Geologia Croatica | 67/1 | 45–58 | 6 Figs. | 5 Tabs. | Zagreb 2014

Distribution and bioavailability of manganese in soil in the vicinity of the „Bužim" abandoned mine

Safeta Redžić[1], Galiba Sijarić[1], Tidža Muhić-Šarac[2], Ekrem Pehlić[1] and Damir Hrnjica[1]

[1] University of Bihać, Biotechnical faculty Bihać, Bosnia and Herzegovina; (corresponding author: safetabtf@gmail.com)

[2] University of Sarajevo, Faculty of Natural Sciences and Mathematics Sarajevo, Bosnia and Herzegovina

doi: 10.4154/gc.2014.04

Geologia Croatica

ABSTRACT

Soil samples from the industrial area in the town of Bužim, Bosnia and Herzegovina were analysed in order to determine their different manganese species. Samples were extracted from seven locations – at the manganese mine and the surrounding area. The paper aims to present the use of the sequential extraction method in determination of the specific distribution of Mn in soil, as well as in estimation of its origin, mobility and bioavailability in the sampling locations.

Sequential extraction used here included determination of the amount of Mn in various soil fractions: the water-soluble fraction, exchangeable fraction, carbonate fraction, easily reduced fraction and the organic fraction. Additionally, it included manganese oxides or moderately reduced oxides, amorphous iron oxide, crystalline iron oxide and the residual fraction. It was determined that chemical properties of soil considerably affect the distribution of heavy metals within different soil fractions.

The highest percentage of natural Mn was determined in the residual fraction (27.00%) at Popović polje, while the highest percentage of anthropogenic origin Mn was determined at Bućevci (57.00%) in the Fe-Mn oxides fraction. The highest near-total content of Mn was determined at Popović polje (20950.00 mg/kg). The highest percentage of natural Mn (27.00%) was determined in the same area. The highest percentage of Mn of an anthropogenic origin (57.00%) was determined at Bućevci.

Keywords: sequential extraction, manganese, manganese bioavailability, manganese mine „Bužim", manganese speciation, soil

1. INTRODUCTION

Interest in the geochemical pattern of soil contamination has increased within the last few decades, due to the fact that soils serve as a depot for metals in an environment (WARREN & BIRCH, 1987; LI & THORNTON, 2001; OREŠČANIN et al., 2003; MARTLEY et al., 2004). MACKLIN (1992) provides a description of soil and sediment contamination by metals as a result of mining activities.

An ever-growing number of research papers are directed towards the determination of soil contamination by manganese (PIPER, 1931; BROMFIELD & DAVID, 1987; HAJDAREVIĆ et al., 1988; MARIKA & MARKKU, 2003; RUTTEN & GERT, 2003; ALVAREZ et al., 2006; MARSCHNER & RENGEL, 2003; MOSSOP & DAVIDSON, 2003; NADASKA et al., 2009; ROUHOLLAH & FARZANEH, 2010; ZAKIR & SHIKAZONO, 2011).

HORSTMAR (1851) conducted an early study investigating the influence of manganese content in soil on manganese content in plants. According to the research conducted by other researchers (MIHALJEVIĆ et al., 2003; SALETOVIĆ

Figure 1: Map of sample collection area near the manganese mine in „Bužim". a) http://www.360.ba/buzim360/ b) Base from HODŽIĆ & ABDURAHMANOVIĆ (1998)

et al., 2011) Mn has an important role in the efficient utilization of other nutrients in the soil.

The total amount of Mn in soils is 200-3000 ppm, where 0.10–1.00% is available to plants. In soils it generally originates from MnO_2, occurring in different oxides with oxidation states from +2 to +7 (NOGALES et al., 1997; ZHANG et al., 2012). The availability of Mn greatly depends on the oxidation-reduction conditions of soil (PIPER, 1931., DOLAR & KEENEY, 1971; BROMFIELD & DAVID, 1987), being reduced in neutral and alkaline environments, and increasing with acidity as Mn^{2+} reduces (VUKADINOVIĆ & LONČARIĆ, 1998). According to ZHANG et al. (2012) the acidity of soil may cause Mn oxide minerals to dissolve and release a significant amount of Mn ions in soil, therefore increasing the toxicity of soil for many plants.

The aim of this research is to determine the specific distribution of Mn and its origin, bioavailability (TRUDINGER & SWAINE, 1979; PERIN et al., 1985; LI et al., 1995) and the mobility (PERTSEMLI & VOUTSA, 2007; MOSSOP & DAVIDSON, 2003; HLAVAY et al., 2004; KALEMBKIEWICZ & SITARZ-PALCZAK, 2004; OLAYINKA et al., 2011) of certain Mn forms in soil at the „Bužim" mine and the surrounding area.

The research included analysis of water-soluble species, exchangeable species, carbonate species, easily reduced species, organic species, manganese oxides or moderately reduced oxides, amorphous iron oxide, crystalline iron oxide and the residual fraction of Mn in soil in order to determine how mining activity affected the amount and origin of Mn in soil.

Therefore, the sequential extraction method was employed in this research (TESSIER et al., 1979; TESSIER & CAMPBELL, 1987; CALMANO et al., 1993; ZOUMIS et al., 2001; FILGUEIRAS et al., 2002; SAHUQUILLO et al., 2003; HLAVAY et al., 2004).

The procedure of sequential extraction applied in this research is combined and modified according to the standardized procedure of sequential extraction in the European Community Bureau of Reference (BCR), TESSIER et al. (1979, 1987), AGNIESZKA & WITOLD (2004), MING et al. (2008), SILVEIRA et al. (2006) and other references dealing with the same issues (KAZI et al., 2005; PUEYO et al., 2008; DAVIDSON et al., 2006; JOSE et al., 2006; KAASALAINEN & YLI-HALLA, 2003; ROUHOLLAH & FARZANEH, 2010). A modified procedure of sequential extraction includes the determination of Mn bound to particular soil phases in nine fractions: water-soluble fraction, exchangeable fraction, carbonate fraction, easily reduced fraction, organic fraction, manganese oxides or moderately reduced oxides, amorphous iron oxide, crystalline iron oxide and the residual fraction of Mn. The first three steps of sequential extraction provide further data on the bioavailability of metals (JAIN, 2004).

2. AREA OF INVESTIGATION

The research was conducted in the farthest northeast part of Bosnia and Herzegovina in the town of Bužim. Bužim has a population of about 20.000 inhabitants. It borders with the towns of Bosanska Krupa (east), Cazin (south), Velika Kladusa (west and north) and the Republic of Croatia (northeast). A well-known manganese mine in Bosnia and Herzegovina is located in Bužim, but has been out of use since the war in Bosnia and Herzegovina.

The area is characterised by slightly rounded and seldom angular hills. The lowest altitudes occur in the Bužimica river valley (150m). This is an area of mildly continental and mountain climate. The manganese deposit is placed in a synclinal structure which extends in a northeast-southwest direction. It occurs where the volcanogenic-sedimentary series overlie dolomites and dolomitic limestone. The deposit is dark red in colour, due to the high manganese content. Occasionally, greenish tufa and light grey kaolin rich marls can be observed.

