂ O ₅ mg/100 g	7.7	0.6–28.0	8.5	4.2	0.8–17.8	5.0
K ₂ O mg/100 g	34.4	19.0–59.6	11.8	31.1	20.4–53.5	10.4
CEC meq/100 g	25.1	15.5–31.5	5.6	23.8	16.9–34.7	6.6
Sand, %	29.6	21.4–36.0	4.8	32.2	22.3–50.5	9.0
Silt, %	24.6	18.8–31.2	3.6	22.8	11.9–29.4	5.6
Clay, %	45.8	33.5–54.4	7.2	44.9	28.9–64.3	11.1
Silt + Clay, %	70.4	64.0–78.6	4.8	67.7	49.5–77.7	9.0

The examined vertisols showed marked heterogeneity in terms of pH, and most of the studied soil samples were acid to slightly alkaline. In terms of the readily available phosphorus content, the selected locations belong to the class of soils with lower availability of this element but the observed level of P₂O₅ varied widely between the different samples: 0.6–28.0 mg/100 g soil for samples from fields and 0.8–17.8 mg/100 g soil for the samples under meadows. The investigated soils showed a moderate to high content of available K₂O. The selected sites of vertisols also differed in their humus contents, with an average of 3.3 (field) and 3.5 % (meadow), and had a high capacity for cation adsorption, range from 15.5 to 34.7 meq/100 g soil.

The average value of total iron (HNO₃–HF–HClO₄ extraction) in the tested vertisols was 3.7 (field) and 3.6 % (meadows), ranging from 0.5 to 5 % which are typical values for “normal” land. The variations between the samples could be explained by the differences in the basic physical and chemical properties of the soil. Thus, soils with higher clay contents and higher values of CEC contained higher levels of iron. This indicates that the metals in soils with the higher values

of CEC are strongly bounded and could not be subjected to leaching out in the deeper layers. Consequently, the total content of the iron was the higher compared with soils with a less pronounced CEC thus metals are not in form that could be easily adopted by plants, what determines their low accessibility.^{5,19}

The extraction of accessible forms of iron using mild extraction agents (0.1 M HCl and 0.005 M DTPA) showed extremely low contents of soluble iron compared to the total iron contents. The solution of 0.1 M HCl extracted two times more iron compared with the 0.005 M DTPA solution, ranging from 53.5 (field) to 60.6 mg/100 g soil (meadow). This observation confirms that the application of 0.1 M HCl solution also transformed the part of iron cations specifically adsorbed on organic and mineral components (oxides, carbonates and silicates), as well as occluded and precipitated iron. The acids also released coordinated bound iron ions from the surface of silica, but these amounts vary considerably depending on the mineralogical composition of soil.^{20–22}

Lindsay and Norvell²³ using the DTPA-accessible content of microelements (iron) successfully separated Colorado soils into deficient and well supplied. Based on the plants response to the application of microfertilizers (Fe), the critical content of DTPA-extracted iron was determined, which was 4.5 mg kg⁻¹ for corn and 2.5 mg kg⁻¹ for sorghum (sorghum plants are less susceptible to a lack of microelements). Below these values, plants responded to the application of iron, hence it could be considered that this soil was deficient in Fe. Above the value of 4.5 mg kg⁻¹ extracted iron, the plants showed no response to the application of iron microfertilizers, therefore these soils were characterized as well supplied.

The relative values of the extracted iron in HNO₃ solution, obtained from the pseudo-total metal contents,¹³ show a similar variation in both groups of vertisols, since the decomposition of the crystal lattice of the primary and secondary minerals was not complete. From the vertisol of arable soils, 84.9 % of its total content was extracted by HNO₃, while from the meadows 83.4 %. These data indicate that at least 15–17 % of the total iron content is most likely located in the structures of primary and secondary minerals. These results correspond with those of Hang *et al.*,²⁵ who found that the average extractability of 4 M HNO₃ for iron was between 76 to 85 % of that of HF for vertisols of the Mississippi River Delta.

In the case of vertisols originating from the fields that are richer in iron, HNO₃ extracts a greater part of the total iron, compared with vertisols from the meadows. However, it was observed that the relative values of the extraction of iron show similar variation in both groups of soil. Based on this, it could be concluded that the higher concentrations of iron in the arable soil was not a prerequisite for its greater solubility and its greater occurrence in the weaker forms of bondage.

