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Distribution and forms of manganese in vertisols of Serbia

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Abstract: Soil samples taken from the Ap horizon of arable land and meadows at ten different localities were analyzed for different forms of manganese, including total (HF), pseudo-total (HNO₃), 0.1 M HCl-extractable and diethylenetriaminepentaacetic acid (DTPA)-extractable. A sequential fractional procedure was used for Mn portioning into fractions: water soluble and exchangeable Mn (I), specifically adsorbed Mn with carbonates (II), reductant releasable Mn in oxides (III), Mn bonded with organic matter (IV) and Mn structurally bonded in silicates (residual fraction) (V). Serbian vertisols have a normal Mn content, comparable with similar soils. The total (HF) and pseudo-total (HNO₃) Mn contents were not correlated with soil properties, whereas the humus content positively influenced the 0.1 M HCl-extractable Mn in soil ($r = 0.49$). Soil pH and CaCO₃ ($r = 0.57$ and 0.43) showed significant negative correlations with the DTPA-extractable Mn, respectively. The different extraction methods showed similar patterns of Mn content in arable and meadow soils. The sequential fractional procedure showed that reductant releasable Mn occluded in oxides of Fe and Mn was the prevailing Mn fraction in soil, however, water soluble and exchangeable Mn and Mn bonded with organic matter had significant correlations with most of the examined soil characteristics. Potential Mn toxicity in vertisols could be observed under lower pH and saturated conditions.

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

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INTRODUCTION

Being a multi-complex system, soil comprises mineral, organic, organic-mineral, liquid and gaseous phases and it possesses certain physical, chemical and biological properties. The original geologic substrate and subsequent geochemical and pedogenic impacts determine the total levels of micronutrients in soils. The total levels are rarely indicative of plant availability, because availability depends on soil pH, organic matter content, adsorptive surfaces, and other physical, chemical, and biological conditions in the rhizosphere.¹

The accumulation of heavy metals in soils represents a potential risk to human health due to the transfer of these elements to aquatic media, their uptake by plants and their subsequent introduction into the food chain. Chemical fractionation schemes for partitioning trace metals in soils and sediments have been used extensively since the 1970s and are based on three to six fractions,²⁻⁵ many of them being slightly modified Tessier's schemes.² Chemical extraction is employed to assess operationally defined metal fractions, which can be related to chemical species, as well as to potentially mobile, bioavailable or ecotoxic phases of a sample. The sequential extraction procedure for environmental studies provides an important tool for the determination of the different chemical forms or ways of binding between trace metals and soil components.⁶ It is generally accepted that the ecological effects of metals (*e.g.*, their bioavailability, ecotoxicology and risk of groundwater contamination) are related to their mobile fractions rather than to the total concentrations.⁷ Sequential extraction was confirmed as a convenient method for the investigation of heavy metals in agro-ecological conditions.⁸

Manganese (Mn) is an essential micronutrient for plant growth. Through its involvement in various enzymes and other physiologically active molecules, this micronutrient affects the gene expression, biosynthesis of proteins, nucleic acids, growth substances, chlorophyll and secondary metabolites, metabolism of carbohydrates and lipids, stress tolerance,⁹ *etc.* of plants. Mn oxides are not only an important solid phase component of soil micronutrients, but also play an important role in the redistribution of micronutrients in soils. Changes in the redox status and consequent transformation of mineral forms of Mn act as an important driving force for the redistribution of trace elements and other heavy metals in soils.¹⁰ Patrick and Jugsujinda,¹¹ and Han and Banin¹² found significant transformations and redistribution of heavy metals among the solid-phase components in soils due to the redistribution of Mn during incubation under a saturated regime. High values of Mn are usually attributed to the presence of Mn-oxides concentrations due to locally reduced conditions.¹³ Therefore, proper land use, *i.e.*, cropped soil, permanent crops or meadows, can strongly influence the soil moisture regime.

The aim of this study was to assess the distribution and forms of manganese occurring in vertisol soils under the environmental conditions of Serbia using different extraction methods and a sequential extraction procedure.