MOJIĆEVIĆ et al. (1984) determined the age of the sediments in the wider area of Bužim, having discovered that these are composed of Triassic, Cretaceous, Palaeocene, Miocene, and Pliocene-Quaternary structures. Figure 1. is a location and sampling scheme map of the collection area near the manganese mine in „Bužim" and the surrounding area.

3. MATERIALS AND METHODS

3.1. Sampling

Sample collection from the soil was conducted by means of the standard pedologic methods of soil sampling, as well as the open pit sampling with reference to ISO 10381 procedures (ISO, 2002). Sampling was conducted by means of the standard pedologic equipment and tools, while the special attention was given to prevention of sample contamination.

Sample collection occurred at the end of March 2010 at the manganese mine „Bužim" and the surrounding area and a total of 10 soil samples from different locations have been used.

Four samples were collected from a soil profile close to the mine at different depths, i.e. from four horizons in loose and solid part using Kopecky cylinders (Figure 2). Clearly visible sequences of genetic horizons have been observed during the process of sample collection from the soil profile at a depth of 100 cm. The four horizons are distinguishable at a 0-26 cm, 26-49 cm, 49-69 cm and 69-100 cm deep.

A total of six ordinary loose samples were taken from the surrounding area of the mine at a depth of 0-25 cm. Locations of these samples were: Popović polje located 2.5-3 km north-west of the mine, Rusija and Bajraktarević polje (2 km to the south-west), Varoška rijeka also 2.5 km south-west of the mine, Radostovo (4 km to the south) and Bućevci 7 km south-east of the mine. These locations were chosen in order to determine the distribution of manganese in horizontal profile at the surrounding area in relation to the manganese mine.

3.2. Sample preparation and analysis

The soil samples were prepared for physico-chemical analyses according to the ISO 11464 procedure (ISO 1994b).

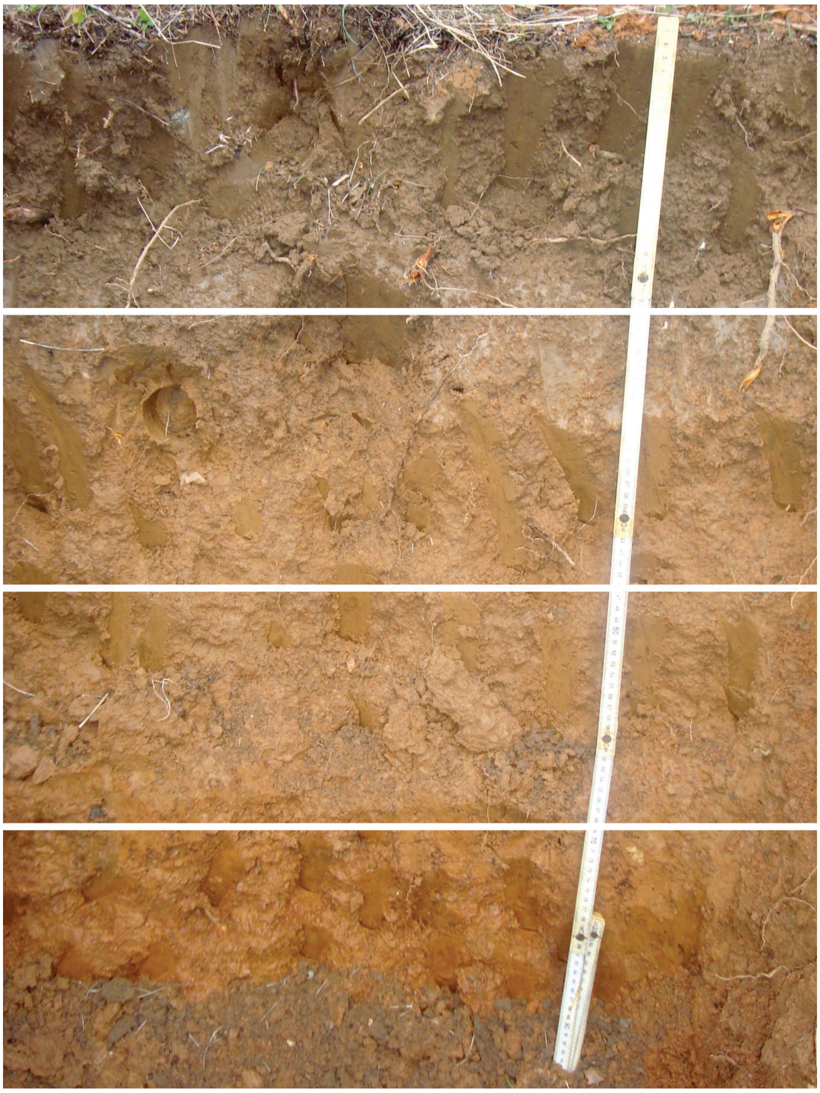

Figure 2: Layout of soil horizons in the soil profile.

Soil samples used in the research were prepared and cleared of impurities (organic matter and visible shells), air-dried, sifted with 2 mm hole diameter sieve, homogenised by the quartering method and sampled for laboratory analysis. Samples prepared in this way were used for physical and chemical analysis of soil. A fragment of prepared samples was dried in dryer at a temperature of 105 °C for an hour, afterwards powdered in agate mortar according to the ISO 11465 procedure (ISO 1993). Samples prepared in this way were used for determination of the near-total content of manganese in all samples, as well as for sequential extraction of manganese in the nine fractions.

3.3. Methods of analysis

Samples were analysed by means of the following methods:

- Determination of the hygroscopic moisture content of the soil (Hy) according to the ISO 11465 procedure (ISO 1993),
- The mineral part of the soil was determined by calcination at 500-600 °C 2 h (ČUSTOVIC & TVICA, 2005),
- Determination of granulometric soil texture was conducted according to the ISO 11277 procedure (ISO 1998). The texture of soil samples was conducted according to Ehwald (RESULOVIC & ČUSTOVIĆ, 2002),
- Bulk density was determined according to the ISO 11272 procedure (ISO 1993),
- Particle density was determined according to the ISO 11508 procedure (ISO 1998),
- Total porosity (%) was calculated using the values of bulk density and particle density (PEKEČ et al., 2013).
- Amount of humus was determined by determination of organic carbon (C) by sulphocromic oxidation as prescribed by ISO 14235 (ISO 1998). A correction factor of 1.724 was used to calculate humus from organic C.
- Amount of carbonate in the soil was determined according to the ISO 10693 procedure (ISO 1995).