In the vertisol of the fields, 0.1 M HCl solution extracted 0.15 % of the total content of iron, whereas 0.005 M DTPA extracted 0.07 %. Considering the indi-

vidual samples, the relative values obtained by extraction with 0.1 M HCl showed greater variation, ranging from 0.06 to 0.22 %, which is in accordance with the greater variation in the total iron content of these soil samples. The relative amounts of iron extracted by 0.1 M HCl solution decreased with increasing total iron content. However, among the individual samples, there were differences in the relative distribution of iron, which is the result of the differences in the pH of the observed soils samples. Particularly important are the samples with the lowest pH values in which the relative iron content, compared to the other samples, was up to nine times higher. Considering the fact that DTPA also extracted the labile forms of microelements from the soil, the amounts of specifically adsorbed iron and iron bound to carbonates was significantly higher in these samples.

Compared to the vertisol of fields, the average value of the relative iron content in the meadow samples extracted with 0.1 M HCl solution was higher (0.18 %), although the average total iron content was lower. The individual samples of vertisol from the meadows showed marked heterogeneity with respect to the relative iron content in the extraction medium (0.03 to 0.38 %), which is most likely caused by differences in the total content of iron and related with variability in the chemical properties of the samples, since the higher prevalence of iron occurs in the samples with the lower pH values. In addition, several soil samples from the meadows, the pH values (in 1 M KCl) of which ranged from 4.7 to 7.0, contained up to 2–6 times more iron. The DTPA iron was not in accordance with the total iron, which confirms the wide incidence of iron-deficiency despite the total amount of iron in the soils.^{8,25}

According to the results of the *t*-test (Table II) between the total and accessible iron contents in the tested vertisols, no statistically significant differences in the distribution of iron between the field and meadows was found, as a result of the similar mineralogical composition of the parent material on which these soils are formed.^{26,27}

TABLE II. Iron content in the tested vertisols of Serbia determined using different extraction methods ($X \pm s_d$ and interval, mg kg^{-1})

Location	HF	HNO ₃	0.1 M HCl	0.005 M DTPA
Field (<i>n</i> = 10)	37000±4516	31200±4036	53.5±14.3	24.6±19.1
	31000–44000	24500–36900	28.0–69.0	7.0–56.0
Meadow (<i>n</i> = 10)	36000±5869	30300±6015	60.6±43.1	30.3±25.3
	28000–44000	22200–36900	25.0–144.0	8.0–86.0
<i>t</i> -Test	0.2117 ^a	0.3709 ^a	0.7726 ^a	1.5102 ^a

^aThere is no statistical significance at $p < 0.05$

The analysis of the correlation coefficients showed that the total iron content and capacity for the adsorption of cations (*CEC*) depended moderately ($r = 0.49$), which correspond with the supposition that soils with higher *CEC* values may

have a greater total content of heavy metals (Table III).¹⁹ In addition, a strong dependence of the total iron content on the clay content and clay content + dust content ($r = 0.72$ and 0.76 , respectively) was observed, due to the capacity of the mechanical fraction to adsorb cations and considerably contribute in the capacity of the whole soil. Accordingly, a negative correlation of the iron content and amount of sand ($r = -0.76$) was found, since a coarsening of the soil particles results in a decrease of soil sorption capacity and less iron in the structure of the minerals (silicates, quartz) in the larger soil particles¹². In general, the observed total iron content in soil was almost entirely controlled by its mechanical composition.⁸ The pseudo-total content of iron, in addition to the observed relationships for the total iron content, has a positive correlation with the pH value.²⁸

TABLE III. The relative content of iron in different extraction agents (in % of HF-total)

Extraction method/Locality	HF	HNO ₃	0.1 M HCl	0.005 M DTPA
Field				
Milutovac	35000	91.1	0.15	0.03
Priština	44000	83.9	0.06	0.03
Trnava	41000	79.5	0.11	0.03
Rekovac	38000	78.9	0.14	0.03
Vranje	35000	91.4	0.19	0.02
Zaječar	34000	78.8	0.10	0.04
Bela Crkva	32000	76.5	0.21	0.17
Blace	35000	94.0	0.15	0.07
Salaš	43000	85.3	0.15	0.10
Kragujevac	31000	89.3	0.22	0.18
<i>X</i>	37000	84.9	0.15	0.07
Meadow				
Milutovac	28000	84.6	0.36	0.07
Priština	41000	90.0	0.35	0.02
Trnava	40000	74.8	0.06	0.04
Rekovac	39000	89.0	0.09	0.06
Vranje	38000	95.8	0.06	0.02
Zaječar	29000	76.6	0.18	0.12
Bela Crkva	28000	80.0	0.38	0.31
Blace	36000	89.3	0.12	0.12
Salaš	44000	83.6	0.03	0.02
Kragujevac	39000	70.4	0.15	0.14
<i>X</i>	36000	83.4	0.18	0.09