EXPERIMENTAL

Samples of the Ap horizon of vertisol soil were taken from the following ten locations in Serbia: 1) Milutovac, 2) Priština, 3) Trnava, 4) Rekovac, 5) Vranje (Neradovac), 6) Zaječar, 7) Bela Crkva, 8) Blace, 9) Salaš and 10) Kragujevac (Fig. 1). Sub-samples were taken from field and meadow ecosystems, from a depth of 0 to 20 cm, after which they were air-dried and crushed in a porcelain mortar to particles of 2 mm in size. A stainless steel screen was used in the preparation for characterization and Mn-fraction analyses.



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

Determination of the soil characteristics

Soil pH was determined in a suspension with water and 1 M KCl mixture, with the ratio of soil:solution 1:2.5 after a 30-min equilibration period; the organic content was determined using the humus method of Kotzmann,¹⁴ the available P₂O₅ and K₂O contents were determined by the AL method of Egner–Riehm.¹⁵ Cation exchange capacity (CEC) was determined using the method with 1 M NH₄OAc, pH 7, and the particle size distribution was determined

by a pipette method.^{16–17} The total manganese was determined by atomic adsorption spectrophotometry (AAS, Carl Zeiss Jena, model AAS 1N). The cold extraction method was used for the determination of the total and pseudo-total manganese where 0.5 ± 0.001 g of sample was transferred into a centrifuge tube, and then 10 cm^3 of 0.5 M HCl were added. The solution was shaken and centrifuged for a short time and then placed on a shaking-table and agitated for 1 h. After agitation, the solutions were centrifuged at 3000 rpm ($1,900 \times g$) for 15 min, and then filtered through a $0.45\text{-}\mu\text{m}$ syringe filter to remove particulates.

Sequential fractional procedures

Manganese (Mn) in different soil fractions was extracted using the procedure proposed by Tessier *et al.*² The methods used for the fractionation procedure are outlined below.

1. Water soluble and exchangeable Mn was determined by extraction with 0.1 M CaCl_2 (pH 7.0); 10 g of soil were agitated in plastic pots with 100 cm^3 of solution for 20 min and then filtered.

2. Specifically adsorbed Mn and Mn bonded with carbonates were determined utilizing extraction with 1 M NaOAc (pH 5.0). Again, 10 g of soil were added to 100 cm^3 of solution, and agitated for 5 h at room temperature and then filtered. In this case, the sum of 1. and 2. was calculated and the value of fraction 2 was obtained by subtraction.

3. Reductant releasable Mn occluded in Fe and Mn oxides was determined in the 2.5 mg of soil placed in a centrifuge tube. After extraction of fractions 1. and 2., 50 cm^3 of 0.04 M hydroxylamine hydrochloride were added (in 25 % HOAc, pH 3). The tubes were then kept in a water bath for 6 h at $85 \text{ }^\circ\text{C}$ under stirring. Subsequently, the total volume of 50 cm^3 was attained by adding distilled water, and the tubes were closed, agitated for 10 min, and centrifuged for 10 min at 3000 rpm. The clear supernatant was removed from the reagent bottles and the remains of the soil were rinsed with 20 cm^3 of distilled water.

4. Mn bonded with organic matter was determined in the following way: 7.5 cm^3 of 0.02 M HNO_3 and 12.5 ml of H_2O_2 pH 2.0 were added to the centrifuge tubes with the soil remaining from the previous three extractions. The tubes were kept in a water bath at $86 \text{ }^\circ\text{C}$ for 2 h and then stirred. After cooling, 7.5 cm^3 of 30 % H_2O_2 were added and again the suspension was kept at $86 \text{ }^\circ\text{C}$ for 3 h. After cooling, 12.5 cm^3 of 3.2 M NH_4OAc in 20 % HNO_3 were 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 resulting clear supernatant was transferred to reagent bottles.

5. Mn structurally bonded in silicates (residual fraction) was determined by calculating the difference between the total content determined with $\text{HNO}_3\text{--HF--HClO}_4$ and the sum of the first four fractions.