- Determination of soil pH value was conducted according to the ISO 10390 procedure (ISO 1994c),
- Sum of the absorbed base cations and hydrolytic acidity were determinedby Kapenn's method (ČUSTOVIĆ & TVICA, 2005)
- The total adsorption capacity (T) was calculated from the total adsorbed basic cations (S) and total adsorbed H^+ ions (H).
- The degree of base saturation was calculated from the proportions of base cations (S) relative to the total adsorption capacity (T) and was expressed as a percentage.
- Easily accessible phosphorus and potassiumin the soil, are determined through AL-method (Enger-Riehm-Domino) by ammonium lactate-acetic acid extractaction described by EGNER et al. (1960),
- Near -total Mn content in the soil was determined by AAS after digestion of soil samples in a microwave oven,
- Methods of Mn sequential extraction of soil samples are presented in Table 1.

3.3.1. Method for determining the near-total Mn content in soil samples

Near-total contents of Mn in all soil samples were determined from their extracts (SILVEIRA et al., 2006). Sample extracts were processed by microwave digestion with the addition of 6 ml HCl (36%) and 2 ml HNO_3 (65%) - microwave technique on a MARSXpress system (CEM) according to the EPA 3050 (USEPA, 1996). The microwave digestion programme included two phases: first, 8 minutes at 160°C, and 1200W; and second 10 minutes at 160°C, and 1200W.

After completion of digestion and cooling, extracts were filtered (Whattman type 50 filter paper) in glass bottles of 50 ml and diluted with distilled water to the level line (MOSSOP & DAVIDSON, 2003). Extracts prepared in this way were stored at 4°C until further analysis by AAS according to the procedures of ISO 11047 (ISO 1998).

3.3.2. Methodology for the sequential extraction of manganese from the soil

The defined steps and reagents used in the process of sequential extraction are shown in Table 1.

Extracts from different soil fractions were separated by centrifugation at a speed of 3000 rpm for a period of 30 minutes, collected in polyethylene bottles and stored at 4 °C until analysis according to the references (AGNIESZKA & WITOLD, 2004; MING et al., 2008; SILVEIRA et al., 2006; KAZI et al., 2005; PUEYO et al., 2008; DAVIDSON et al., 2006; JOSE et al., 2006; KAASALAINEN & YLI-HALLA, 2003; ROUHOLLAH & FARZANEH, 2010).

The extracts from the residual fractions were processed by microwave digestion using the same procedure as for determination of the near-total content of manganese in soil samples. Manganese concentrations in acidic residues were measured by Atomic Absorption Spectrophotometer (Zeeman, Varian), using a calibration curve method (LI et al., 2000).

3.3.3. Quality assurance and quality control (QA/QC)

Quality assurance (QA) of the research has been realised by means of the appropriate laboratory facilities, specialised work procedures, use of distilled water, high-purity chemicals, and measurements conducted on the equipment with satisfying performance (analytical scales, pH meter, AAS).

Quality control (QC) has been realised by an analysis of the relevant blind experiments, calibration of the equipment using standardised solutions, and repetition of the analyses using the same methodology with reference to ISO 17025 procedures (ISO, 2005).

4. Results and discussion

4.1. Physical and chemical soil analysis

The determined values of specific physical and chemical soil properties are shown in Tables 2 and 3. Research has shown that particle density decreases in a vertical soil profile with

Table 1: Sequential extraction of Mn from soil.

Step	Fraction	Reagents	References
1.	Water-soluble	30 ml distilled water	(AGNIESZKA & WITOLD, 2004)
2.	Exchangeable fraction	20 ml 1 M $CaCl_2$ (pH=7)	(AGNIESZKA & WITOLD, 2004; MING et al., 2008)
3.	Carbonate fraction	20 ml 1 MNaOAc (pH=5 adjusted with HOAc)	(MING et al., 2008; SILVEIRA et al., 2006; KAZI et al., 2005, BAEYENS et al., 2003)
4.	Easily reduced substances	40 ml 0.04 M $NH_2OH \cdot HCl$ (pH=2 adjusted with CH_3COOH)	(MING et al., 2008; PUEYO et al., 2008; DAVIDSON et al., 2006; JOSE et al., 2006; KAASALAINEN & YLI-HALLA, 2003)
5.	Organic fraction	20 ml 1 M $Na_4P_2O_7$	(ROUHOLLAH & FARZANEH, 2010)
6.	Manganese oxides or moderately reduced oxides	40 ml 0.05 M NH_2OH/HCl (pH=2)	(MING et al., 2008; SILVEIRA et al., 2006)
7.	Amorphous iron oxide	30 ml 2 M ($H_2C_2O_4$) +0.2 M $(NH_4)_2C_2O_4$(pH = 3)	(MING et al., 2008;SILVEIRA et al., 2006)
8.	Crystalline iron oxide	20 ml 6M HCl	(MING et al., 2008)
9.	Residue (residual fraction)	HCl : HNO_3 (3:1) microwave digestion USEPA, 1996	(SILVEIRA et al., 2006)

Table 2: Physical properties of soil.

Soil test / sample	PARTICLE DENSITY ($kgdm^{-3}$)	BULK DENSITY ($kgdm^{-3}$)	TOTAL POROSITY (%)	PARTICLE CONTENT IN SOIL (%) SIZE OF PARTICLES IN (mm)			TEXTURAL TYPES according to HWALD
				0.02–2.00 sand	0.002–0.02 silt	< 0.002 clay	
	a	b	c	d			
MINE SECTION 1st horizon (0-26 cm)	2.51	1.46	41.80	37.50	42.50	20.00	Loam
MINE SECTION 2nd horizon (26-49 cm)	2.55	1.44	43.50	30.70	38.00	31.30	Clay loam
MINE SECTION 3rd horizon (49-69 cm)	2.46	1.49	39.40	30.80	35.80	33.40	Clay loam
MINE SECTION 4th horizon (69-100 cm)	2.30	1.41	38.60	12.50	16.20	71.30	Clay
Popović polje (0-25 cm)	–	–	–	47.40	37.70	14.90	Sandy loam
Rusija (0-25 cm)	–	–	–	33.20	47.40	19.40	Loam
Bajraktarević polje (0-25 cm)	–	–	–	45.90	45.00	9.10	Sandy loam
Varoška rijeka (0-25 cm)	–	–	–	80.30	17.20	2.50	Loamy sand
Radostovo (0-25 cm)	–	–	–	39.20	49.40	11.40	Sandy loam
Bućevci (0-25 cm)	–	–	–	73.30	22.10	4.60	Silty sand

increasing depth, i.e. from 2.51 g/cm^3 in the 1st horizon to 2.30 g/cm^3 in the 4th horizon. Bulk density displays different values within horizons of the vertical soil profile. The average amount in the 1st horizon is 1.46 g/cm^3, 1.44 g/cm^3 in the 2nd, 1.49 g/cm^3 in the 3rd, and 1.41 g/cm^3 in the 4th horizon. Based on the particle density and bulk density, it is possible to determine whether the soil is arable compacted soil. Based on the research of soil porosity we determined soil with low porosity, with a total amount of pore space of 38.60% in 4th horizon to 43.50% in 2nd horizon.