The amount of iron extracted from vertisols with a solution of 0.1 M HCl showed no dependence on any set of properties of this type of soil (Table IV).

The greatest influence on the DTPA accessible iron in the Serbian vertisols had the acidity ($r = -0.92$) and potential acidity ($r = -0.89$), and to a lesser extent, the content of available potassium and the *CEC*, the correlation coefficients of which were 0.57 and 0.69, respectively. Regarding the fact that the obtained cor-

relation coefficients were negative, it can be concluded that increasing soil acidity increases the solubility of iron, while an increasing content of clay increases the strength of the binding between the clay and iron, and consequently reduces its solubility.

TABLE IV. Correlation coefficients between the total and available content of iron and some soil properties

Soil property	Iron	
	Total (HF)	Pseudo-total (HNO ₃)
pH (H ₂ O)	NS ^a	0.51 ^b
pH (1 M KCl)	NS	0.51 ^b
Humus content	NS	NS
CaCO ₃	NS	NS
P ₂ O ₅	NS	NS
K ₂ O	NS	NS
CEC	0.49 ^c	0.52 ^b
Sand	-0.76 ^c	-0.66 ^b
Silt	NS	NS
Clay	0.72 ^c	0.52 ^b
Silt + Clay	0.76 ^c	0.66 ^c
	Available content (0.1 M HCl)	Available content (DTPA)
pH(H ₂ O)	NS	-0.92 ^c
pH(nKCl)	NS	-0.89 ^c
Humus content	NS	NS
CaCO ₃	NS	NS
P ₂ O ₅	NS	NS
K ₂ O	NS	-0.57 ^b
CEC	NS	-0.69 ^c
Sand	NS	NS
Silt	NS	0.64 ^c
Clay	NS	-0.60 ^c
Silt + Clay	NS	NS

^aThere was no statistical significance; ^bstatistically significant at the probability level 0.05; ^cstatistically significant at the probability level 0.01

A similar result was presented in Sharma *et al.*⁸ Additionally, they observed a positive correlation with the content of organic matter, following the formation of chelates and the reduction of iron(III) to iron(II), which upon oxidation, precipitates as amorphous iron compounds thereby increasing the solubility of the iron. The DTPA soluble iron in the vertisols showed a statistically significant positive correlation with the content of the mechanical silt fraction, which indicates that coarsening of the soil particles could potentially provide a readily available fraction of iron.

Sequential extraction analysis

Considering the fact that the tested vertisols in Serbia were established at locations with deficient iron content in the parent material, from their sequential extraction (Table V), it is possible to determine the form of their location in the soil, allowing for a clear understanding of their potential mobility and accessibility for plants.

TABLE V. Distribution of iron in the different fractions of vertisols obtained by sequential analyses procedures (mg kg^{-1})

Fraction	I	II	III	IV	V
Field Fe $\pm SD$	0.11 \pm 0.32	2.62 \pm 2.04	4024 \pm 1777	221 \pm 127	32552 \pm 4301
Meadow Fe $\pm SD$	0.18 \pm 0.22	4.0 \pm 5.07	4094 \pm 1181	231 \pm 146	31970 \pm 58881

Based on statistical correlation analysis (Table VI), a highly significant correlation was found between the exchangeable and specifically adsorbed iron ($r = 0.89$), which indicates mutual influences of these two fractions. The quantities of exchangeable (fraction I) and specifically adsorbed iron (fraction II) in the investigated vertisols of Serbia showed no dependence on its contents in the other extracted fractions, indicating low mobility of iron in these soils. The negative correlations between the total and residual Fe (fraction V) with the Fe in fraction II ($r = -0.46$ and -0.51 , respectively) and the positive correlation of the total with the residual Fe ($r = 0.96$) indicate that the mobility of iron is small and that the stable fraction V is correlated with the total iron content. The content of iron in the first fraction has no significant correlation with any soil properties, except pH (Table VII).