The total Mn content was determined by destructing the samples with a mixture of the acids HNO_3 , HClO_4 and HF. Through this procedure, all the forms of Mn present in the soil were transferred into solution. The pseudo-total content of the Mn was obtained by application of concentrated HNO_3 and H_2O_2 .^{18–20}

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

Statistical analysis

The results obtained for the different contents of manganese (total, accessible and different chemical fractions) in the vertisol samples were statistically processed by the Student's *t*-test and Pearson correlation coefficients.²¹

RESULTS AND DISCUSSION

Basic soil characteristics of the investigated vertisols are given in Table I. The vertisols showed marked heterogeneity in terms of pH. Most of the studied soil samples were acid to slightly alkaline. In terms of the content of readily available phosphorus, the selected samples belonged to the class of soils with a low P availability, but the observed levels of P₂O₅ varied widely among the samples: from 0.6–28.0 mg 100 g⁻¹ soil in the samples from cultivated fields to 0.8–17.8 mg 100 g⁻¹ soil in the samples from meadows. The investigated soils showed a moderate to high content of available K₂O. The selected sampling sites also differed in the humus concentration with an average range from 3.3 % (field) to 3.5 % (meadow) and with a high capacity for cation adsorption, ranging from 15.5 to 34.7 meq per 100 g soil.

TABLE I. Examined physical-chemical characteristics of vertisol in Serbia (mean, standard deviation and range)

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 content, mg 100g ⁻¹	7.7	0.6–28.0	8.5	4.2	0.8–17.8	5.0
K ₂ O content, mg 100g ⁻¹	34.4	19.0–59.6	11.8	31.1	20.4–53.5	10.4
CEC, m.e 100g ⁻¹	25.1	15.5–31.5	5.6	23.8	16.9–34.7	6.6
Sand content, %	29.6	21.4–36.0	4.8	32.2	22.3–50.5	9.0
Silt content, %	24.6	18.8–31.2	3.6	22.8	11.9–29.4	5.6
Clay content, %	45.8	33.5–54.4	7.2	44.9	28.9–64.3	11.1
Silt + clay content, %	70.4	64.0–78.6	4.8	67.7	49.5–77.7	9.0

The mean value of the total Mn content in the field and meadow vertisols amounted to 927 and 882 mg kg⁻¹, respectively (Table II). However, the examined samples showed high heterogeneity regarding the total Mn content.

TABLE II. Manganese content in the tested vertisols of Serbia determined using different extraction methods ($X \pm SD$ and interval, mg kg⁻¹)

Location	HF	HNO ₃	0.1 M HCl	0.005 M dtpa
Field (<i>n</i> = 10)	927±311	850±306	117±17.1	52.5±21.7
	650–1675	550–1600	89.0–154.0	21.0–90.0
Meadow (<i>n</i> = 10)	882±252	803±286.5	113±32	59.8±22.2
	560–1460	500–1490	49–178	28.0–106.0
<i>t</i> -Test (field and meadow)	0.40 ^b	0.35 ^b	0.05 ^a	0.74 ^b

^aThe Student *t*-test showed that there is a statistical significance between the examined characteristic of the field and meadow soil; ^bThe Student *t*-test showed that there was no statistical significance between the examined characteristic of the field and meadow soil

The average values of Mn extraction from the samples of arable land, when mild extraction agents were used, were 117.0 mg kg^{-1} in 0.1 M HCl and 52.5 mg kg^{-1} in 0.005 M diethylenetriaminepentaacetic acid (DTPA), indicating that the soils were sufficiently provided with this element. The high values of available Mn in the arable soil samples indicated a low strength of its binding with the solid soil phase. The meadow soil samples were also adequately supplied with readily available Mn, although the Mn concentrations found by 0.1 M HCl extraction (113 mg kg^{-1}) were slightly lower and by DTPA extraction (59.8 mg kg^{-1}) slightly higher compared with the corresponding values found for the arable vertisols. Thus, a solution of 0.1 M HCl extracted twice the amount of Mn extracted by a DTPA solution.

On average, about 91 % of the total content of Mn in vertisols from arable land and meadows was extracted with HNO_3 (pseudo-total content), *i.e.*, 850 and 803 mg kg^{-1} , respectively (Table III). Conversely, 0.1 M HCl extracted about 13.5 % of the total content of Mn in vertisol from the arable and the meadow samples. The relative values of the individual Mn extractions with 0.1 M HCl solution, between the two land uses, varied over a wide range (7.6–16.5 % from the arable soil samples and 5.8–21.7 % from the meadow samples).