The results of granulometric analysis indicate that samples from the 2nd and 3rd horizons of the vertical profile are similar in granulometric properties and can be regarded as a clay loam. Samples taken from the locations surrounding the manganese mine (Popović polje, Rusija, Bajraktarević polje, Varoška rijeka, Radostovo and Bućevci) at depth of 0-25 cm displayed similar granulometric properties, which are: sandy loaml, loam, loamy sand and silty sand. This can be regarded as being caused by intensive deep erosion.

The soils pH values range from moderately acidic to mildly alkaline, from pH=4.64 at the manganese mine location in the deepest horizon to pH=7.26 at the location of Varoška rijeka. At different horizons in vertical profile, pH value decreases from the 1st to 4th horizons.

All soil samples displayed lower pH values of KCl than the pH values of H_2O, especially in soils where pH value is usually high. Soils with delta pH higher than 0.10, are said to have geric properties, i.e. are very exposed to erosion and have low adsorption capacity or a low number of exchangeable bases (RESULOVIĆ, 1997). Delta pH had the highest value (pH=0.65) at the 4th horizon (100 cm) at the manganese mine.

The amount of $CaCO_3$ in all samples was lower than the limit set by the method, since the dissolution of soil samples was conducted by using diluted hydrochloric acid. Based on the results of research and values obtained for the level of base saturation (V), ranging from 73.58% at Popović polje to 99.47% at Varoška rijeka, it can be stated that all tested locations are Eutric Cambisols.

4.2. Near-total content of manganese

The near-total content of manganese for each sample location in the vertical profile are presented in Table 4, as well as for each sample location surrounding the „Bužim“ man-

Table 3: Chemical properties of soil.

Soil test / sample	pH-VALUE IN (1:2.5)		HIGROSCOPIC HUMIDITY (t=105°C) (%)	RESIDUE AFTER CALCINATION (t=550°C) (%)	AMOUNT OF HUMUS (%)	AMOUNT OF PHYSIOLOGICAL ACTIVITY (mg/100 g of soil)		AMOUNT OF $CaCO_3$ (%)	HYDROLYTIC ACIDITY „H" (mmol/100 g of soil)	AMOUNT OF ALKALINE ADSORPT-ION „S" (mmol/ 100g of soil)	TOTAL ADSORPTION CAPACITY „T" (mmol/ 100 g of soil)	DEGREE OF ALKALI-NE SATUR-ATION „V" (%)
	H_2O	KCl				P_2O_5	K_2O					
	a		b		c	d		e	f	g	h	j
MINE SECTION 1st horizon (0-26 cm)	5.53	5.29	2.17	91.63	2.65	< 0.10	10.52	< 0.10	1.50	8.77	10.27	85.40
MINE SECTION 2nd horizon (26-49 cm)	5.46	5.45	2.25	93.55	0.64	< 0.10	6.75	< 0.10	0.75	5.98	6.73	88.85
MINE SECTION 3rd horizon (49-69 cm)	5.34	5.14	2.41	93.74	0.47	< 0.10	7.01	< 0.10	0.75	5.58	6.33	88.16
MINE SECTION 4th horizon (69-100 cm)	4.64	3.99	4.22	89.62	0.47	< 0.10	6.66	< 0.10	1.35	5.58	6.93	80.53
Popović polje (0-25 cm)	5.23	4.85	2.97	87.07	3.52	< 0.10	17.98	< 0.10	3.15	8.77	11.92	73.58
Rusija (0-25 cm)	5.79	5.42	2.68	89.50	4.15	< 0.10	21.66	< 0.10	2.10	9.97	12.07	82.60
Bajraktarević polje (0-25 cm)	6.76	6.55	2.02	91.67	2.33	< 0.10	7.71	< 0.10	1.50	27.94	29.44	94.90
Varoška rijeka (0-25 cm)	7.26	7.21	1.41	91.92	3.36	7.22	12.36	< 0.10	0.45	85.45	85.90	99.47
Radostovo (0-25 cm)	6.99	6.56	2.26	90.93	3.48	2.88	21.92	< 0.10	0.75	15.56	16.31	95.40
Bućevci (0-25 cm)	7.08	7.06	3.15	89.11	3.07	< 0.10	15.43	< 0.10	0.75	39.12	39.87	98.10

ganese mine. Relatively equable Mn concentrations were measured through all horizons, at three depths of the vertical profile, ranging from 1190.00 to 1160.00 mg/kg with increasing depth.

Table 4: Near-total content of Mn for each sample location.

	Symbols of samples	Amount Mn (mg/kg)
MINE SECTION	1st horizon (0-26 cm)	1190.00
	2nd horizon (26-49 cm)	1170.00
	3rd horizon (49-69 cm)	1160.00
	4th horizon (69-100 cm)	780.00
	(0-25 cm)	
	Rusija (0-25 cm)	
	Bajraktarević polje (0-25 cm)	
	Varoška rijeka (0-25 cm)	
	Radostovo (0-25 cm)	
	Bućevci (0-25 cm)	

The amount of Mn was significantly decreased at the 4th horizon (780.00 mg/kg), as displayed in Figure 3.

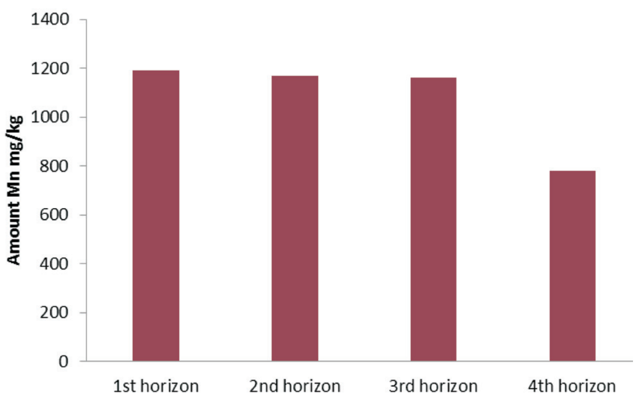

Figure 3: Near-total content of Mn at the mining area.

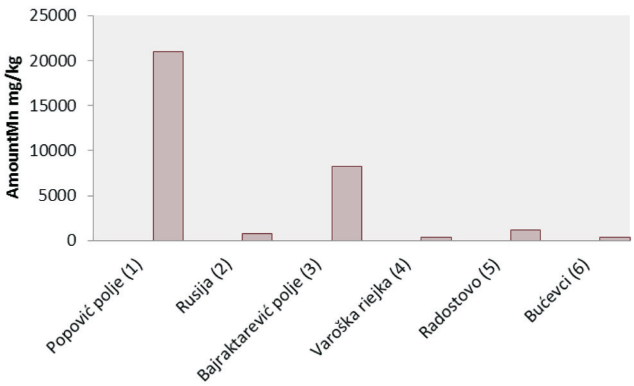

Figure 4: Near-total content of Mn in the surrounding area.

Figure 4. indicates that within the examination of all locations at a depth of 0-25 cm, the highest near-total content of 20950.00 mg/kg of Mn, was measured at the area of Popović polje, while the lowest amount was measured at the area of Bućevci of 418.00 mg/kg. The high content of Mn in certain locations is probably due to the close proximity of the sampling areas to the mine.