TABLE VI. Correlation coefficient between the iron content in different chemical fractions in soil from fields and meadows

Fraction	I	II	III	IV	V	Fe content total (HF)
I	1.00					
II	0.89 ^a	1.00				
III	NS ^b	NS	1.00			
IV	NS	NS	NS	1.00		
V	NS	-0.51 ^c	NS	NS	1.00	
Fe content total	NS	-0.46 ^c	NS	NS	0.96 ^c	1.00

^aStatistically significant at the probability level 0.01; ^bthere was no statistical significance; ^cstatistically significant at the probability level 0.05

Specifically adsorbed iron and iron related to carbonates (fraction II) gave significant differences and negative correlations with some soil properties, such as pH, clay content and CEC. The positive correlation with the silt implies that these factors had a dominant influence on the distribution of iron in this fraction. The negative correlation between the iron content in the specifically adsorbed

iron fraction and the pH value of the soil indicates that the solubility of iron in this fraction decreases with increasing soil pH because high pH values favour the oxidation of Fe^{2+} to Fe^{3+} , which results in the precipitation of iron(III) salts and oxides. The significant negative correlation between the specifically adsorbed iron and the clay content indicates that with increasing clay content, the CEC value increases and hence the association of iron and the solid soil phase, which resulted in reduced mobility and accessibility of the iron in this fraction.

TABLE VII. Correlation coefficients between the iron content in different chemical fractions and some soil characteristics

Soil characteristics	Fraction					Fe content total
	I	II	III	IV	V	
pH (H ₂ O)	-0.48 ^a	-0.70 ^b	-0.45 ^a	NS ^c	0.54 ^a	NS
pH (1M KCl)	NS	-0.64**	-0.46 ^a	NS	0.54 ^a	NS
Humus content	NS	NS	NS	NS	NS	NS
P ₂ O ₅	NS	NS	-0.66 ^b	NS	NS	NS
K ₂ O	NS	NS	-0.70 ^b	NS	0.53 ^a	NS
CEC	NS	-0.55 ^b	-0.49 ^a	0.50 ^a	0.63 ^b	0.49 ^a
Sand	NS	NS	NS	NS	-0.78 ^b	-0.76 ^b
Silt	NS	0.55 ^b	NS	NS	NS	NS
Clay	NS	-0.50 ^a	NS	0.43 ^a	0.80 ^b	0.72 ^b
Silt + Clay	NS	NS	NS	NS	0.78 ^b	0.76 ^b

^aStatistically significant at the probability level 0.05; ^bstatistically significant at the probability level 0.01; ^cthere was no statistical significance

The positive correlation between the iron content in Fraction II and the silt content indicates iron unstably bound with the silt particles, since increasing particle size led to increasing solubility of the iron in this fraction.

The content of extracted iron from the oxide fractions of Fe (Fraction III) is negatively correlated with some soil properties, such as pH value, content of available P₂O₅ and K₂O and the values of CEC. Increasing soil pH values decreased the iron content in the third fraction due to the high degree of oxidation of Fe^{2+} compounds and depositions with phosphate. The negative correlation between the iron content in this fraction and the CEC value indicates that the increase in surface adsorption increases the bond strength between the solid soil phase and iron, which affects the lower solubility of iron in this fraction.

The amount of iron extracted from the organic matter was positively correlated with the CEC values and the clay content. This indicates that the clay and the CEC are the dominant factors affecting the distribution of iron in this fraction.

The iron associated with the residual fraction was negatively correlated with sand content and positively with the soil pH values, readily available K₂O, clay, CEC and the silt + clay fractions. The negative correlation between the residual iron and sand and a positive correlation with the clay content and silt + clay indi-

cates that most of iron in this fraction is bound to clay particles and silt. The clay fractions usually contain high amounts of metals (Fe) due to high adsorption, as well as the content present in the crystal lattice. These variations in the amounts of residual iron with clay are in accordance with the conclusions of other authors.^{28,29}

The positive correlation between iron in residual fractions and soil pH indicates that base oxidation and environmental conditions cause iron deposition but reducing conditions its hydrolysis.⁴

Based on the attained results of correlation coefficients given in Table VIII, DTPA extracted iron gives highly significant positive correlations with the iron content in Fractions I and II ($r = 0.689$ and 0.907 , respectively) and a negative correlation with the content in fraction V.