The average relative values of Mn extracted with DTPA were 5.6 (arable soil) and 7.4 % (meadow). The individual values varied widely and were related to the soil pH. The highest relative amount of DTPA-extractable Mn was extracted from the soil with the lowest pH value. The extraction with 0.1 M HCl and DTPA 0.005 extracted much greater amounts of Mn (2–3 times more) from the arable land samples 7 and 10.

These results are in agreement with a number of previous observations.²² Han and Banin²³ reported that Mn in arid-zone soils was mainly in the easily reducible oxide-bound fraction and it redistributed into the carbonate-bound and soluble plus exchangeable fractions after a year of water saturation. The EDTA-extractable Mn in savanna soils ranges from 13 to 54 mg kg^{-1} soil, which is far greater than the 1.0 mg kg^{-1} considered critical for most soils, suggesting that savanna soils have adequate reserves of available Mn.²⁴

Generally, the contents of total and readily available Mn in the analyzed vertisols were not dependent on the properties of the investigated soils. However, this finding was not confirmed for Indian vertisols, where the total Mn was negatively correlated with coarse clay and silt but positively correlated with fine clay. Contrary to this, the DTPA-available form of Mn was negatively correlated with pH ($r = -0.55$ and -0.57) and the CaCO_3 content (-0.43). Similar results for DTPA-Mn were presented by Verma *et al.*²⁵ and for Indian vertisols.²⁶ From this association, it can be inferred that the addition of organic matter increases the availability of Mn and, as the soil become coarser, Mn deficiency becomes a problem.²⁷ Manganese extracted with 0.1 M KCl is positively correlated with the

humus content ($r = 0.49$). Bloom²⁸ reported that Mn^{2+} formed outer-sphere complexes (non-specific sorption) with the carboxyl groups of the soil organic matter (SOM); this mechanism explains the weak association of Mn with the soil organic matter. The Mn content in soil showed no relation with the soil texture of the investigated vertisols. Some studies also found that Mn movement is independent of clays, as shown by the weak correlation between Mn and the clay distribution in soils.^{29,30}

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

Locality	Extraction method			
	HF	HNO ₃	0.1 M HCl	0.005 m dtpa
Field				
Milutovac	720	81.9	14.4	3.8
Priština	1675	95.5	7.6	5.0
Trnava	778	99.6	14.0	4.6
Rekovac	780	83.3	13.7	5.1
Vranje	740	94.6	16.5	3.9
Zaječar	760	97.4	15.5	7.0
Bela Crkva	650	84.6	13.7	7.1
Blace	1020	97.0	11.8	5.4
Salaš	950	96.3	12.5	6.8
Kragujevac	1200	82.9	12.8	7.5
X	927	91.3	13.3	5.6
Meadow				
Milutovac	813	87.9	14.4	7.4
Priština	1460	102.0	9.0	4.1
Trnava	1041	86.9	11.5	6.4
Rekovac	764	85.7	15.8	6.8
Vranje	800	93.8	13.6	5.6
Zaječar	620	80.6	15.3	7.4
Bela Crkva	560	88.4	21.2	15.2
Blace	995	97.0	9.5	4.9
Salaš	900	99.4	5.8	3.3
Kragujevac	820	86.6	21.7	12.9
X	877.3	90.8	13.8	7.4

Sequential extraction analysis

Considering that the tested vertisols from Serbia were established at locations with manganese deficiency in the parent material, sequential extraction enabled the determination the form of its presence in the soil, allowing a clear understanding of its potential mobility and accessibility to plants. The Mn distribution among the various chemical fractions of the examined vertisols showed that Mn was predominantly located in the fraction of oxides of Fe and Mn(III). Its presence in this fraction was 56.4 % of its total content in the meadow vertisols and 54.2 % in the arable soils. Similar Mn values in the fraction of metals

associated with Fe and Mn oxides were found by other authors. Sims *et al.*³¹ found that the reduced fraction contained approximately 45 % of the total content of Mn, and Maria Isabel *et al.*³² found 33.1 % in oxide-bound phase according to a modified Tessier procedure and 48.9 % according to Community Bureau of Reference Protocol for Spanish Soils. The high content of extractable Mn in this fraction was derived from the fixed Mn and Mn coupled with oxides (MnO and MnO₂).² The individual samples from the fields and meadows showed a marked heterogeneity in terms of the Mn content in this fraction, which could be explained by the fact that the content of Mn in this fraction occurs in samples with larger Mn contents.