Results indicate that, the sample locations contain extremely high concentrations of manganese, which can be related to the former mining activities in the area.

4.3. The distribution of Mn in different soil fraction determined from sequential extraction

Table 5. presents the Mn contents in the individual fractions as determined by the process of sequential extraction. The sum of all the examined Mn fractions displays relatively good correlation with near-total content of Mn at the same soil samples, while this type of correlation was not displayed at the area of Popović polje. According to ZEMBERYOVA et al. (2006) figures 5 and 6 display the extracted percentages of Mn among the examined fractions (in relation to the certified value of 100).

MEERS et al. (2007) define the water-soluble fraction as being easily mobilised and a highly available fraction. In the first soluble fraction, the percentage of Mn in the vertical profile of horizons at the manganese mine location is lower than 1.00%, thus posing no threat according to the assessment code. The percentage of soluble fraction in soil samples from the area surrounding manganese mine at all sampling locations is lower than 1.00%, thus having no detrimental effect on the environment.

The exchangeable metal fraction is loosely bound to colloidal soil particles (AGNIESZKA & WITOLD, 2004).

NOVOZAMSKI et al. (1993) proposed the use of $CaCl_2$ as a reagent for evaluation of metal and nutrient bioavailability in air-dried soil sample. HOUBA et al. (1996, 2000) state the advantages of this reagent. In the second exchangeable fraction, the percentage of Mn in the vertical profile (sampled in the mine) is as follows: 2.00 % in 1st horizon, 1.00% in the 2nd and 3rd horizon and 3.00 % in the 4th horizon. The highest percentage of the exchangeable manganese fraction is obtained in the 4th horizon, probably due to an increased ionic exchange which occurs as the soil depth and amount of cations in the soil increase.

The percentage of exchangeable fractions at locations surrounding the manganese mine (1st horizon) is as follows: <0.10% in Popović polje and Bajraktarević polje, 2.00% in Rusija and Varoška rijeka, 1.00% in Radostovo and Bućevci. The percentage of Mn in the exchangeable fraction (mobile metal fraction) at all sample locations, according to the assessment code, has no detrimental effect on the environment.

The carbonate fraction is regarded as an easily mobilised fraction. Extraction within this fraction was conducted by means of reagent 1M NaOAc solution, pH=5 adjusted with acetic acid in order to transfer most of the absorbed Mn into solution (BAEYENS et al., 2003), as the fraction is highly sensitive to changes of pH value (TESSIER et al., 1979).

Table 5: The amount of Mn in certain fractions after sequential extraction procedure (mg/kg).

SAMPLE / FRACTION	MINE SECTION				Popović polje (0-25 cm)	Rusija (0-25 cm)	Bajraktarević polje (0-25 cm)	Varoška rijeka (0-25 cm)	Radostovo (0-25 cm)	Bućevci (0-25 cm)
	1st horizon (0-26 cm)	2nd horizon (26-49 cm)	3rd horizon (49-69 cm)	4th horizon (69-100 cm)						
Water-soluble fraction	1.50	1.50	1.50	1.50	0.60	0.90	0.90	0.90	1.20	0.90
Exchangeable fraction	29.20	8.40	8.60	17.40	56.80	17.80	10.40	8.60	15.20	5.20
Carbonate fraction	31.80	8.80	7.40	9.20	52.80	22.40	48.60	52.80	34.80	42.60
Easily reduced substances	393.60	181.60	162.00	186.80	2916.00	92.80	2644.00	207.20	217.20	255.60
Organic fraction	992.00	516.00	556.00	183.00	5200.00	424.00	2600.00	40.00	505.00	48.00
Manganese oxides	158.00	67.20	74.40	34.40	2832.00	73.20	784.00	17.60	70.80	19.60
Amorphous iron oxide	48.30	47.70	50.70	21.00	2664.00	41.10	1296.00	8.40	56.70	9.30
Crystalline iron oxide	80.20	86.00	91.20	52.00	5880.00	63.80	900.00	67.60	67.20	38.00
Residual amount of Mn	147.00	168.50	149.50	124.50	7125.00	114.50	520.00	29.50	178.50	41.00
Total amount of fractions	1881.60	1085.70	1101.30	629.80	26727.20	850.50	8803.90	432.60	1146.60	460.20

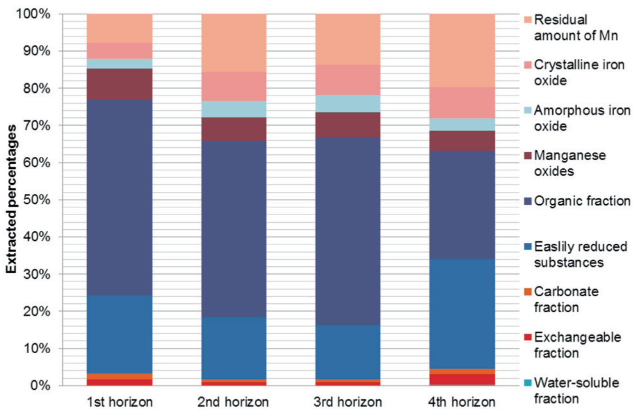

Figure 5: Distribution of Mn at the mining area using the sequential extraction procedure.

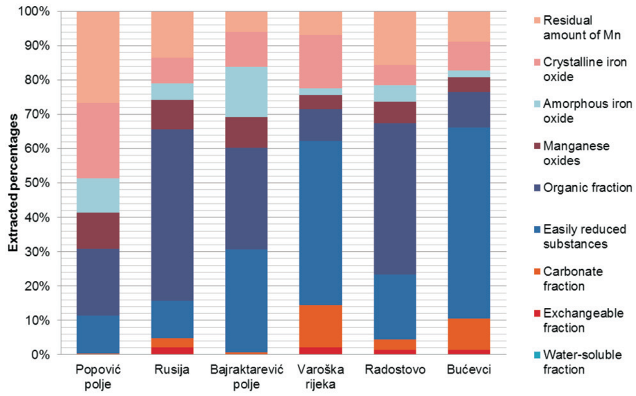

Figure 6: Distribution of Mn in the area surrounding the mine using sequential the extraction procedure.

According to ROBBINS et al. (1984) the reagent releases 99.90% of the carbonate fraction and has minimum influence on other fractions. The percentage of carbonate fraction in vertical profile (sampled in the mine) of horizons ranges from 1.00% in 2nd, 3rd and 4th horizon, to 2.00% in 1st horizon, thus posing low risk to the environment according to the assessment code. The highest percentage of carbonate fraction in the 1st horizon can be explained by the susceptibility of the fraction to changes of pH value (TESSIER et al., 1979).

Consequently, it was observed that the highest percentage of carbonate fraction correlates with the highest measured pH value (5.53) at the 1st horizon soil sample in the vertical profile in the area of the mine.