TABLE VIII. The correlation coefficients between the content of iron in different chemical fractions of soil and its contents obtained using different extraction procedures

Extraction procedures	Fraction				
	I	II	III	IV	V
HF	NS ^a	-0.463 ^b	NS	NS	0.956 ^c
HNO ₃	NS	-0.519 ^b	NS	NS	0.812 ^c
0.1 M HCl	NS	-0.441 ^b	NS	NS	NS
0.005 M DTPA	0.689 ^c	0.907 ^c	NS	NS	-0.557 ^c

^aThere was no statistical significance; ^bstatistically significant at the probability level 0.05; ^cstatistically significant at the probability level 0.01

Since the DTPA extractant gives highly significant correlation coefficients with fractions I and II, it can be used to evaluate the accessibility of iron for plants, and this interpretation agrees with the negative correlation ($r = -0.557$) between the DTPA extracted iron and the iron content in the structures of the primary and secondary minerals.

Unlike the DTPA extractant, 0.1 M HCl showed less pronounced statistical significance ($r = 0.441$) only with the iron content in the second fraction and, therefore, cannot be used as a reliable factor in the interpretation the bioavailability of the iron in soils.

The less pronounced but significant negative correlation coefficients ($r = -0.519$ and -0.463) found between the HNO₃ and HF extracted iron and its contents in fractions I and II, respectively, showed that the iron extracted with these acids is not weakly bound iron which is easily accessible to plants. Moreover, this interpretation agrees with the existence of strong positive correlations ($r = 0.812$ and 0.956) between the content of iron in HNO₃ and HF and its contents within the structure of primary and secondary minerals (residual fraction V).

CONCLUSIONS

Analyses using the procedures of sequential extraction showed that the soil samples from arable soils and meadows were similar in the relative distribution of iron among the different fractions. The sequential extraction procedures showed that the iron was mostly built into the lattice of primary and secondary minerals and in the clay minerals of the residual fraction. The iron content in the soils was correlated with the pH value, CEC and the aggregate size fraction of silt and clay. The low plant availability of the iron in the vertisols could be explained by its occurrence in the least soluble fraction (Fraction V). The appropriate selection of genotype, foliar application and liming are required for the successful growth of agricultural crops on the examined soils.

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ИЗВОД

ДИСТРИБУЦИЈА И ФОРМЕ ГВОЖЂА У ВЕРТИСОЛИМА СРБИЈЕ

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У циљу одређивања различитих облика гвожђа у неким варијететима вертисола са подручја Србије (оранице и ливаде) пореклом са десет различитих локалитета анализиран је укупан садржај гвожђа (HF), псеудо-укупан садржај (HNO₃), 0,1 М HCl растворљиво и ДТРА растворљиво гвожђе. Секвенцијалном екстракцијом извршено је раздвајање фракција гвожђа на растворљиво у води и разменљиво Fe (I), специфично абсорбовано гвожђе са карбонатима (II), оклудовано Fe у оксидима (III), Fe везано за органску материју (IV) и Fe структурно везано у силикатима (резидуални део, V). pH вредност земљишта, СЕС и величина фракција (глина и прах) имали су значајан утицај на дистрибуцију различитих облика гвожђа. Различите методе екстракције су показале сличан облик садржаја Fe у обрадивом земљишту и ливади. Међутим, садржај ДТРА растворљивог гвожђа не одговара укупном садржају, што потврђује да је учесталост недостатка гвожђа у вертисолима на подручју Србије независна од укупног гвожђа у земљиштима. Износ разменљивог гвожђа (фракција I) и адсорбованог (II) гвожђа није показала зависност од његовог садржаја у другим фракцијама, што указује на ниску мобилност гвожђа у проучаваним вертисолима. Јака позитивна корелација ($r = 0,812$ и $0,956$) између садржаја гвожђа у HNO₃ и HF и његовог садржаја у примарним и секундарним минералима (фракција V) показују низак ниво гвожђа доступног биљкама у испитиваним вертисолима. Коришћењем секвенцијалне екстракције могуће је утврдити садржај и приступачност гвожђа у вертисолима Србије.

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