The fraction of specifically adsorbed Mn and Mn bound to carbonates (II) was the second largest Mn pool. In the arable soil samples, this fraction accounted for 13.7 % of the total Mn content, while in the meadow vertisols, the value was 15.45 %. The higher relative content of Mn in the meadow samples might indicate that the Mn in the arable soils could have a stronger association to the solid phase of the soil, despite its higher content. This finding was confirmed by the fact that the relative content of Mn in the arable soils was significantly lower in the exchangeable fraction of adsorbed metal (fraction I), which leads to weak associations with the soluble part of the total Mn, which is directly accessible to plants. In addition, the extracted amount of Mn and its relative prevalence in this fraction, in individual samples, varied over a wide range, which were significantly higher in samples of the arable soils (9.7–28.4 %) compared with the meadow soil. It was also found that the largest amounts of Mn were extracted from samples with the highest total content. Contrary to the above, the samples with the highest total contents of Mn had lower values of relative Mn abundance, indicating that the increase in the total Mn content reduces its percentage in the fractions of specifically adsorbed Mn and Mn bonded to carbonates. Based on those findings, it could be assumed that the potential availability of Mn is determined by specific soil properties and less by its total content.

In the arable vertisols, the relative content of Mn in the organic (IV) fraction averaged 13.2 %, while in the meadow vertisols, the average was 12.8 %. Similar differences were observed for the Mn content in the third fraction. These differences probably derived from the chemical and mineralogical properties of the individual soil samples and, similarly, the lowest soil pH values led to the least amount of organically bound Mn. Another observation was that the samples with the highest relative content of organically bound Mn were the highest in K₂O, the texture clay fraction and the CEC. This could be explained by the fact that the complexes of organic matter with Mn can be easily adsorbed to the clay particles of soil, which affects the content of organically bound Mn. The positive relationship between the organic bound Mn and the available potassium is probably due to their appearance in the same forms of bonds, since the investigated vertisols

had sufficient clay contents, which explains the considerable amount of potassium in the soil.

The fraction of exchangeable adsorbed metal (fraction I) was relatively high in Mn (3.7 % of the total content of Mn) in the arable land samples (35.9 mg kg⁻¹) and 5.6 % of the total Mn content in the meadow samples (42.3 mg kg⁻¹). This fraction is dependent on soil pH, content of K₂O, clay (*CEC*), silt and CaCO₃, respectively.

The *t*-test found no significant differences between the respective chemical fractions for both uses of the vertisols, indicating the same geochemical origin of the soils at the examined locations and no effects of cropping technology on the distribution of Mn among the different fractions.

Positive correlation coefficients for the Mn content were found between fractions I and II, III and IV, III and the total content and IV and the total content, whereas negative correlations were observed between fractions I and IV, II and IV and the total content (Table IV). The negative correlation between the content of Mn in fractions I and IV indicates that the increase of Mn in the organic matter (fraction IV) was a result of the high complexation of Mn and its decrease in the soluble fractions. The results also showed that all of the stable fractions (II, III and IV) were correlated with the total Mn, but not with the residual fraction. Medium to high correlations ($r = -0.51$ and 0.96) were observed between total Mn and Mn in fractions II–IV. The coefficients indicate that the individual forms of Mn were in a state of dynamic equilibrium.

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

Fraction	I	II	III	IV	V	Mn content total (HF)
I	1.00					
II	0.52 ^a	1.00				
III	NS ^b	NS	1.00			
IV	-0.61 ^c	NS	0.57 ^c	1.00		
V	NS	-0.51 ^c	NS	NS	1.00	
Mn content total	NS	-0.46	0.96 ^c	0.53 ^a	NS	1.00

^aStatistically significant at the probability level of 0.05; ^bthere is no statistical significance, ^cstatistically significant at the probability level of 0.01

The correlation coefficients between the Mn content in different chemical fractions and selected soil properties are presented in Table V. The analysis showed that the content of Mn in fraction I decreased significantly (-0.49 and -0.90) as the soil pH and the contents of clay (*CEC*), K₂O and CaCO₃ increased. Conversely, plots with high values of silt had an increased Mn content in fraction I ($r = 0.52$).