The percentages of carbonate fraction at the other sample locations surrounding the manganese mine (1st horizon) are: <0.10% in Popović polje, 3.00% in Rusija, 1.00% in Bajraktarević polje, 12.00 % in Varoška rijeka, 3.00% in Radostovo and 9.00% in Bućevci. The highest percentage of the carbonate fraction was detected at the location of Varoška rijeka (12.00%) correlating with the highest measured pH value at the same location (7.26), which confirms the fact that the fraction is susceptible to changes of pH value. Moreover, it proves the sensitivity of the fraction to changes of pH-value and indicates that as the soil pH value increases, so does the percentage of carbonate and consequently of the bioavailable manganese fraction in the soil. The percentage of Mn in the carbonate soil fraction at the location of Varoška rijeka has a limited effect on the environment.

Easily reduced substances (Fe-Mn bound oxides) display moderate mobility, depending on the redox conditions of the environment. According to SILVERA et al. (2006) the redox potential of soil can significantly increase the solubility of Fe and Mn oxides.

Fe and Mn oxides have a great effect on control and mobility of other metals in the environment. In the reduced fraction (Fe-Mn bound oxides), the percentages of Mn in the vertical profile (sampled in the mine) of individual horizons are: 1st horizon 21.00%, 2nd horizon 17.00%, 3rd horizon 15.00% and 4th horizon 31.00%. The highest percentage of Mn in the vertical profile was determined at the 4th horizon (31.00%), which could be due to an increased redox potential there, leading to an increased solubility of the fraction. The highest percentage of Mn in this fraction correlates with the lowest measured pH value at the 4th horizon.

Percentages of the reduced fraction at the locations surrounding the manganese mine (1st horizon) are: Popović polje and Rusija 11.00%, Bajraktarević polje 29.00%, Varoška rijeka 48.00%, Radostovo 19.00% and Bućevci 57.00%. The percentage of the reduced fraction at all sample locations is relatively high, due to numerous natural and anthropogenic sources of Mn over the area.

The highest percentage of the easily reduced fraction is determined in the area of Bućevci (57.00%), which can be explained by manganese oxidation resulting from mining activity there (NADASKA et al., 2009).The fact that Mn dominates in the fraction of Fe-Mn oxide at the area of Bućevci indicates they share a common origin.

According to HAUNG et al. (2007) Mn bound to the organic fraction displays moderate mobility, although it can be increased due to the oxidation of organic matter. The solubility of the Mn fraction bound to organic matter, precedes those of Mn oxides, amorphous and crystalline iron oxides. This enables organic phase degradation, providing better conditions for the extraction of fractions bound to Mn (ALVAREZ et al., 2006).

The percentage of the organic fraction in the vertical profile (sampled in the mine) of individual horizons is: 1st horizon 52.00%, 2nd horizon 47.00%, 3rd horizon 49.00% and 4th horizon 29.00%. The percentage of the organic fraction at sample locations surrounding the „Bužim“ manganese mine (1st horizon) is: Popović polje 19.00%, Rusija 49.00%, Bajraktarević polje 30.00%, Varoška rijeka 9.00%, Radostovo 44.00% and Bućevci 10.00%. Due to a high affinity of bonding to organic matter (RESULOVIĆ, 1997) Mn is dominant in this fraction with the highest percentage (52.00%) in the 1st horizon of the vertical profile (sampled in the mine).

The percentage of manganese oxides or moderately reduced oxides in horizons of vertical profiles (sampled in the mine) is: 1st horizon 8.00%, 2nd horizon 6.00%, 3rd horizon 7.00% and 4th horizon 5.00%. The percentage of this fraction at other locations surrounding the manganese mine (1st horizon) is: Popović polje 11.00%, Rusija i Bajraktarević polje 9.00%, Varoška rijeka and Bućevci 4.00%, Radostovo 6.00%. The highest percentage of the fraction was measured at the Popović polje location (11.00%), which can be related to relatively low pH-values of the location (5.23) (SILVEIRA et al., 2006).

The percentage of Mn bound to the amorphous iron oxide fraction in the horizons of the vertical profile (sampled in the mine) is:1st and 4th horizon 3.00%, 2nd horizon 4.00% and 3rd horizon 5.00%. At locations surrounding the manganese mine (1st horizon) it is as follows: Popović polje 10.00%, Rusija 5.00%, Bajraktarević polje 15.00%, Varoška rijeka and Bućevci 2.00% and Radostovo 5.00%. The highest percentage of this fraction is measured in the area of Bajraktarević polje (15.00%).

SCHWERTMANN (1991) proved the efficacy of 6 M HCl used for dissolution of the crystalline iron oxide fraction. In his research, the author stated that nearly 60.00% of Fe dissolves with 6M HCl solution (SILVIERA et al., 2006). The percentage of Mn bound to the crystalline iron oxide fraction in individual horizons of vertical profile (sampled in the mine) is determined as: 1st horizon 4.00%, 2nd, 3rd and 4th horizon 8.00%. At locations surrounding the manganese mine (1st horizon) it is as follows: Popović polje 22.00%, Rusija 8.00%, Bajraktarević polje 10.00%, Varoška rijeka 16.00%, Radostovo 6.00% and Bućevci 8.00%. The highest percentage of the fraction was measured in the Popović polje (22.00%).

The highest percentage of Mn in this fraction correlates with the highest percentage in manganese oxides and moderately reduced oxides fraction, which can be due to the size of their ionic radii and isomorphic substitution of Mn and Fe (SILVEIRA et al., 2006).

According to SUTHERLAND et al. (2000), metals extracted in non-residual fractions indicate an anthropogenic origin, and metals extracted in the residual fraction indicate a natural origin (FORSTNER, 1983; BLASCO et al., 2000; JAIN, 2004; RAMIREZ et al., 2005). PRICA (2011) states that the residual fraction cannot be mobilised from geological material and is not bioavailable.

The percentage of the residual fraction in horizons of the vertical profile (sampled in the mine) is: 1st horizon 8.00%, 2nd horizon 16.00%, 3rd horizon 14.00% and 4th horizon 20.00%. At locations surrounding the manganese mine (1st horizon) it is as follows: Popović polje 27.00%, Rusija 13.00%, Bajraktarević polje 6.00%, Varoška rijeka 7.00%, Radostovo 16.00% and Bućevci 9.00%.

A rather high percentage of Mn at the aforementioned locations is probably due to extremely strong bonds of Mn and the soil solid phase. The highest percentage of the fraction is determined at the area of Popović polje (27.00%). The highest percentage of Mn in this fraction in the area correlates with the crystalline iron oxide fraction and Mn oxide and moderately reduced oxide fraction.

5. CONCLUSIONS

According to the research conducted at the „Bužim“ manganese mine and the surrounding area, the following conclusions can be drawn:

According to pH values the soils are moderately acidic to mildly alkaline, thus being considered as Eutric Cambisols. The results of sequential extraction indicate that chemical soil properties significantly affect Mn distribution in the different soil fractions. The highest percentage of bioavailable Mn was measured at the „Bužim“ manganese mine (in 1st fraction) and in Popović polje (in 2nd fraction), since there are numerous natural and anthropogenic sources of Mn at these areas. The percentage of Mn soluble fraction is less than 1.00% at all locations, thus having no detrimental effect on the environment. The highest percentage of exchangeable manganese fraction (3.00%) was measured in the 4th horizon of the vertical profile, probably due to an increased ionic exchange which occurs as depth increases, thus having no detrimental effect on the environment according to the assessment code. The highest percentage of the carbonate fraction (12.00%) was determined at the location of Varoška rijeka correlating with pH=7.26. The percentage of Mn in the carbonate fraction at the location of Varoška rijeka moderately affects the environment.