The high negative correlation coefficients between the content of Mn in the first fraction and soil properties, such as pH, clay content (*CEC*) and K₂O, in-

indicated that these soil properties had a dominant influence on the distribution of Mn in this fraction. When the pH value of the soil is high, Mn is less soluble due to the oxidation process that occurs in an alkaline reaction and the transition of Mn oxides into the more inaccessible forms. As the clay content and pH influence the *CEC* to a large extent, the increase of *CEC* strengthens the bond between cations (Mn) and the solid phase of soil, which reduces the mobility and solubility of Mn in this fraction.

TABLE V. Correlation coefficient between the manganese content in different chemical fractions and some soil characteristics

Soil characteristic	Fraction					Mn content total
	I	II	III	IV	V	
pH (H ₂ O)	-0.90 ^a	NS ^b	NS	0.71 ^a	NS	NS
pH (nKCl)	-0.90 ^a	NS	NS	0.70 ^a	NS	NS
Humus content	NS	NS	NS	NS	-0.46 ^c	NS
P ₂ O ₅	NS	NS	NS	NS	NS	NS
K ₂ O	-0.60 ^a	NS	NS	0.57 ^a	NS	NS
<i>CEC</i>	-0.64 ^a	NS	NS	0.76 ^a	NS	NS
Sand	NS	NS	NS	-0.61 ^a	NS	NS
Silt	0.52 ^c	NS	NS	-0.61 ^a	NS	NS
Clay	-0.49 ^a	NS	NS	0.79 ^a	NS	NS
Silt + clay	NS	NS	NS	0.61 ^a	NS	NS

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

The positive correlation between the Mn content in fraction I and silt is caused by weaker bond strengths between the silt and Mn, since silt particles are coarse and positioned at the junction between sand and clay. It could be assumed that the solubility of Mn (fraction I) is higher in soil with a coarser texture than clay soil with a similar total content of Mn. Specifically adsorbed Mn and Mn bound to carbonates (fraction II) and Mn bound to oxides (fraction I) were not significantly correlated with any of the studied soil properties (Table V).

The amounts of Mn extracted from the organic fraction (IV) had significantly high positive correlations with soil pH, clay (*CEC*) and K₂O (from 0.57 to 0.79), and negative correlations with coarse soil particles (silt and sand). The high and positive correlation of Mn in the organic fraction and clay showed that most of the Mn was associated with clay organic matter. Therefore increasing the content of fine particles (clay with organic matter) results in increases in the free surface, and therefore the *CEC*, as well as bond strength compared to the coarser particles (silt and sand).

The positive correlation ($r = 0.70$ and 0.71) between soil pH and Mn content in the organic fraction indicates that the pH had a positive effect on the Mn con-

tent in the organic fraction. These results are similar to the results of other authors.^{25,33–35}

Based on the correlation coefficients shown in Table VI, it was found that the applied extraction techniques extracted significantly higher amounts of dissolved Mn compared with the amounts that plants could adopt. With 0.005 M DTPA and 0.1 M HCl addition, besides the water-soluble + exchangeable amounts of Mn, specifically adsorbed forms also dissolve. HF and HNO₃ dissolve metals that are bound with much stronger bonds (fraction II–V). These metals are not accessible to plants and, therefore, this method cannot be used as an indicator of Mn accessibility to plants. The availability of micronutrients to crops is controlled by many soil factors, such as pH, soil organic matter, temperature and moisture.^{36–37} Increased microbial activity can also result in a decrease in the oxidation–reduction potential of the soil, increasing Mn availability; consequently, manganese (II) forms only relatively weak bounds with organic ligands.³⁸ According to Fageria *et al.*, the main ionic Mn species in a soil solution is Mn²⁺, and its concentrations decrease 100-fold per unit increase in soil pH.³⁷ This is in agreement with the results obtained in other studies on Brazilian soils.^{37,39}

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

Extraction procedure	Fraction				
	I	II	III	IV	V
HF	NS ^a	0.512 ^b	0.959 ^c	0.534 ^b	NS
HNO ₃	NS	0.443 ^b	0.966 ^c	0.572 ^c	NS
0.1 M HCl	0.516 ^b	0.703 ^c	NS	NS	NS
0.005 M DTPA	0.786 ^c	0.882 ^c	NS	NS	NS