The highest percentage of natural Mn was determined in the residual fraction (27.00%) at Popović polje, while the highest percentage of anthropogenic origin Mn was determined at Bućevci (57.00%) in the Fe-Mn oxides fraction. The highest near-total content of Mn was determined at Popović polje (20950.00 mg/kg). The highest percentage of natural Mn (27.00%) was determined in the same area. The highest percentage of Mn of an anthropogenic origin (57.00%) was determined at Bućevci. The results are possibly due to mining activity which took place there in the past.

Further research shall be directed towards additional techniques such as X-ray analysis, which is highly important in the research of mineral phases enabling the determination of any correlation between certain chemical forms (species) of Mn at the aforementioned soil areas.

ACKNOWLEDGEMENT

We would like to acknowledge the help in sample collection and soil analysis, provided by the director of the Agricultural Institute of Una-Sana Canton and Head of Laboratory Muhamed Ajaz.

REFERENCES

AGNIESZKA, M. & WITOLD, W. (2004): Three-step extraction procedure for determination of heavy metals availability to vegetables.– Anal. Bioanal. Chem., 380, 813–817.

ALVAREZ, J.M., LUIS, M., VALDIVIA, L., NOVILLO, J., OBRADOR, A. & RICO, M. (2006): Comparison of EDTA and sequential extraction tests for phytoavailability prediction of manganese and zinc in agricultural alkaline soils.– Geoderma, 132, 450–463.

BAEYENS, W., MONTENY, F., LEERMAKERS, M. & BOUILLON, S. (2003): Evalution of sequential extractions on dry and wet sediments.– Anal. Bioanal. Chem., 376, 890–901.

BLASCO, J., SAENZ, V. & GOMEZ-PARRA, A. (2000): Heavy-metal fluxes at the Sediment-water interface of three coastal ecosystems from south-west of the Iberian Peninsula.– Science of the Total Environment, 247, 189–199.

BROMFIELD, S.M. & DAVID, D.J. (1987): Properties of biologically formed manganese oxide in relation to soil manganese.– Australian Journal of Soil Research,16, 79–89.

CALMANO, W., HONG, J. & FÖRSTNER, U. (1993): Binding and mobilisation of heavy metals in contaminated sediments affected by pH and redox potential.– Water Science and Technology, 28/8–9, 223–35.

CUSTOVIC, H. & TVICA, M. (2005): Praktikum za pedološka istraživanja, Univerzitet u Sarajevu Poljoprivredni fakultet.

DAVIDSON, C.M., URQUHART, G.J., AJMONE-MARSAN, F., BIASIOLI, M., DA COSTA, D., ARMANDO, (?)., DÍAZ-BARRIENTOS, E., GRČMAN, H., HOSSACK, I., HURSTHOUSE, A.S., MADRID, L., RODRIGUES, S. & ZUPAN, M. (2006): Fractionation of potentially toxic elements in urban soils from five European cities by means of a harmonised sequential extraction procedure.– Analytica Chimica Acta, 565, 63–72.

DOLAR, S.G. & KEENEY, D.R. (1971): Availability of Cu, Zn and Mn in soils: Influence of soil pH, organic matter, and extractable phosphorus.– Journal of the Science of Food and Agriculture, 22/6, 273–278.

EGNER, H., RIEHM, H. & DOMINO, W.R. (1960) Untersuchungen uber die chemische Bodenanalyse als Grundlage fur die Beurteilung des Nahrstoffzustandes der Boden, II: Chemische Extractionsmetoden zu Phosphorun Kaliumbestimmung.– Kungliga LantbrukshugskolansAnnaler, 26, 199–215.

FILGUEIRAS, A.V., LAVILA, I. & BENDICHO, C. (2002): Chemical sequential extraction for metal partitioning in environmental solid samples.– J. Environ. Monit., 4, 823–857.

FORSTNER, U. (1993): Metal speciation: general concepts and applications. An account for the improvement and harmonisation of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities.– International Journal of Environmental Analytical Chemistry, 51, 5–23.

HAJDAREVIĆ, S., SIJARIĆ, G., VUJNOVIĆ, D. & ŠIBENIK-STUDEN, M. (1988): Manganonosno područje Uzolomca i gorja.– Zbornik ref. Naučnogskupa ''Minerali, stijene, izumrli i živi svijet BiH''. Zemaljski muzej BiH, 49–61.

HAUNG, J., HAUNG, R., JIAO, JJ. & CHEN, K. (2007): Speciation and mobility of heavy metals in mud, in coastal reclamation areas in Chenzhen, China.– Environ Geol., 53, 221–228.

HLAVAY, J., PROHASKA, T., WEISZ, M., WENZEL, W.W. & STINNGEDER, G.J. (2004): Determination of trace elements bond to soils and sediment fractions.– Pure and Applied Chemistry, 76/2, 415–442.

HODŽIĆ, T. & ABDURAHMANOVIĆ, A. (1998): Školski atlas IP "Svjetlost" dd. Zavod za udžbenike i nastavna sredstva, Sarajevo, 1999. BiH.

HORSTMAR, P.S. (1851): Sur la nutrition de l'avoine, particulierement en ce qui concerne les matieresinorganiques qui sontnecessaires a cette nutrition.– Ann. Chim. Phys., 32, 461–510.

HOUBA, V.J.G., LEXMOND, T.M., NOVOZAMSKY, I. & VAN DER LEE, J.J. (1996): State of the art and future developments in soil analysis for bioavailability Assessment.– The Science of the Total Environment., 178, 21–28.

HOUBA, V.J.G., TEMMINGHOFF, E.J.M., GAIKHORST, G.A. & VAN VARK,W. (2000): Soil analysis procedures using 0.01 M calcium chloride as extraction reagent.– Communications in Soil Science and Plant Analysis., 3, 1299–1396.

ISO – International Standard Organisation (2002): Soil quality – Sampling – Part 1: Guidance on the design of sampling programmes. ISO 10381-1:2002

ISO – International Standard Organisation (2002): Soil quality – Sampling - Part 2: Guidance on sampling techniques. ISO 10381-2:2002.

ISO – International Standard Organisation (1994): Soil quality pretreatment of samples for physico-chemical analyses. ISO 11464: 1994 (1994b).

ISO – International Standard Organisation (1995): Soil quality – determination of carbonate content-volumetric method. ISO 10693: 1995.

ISO – International Standard Organisation (1993): Soil Quality – Determination of dry matter and water content on a mass basis – Gravimetric method. International Organization for Standardization. Geneva, Switzerland. 9 p. ISO 11465:1993.