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

CONCLUSIONS

The contents of Mn (total and pseudo-total) were found to be similar in the samples of field and meadow vertisols and to have similar levels as the average values determined in other studies. The extraction of Mn with NHO₃ produced values similar to the real total content (about 90 %). The availability of Mn (DTPA–Mn) depends on the pH value and CaCO₃ content, since negative correlations were observed. Reductant releasable Mn occluded in the oxides of Fe and Mn was found to be the most abundant fraction of Mn according to sequential extraction procedures, however, the Mn bonded with organic matter had significant correlations with most of the examined soil properties. Mn availability in soil could be controlled by appropriate water regime and management practices that modify the pH value of soil.

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ИЗВОД

ДИСТРИБУЦИЈА И ФОРМЕ МАНГАНА У ВЕРТИСОЛИМА СРБИЈЕ

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У циљу одређивања различитих облика мангана у вертисолима са подручја Србије (оранице и ливаде) пореклом са десет различитих локалитета анализиран је укупан садржај мангана (HF), псеудо-укупан садржај (HNO₃), 0,1 М HCl растворљив и ДТРА растворљив манган. Секвенцијалном екстракцијом извршено је раздвајање фракција мангана на растворљив у води и разменљив манган (I), специфично адсорбован са карбонатима (II), оклудован у оксидима (III), манган везан за органску материју (IV) и манган структурно везан у силикатима (резидуални део) (V). Садржај мангана у анализираном земљишту (вертисол) поређен је са добијеним резултатима на сличним земљиштима. Укупан садржај мангана (HF) и псеудо-укупан садржај (HNO₃) нису били у корелацији са испитиваним својствима земљишта, док је садржај хумуса позитивно утицао на 0,1 М HCl растворљив манган ($r = 0,49$). Земљишни pH и CaCO₃ ($r = 0,57$ и $0,43$) су показали високо значајну негативну корелацију са ДТРА растворљивим манганом. Различита екстракциона средства су испољила сличан ефекат на садржај Mn у обрадивом земљишту и ливадама. Секвенциона екстракциона анализа је показала да манган оклудован у оксидима чини процентуално највећу фракцију у земљишту, истовремено постоје статистички значајне корелације између мангана растворљивог у води и мангана везаног за органску материју и већине својстава земљишта. Потенцијал екотоксичности мангана се може испољити само у случајавима ниске pH вредности земљишта и појаве засићања земљишта са водом.

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REFERENCES

1. A. Kabata-Pendias, A. Pendias, *Trace elements in soils and plants*, 2nd ed., CRC press, Boca Raton, FL, USA, 2001
2. A. Tessier, P. G. C. Campbell, M. Bisson, *Anal. Chem.* **51** (1979) 844
3. C. Ianni, N. Ruggieri, P. Rivaro, R. Frache, *Anal. Sci.* **17** (2001) 1273
4. F. X. Han, A. Banin, W. L. Kingery, G. B. Triplett, L. X. Zhou, S. J. Zheng, W. X. Ding, *Adv. Environ. Res.* **8** (2003) 113
5. J. T. Hlavay, M. Prohaska, W. Weisz, G. Wenzel, J. Stingeder, *Pure Appl. Chem.* **76** (2004) 415
6. G. J. Rauret, F. Lopez-Sanchez, A. Sahuquillo, R. Rubio, C. Davidson, A. Ure, P. Quevauviller, *J. Environ. Monit.* **1** (1999) 57

7. E. Cordos, R. Rautiu, C. Roman, M. Ponta, T. Frentiu, A. Sarkany, L. Fodorpataki, K. Macalik, C. McCormick, D. Weiss, *Eur. J. Miner. Process. Environ. Prot.* **3** (2003) 324
8. Dj. Petrović, M. Todorović, D. Manojlović, V. D. Krsmanović, *J. Serb. Chem. Soc.* **75** (2010) 1005
9. Z. Rengel, in *Nutrient Cycling in Terrestrial Ecosystems*, P. Marschner, Z. Rengel, Eds., Springer-Verlag, Heidelberg, 2007, p. 121
10. F. X. Han, A. Banin, *Commun. Soil Sci. Plant Anal.* **31** (2000) 943
11. W. H. Patrick Jr., A. Jugsujinda, *Soil Sci. Soc. Am. J.* **56** (1992) 1071
12. F. X. Han, A. Banin, W. L. Kingery, G. B. Triplett, L. X. Zhou, S. J. Zheng, W. X. Ding, *AES BIOFLUX* **8** (2003) 113
13. C. S. Aydinalp, S. Marinova, *Polish J. Environ. Stud.* **12** (2003) 629
14. M. Jakovljevic, M. Pantovic, S. Blagojevic, *Laboratory Manual of Soil and Water Chemistry*, Faculty of Agriculture, Belgrade, 1995, p. 57 (in Serbian)
15. A. M. Ure, in *Heavy metals in soils*, 2nd ed., B. J. Allovay, ed., Blackie Academic & Professional, Glasgow, UK, 1995, p. 58
16. USDA-NRCS, *Soil survey laboratory methods manual*, Soil Survey Investigation Report 42, ver. 3.0, National Soil Survey Center, Lincoln, NE, USA, 1996
17. JDPZ, *Soil survey laboratory methods manual*, Book 5, Belgrade, 1997 (in Serbian)
18. D. C. Martens, W. L. Lindsay, in *Soil Testing and Plant Analysis*, 3rd ed., Soil Science Society of America, Madison, WI, USA, 1980
19. R. J. Haynes, *J. Agric. Sci.* **129** (1997) 325
20. J. J. Wang, D. L. Harrell, R. E. Henderson, P. F. Bell, *Commun. Soil Sci. Plant Anal.* **35** (2004) 145
21. R. Mead, R. N. Curnow, A. M. Hasted, *Statistical methods in agriculture and experimental biology*, Chapman & Hall, London, 1996, p. 410
22. B. Li, Q. Wang, B. Huang, S. Li, *Anal. Sci.* **17** (2001) 1561
23. F. X. Han, A. Banin, *Soil Sci. Soc. Am. J.* **60** (1996) 1072
24. W. L. Lindsay, W. L. Norvell, *Soil Sci. Soc. Am. J.* **42** (1978) 421
25. V. K. Verma, R. K. Setia, P. K. Sharma, C. Singh, A. Kumar, *Int. J. Agric. Biol.* **7** (2005) 243
26. B. D. Sharma, S. S. Mukhopadhyay, J. C. Katyal, *Commun. Soil Sci. Plant Anal.* **37** (2006) 653
27. V. K. Nayyar, U. S. Sadana, P. N. Takkar, *Fertil. News* **8** (1985) 173
28. V. P. R. Bloom, *Chemistry in the Soil Environment*, ASA Special Publication 40, Soil Science Society of America, Madison, WI, USA, 1983, p. 129
29. A. Swarup, S. Anand, *Fertil. News* **34** (1989) 21
30. F. X. Han, W. L. Kingery, J. E. Hargreaves, T. W. Walker, *Geoderma* **142** (2007) 96
31. J. L. Sims, I. W. H. Patrich, *Soil Sci. Soc. Am. J.* **42** (1978) 258
32. R. M. Isabel, J. M. Alvarez, L. M. Lopez-Valdivia, A. Novillo, J. Obrador, *Soil Sci.* **174** (2009) 94
33. V. H. Nguyen, S. Vega, J. A. Silva, *Soil Sci. Soc. Am. J.* **65** (2001) 153
34. P. Polić, P. Pfenđt, *J. Serb. Chem. Soc.* **61** (1996) 1001
35. M. D. Marjanović, M. M. Vukčević, D. G. Antonović, S. Dimitrijević, Đ. M. Jovanović, M. N. Mata vulj, M. Đ. Ristić, *J. Serb. Chem. Soc.* **74** (2009) 697
36. J. C. Katyal, B. D. Sharma, *Geoderma* **49** (1991) 165
37. N. K. Fageria, V. C. Baligar, R. B. Clark, *Adv. Agron.* **77** (2002) 185

38. H. Marschner, *Mineral nutrition of higher plants*, 2nd ed., Academic Press, San Diego, CA, USA, 1995
39. E. Vidal-Vázquez, R. Caridad-Cancela, M. M. Taboada-Castro, A. Páz-Donzález, C. A. Abreu, *Commun. Soil Sci. Plant Anal.* **36** (2005) 717.