ISO – International Standard Organisation (1994): Soil Quality – Pretreatment of samples for physico-chemical analysis. International Organization for Standardization. Geneva, Switzerland. 9 p. ISO 11464 :1994.

ISO – International Standard Organisation (1993): Soil Quality – Determination of dry bulk density. International Organization for Standardization. Geneva, Switzerland. 10 p. ISO 11272:1993.

ISO – International Standard Organisation (1998): Soil Quality – Determination of particle density. ISO 11508:1998.

ISO – International Standard Organisation (1998): Determination of cadmium, chromium, cobalt, copper, lead, manganese nickel and zinc. Flame and electrothermal atomic absorption spectrometric methods. International Organization for Standardization. Geneva, Switzerland. 6 p. ISO 11047:1998.

ISO – International Standard Organisation (1998): Soil Quality – Determination of organic carbon by sulphochromic oxidation. ISO 14235: 1998.

ISO – International Standard Organisation (1998): Determination of particle size distribution in mineral soil material. Method by sieving and sedimentation. ISO 11277:1998.

ISO – International Standard Organisation (2005): General requirements for the competence of testing and calibration laboratories. ISO/IEC 17025:2005.

JAIN, C. K. (2004): Metal fractionation study on bed sediments of River Yamuna, India.– Water Research, 38, 569–578.

JOSE, M.A., LUIS, M.L., JESUS, N., ANA, O. & MARIA, I.R. (2006): Comparison of EDTA and Sequential Extraction Tests for Phytoavailability Prediction of Manganese and Zinc in Agricultural alkaline Soils.– Geoderma, 132, 450–463.

KALEMBKIEWICZ, J. & SITARZ-PALCZAK, E. (2004): Validation and Optimization of Condition for the Sequential Extraction of Manganese from Ash.– Polish Journal of Environmental Studies, 14, 41–47.

KAZI, T.G., JAMALI, M.K., KAZI, G.H., ARAIN, M.B., AFRIDI, H.I. & SIDDIQUI, A. (2005): Evaluating the mobility of toxic metals in untreated industrial wastewater sludge using a BCR sequential extraction procedure and a leaching test.– Anal. Bioanal. Chem., 383, 297–304.

KAASALAINEN, M. & YLI-HALLA, M.(2003): Use of sequential extraction to assess metal partitioning in soils.– Environmental Pollution, 126, 225–233.

LI, W., PETERS, R.W., BREWSTER, M.D. & MILLER, G.A. (1995): Sequentinial extraction evaluation of heavy-metal-contaminated soil: how clean is clean? – Proceedings of the Air and Waste Management Asociation. 88th Annual Meeting and Exhibition, San Antonio, Texas. June, 18–23.

LI, X., SHEN, Z., WAI, O. & LI, Y-S. (2000): Chemical partitioning of heavy metal contaminants in sediments of the Pearl River Estuary.– Chemistry Speciation Bioavailability, 12/1, 17–25.

LI, X. & THORNTON, I. (2001): Chemical partitioning of trace and major elements in soils contaminated by mining and smelting activities.– Applied Geochem., 16, 1693−1706. doi: 10.1016/S0883-2927 (01)00065-8.

MARIKA, K. & MARKKU, Y-H. (2003): Use of sequential extraction to assess metal parttitioning in soil.– Environmental Pollution, 126, 225–233.

MACKLIN, M.G. (1992): Metal contaminated soils and sediment: a geographical perspective.– In: NEWSON, M.D. (ed.): Managing the human impact on the natural environment: patterns and processes. Belhaven Press, London, 172−195.

MARTLEY, E., GULSON, B., LOUIE, H., WU, M. & DI, P. (2004): Metal partitioning in soil profi les in the vicinity of an industrial complex, New South Wales, Australia.– Geochem. Explor. Env., A4, 171−179. doi: 10.1144/1467-7873/03-030.

MARSCHNER, P., FU, Q. & RENGEL, Z. (2003): Manganese availability and microbial populations in the rhizosphere of wheat genotypes differing in tolerance to Mn deficiency.– Journal of Plant Nutrition and Soil Science, 166/6, 712–718.

MIHALJEVIČ, M., POŇAVIČ, M., ETTLER, V. & ŠEBEK, O. (2003): A comparison of sequential extraction techniques for determining arsenic fractionationin synthetic mineral mixtures.– Anal. Bioanal. Chem., 377, 723–729.

MING, L., BO-HAN, L., QING-RU, Z., PU-FENG, Q. & SARDAR, K. (2008): Fraction Distributions of Lead, Cadmium, Copper, and Zinc in Metal-Contaminated Soil before and after Extraction with Disodium Ethylenediaminetetraacetic Acid.– Communications in Soil Science and Plant Analysis, 39, 1963–1978.

MOJIĆEVIĆ, M., ČAČIĆ, S. & PAPEŠ, J. (1984): Geologija Bosne i Hercegovine, knj. II Mezozojske periode „Geoinženjering" Sarajevo.

MOSSOP, K.F. & DAVIDSON, C.M. (2003): Comparison of original and modified BCR sequential extraction procedures for the fractionation of copper, iron, lead, manganese and zinc in soils and sediments.– Analitica Chimica Acta, 478, 111–118.

MEERS, E., LAING, G., UNAMUNO, V., RUTTENS, A., VANGRONSVELD, J., TACK, F.M.G. & VERLOO, M.G. (2007): Comparison of cadmium extractability from soils bycommonly used single extraction protocols.– Geoderma, 141, 247–259.

NADASKA, G., POLČOVA, K. & LESNY, J. (2009): Manganese fractionation analysis in specific soil and sediment samples.– Nova Biotechnologica, 9–3.

NOGALES, R., GALLARDO-LARA, F., BENITEZ, E., SOTO, J., HERVAS, D. & POLO, A. (1997): Metal extractability and availability in a soil after heavy application Of either nickel or lead in different forms.– Water, Air, and Soil Pollution, 94, 33–44.

NOVOZAMSKY, I., LEXMON, T.M. & HOUBA, V.J.G. (1993): A single extraction procedure of soil for evaluation of uptake of some metals by plants.– International Journal of Analytical Chemistry, 51, 47–58.

OLAYINKA, K.O., OYEYIOLA, A.O., ODUJEBE, F.O. & OBOH, B. (2011): Uptake of potentially toxic metals by vegetable plants grown on contaminated soil and their potential bioavailability using sequential extraction.– Journal of Soil Science and Environmental Management, 2/8, 220–227.

OREŠČANIN, V., KATUNAR, A., KUTLE, A. & VALKOVIĆ, V. (2003): Heavy metals in soil, grape, and wine.– J. Trace Microprobe T., 21, 171–180. doi: 10.1081/TMA-120017912.

PERTSEMLI, E. & VOUTSA D. (2007): Distribution of heavy metals in Lakes Doirani and Kerkini, Northern Greece.– Journal of Hazardous Materials, 148/3, 529–537.

PERIN. G., CRABOLEDDA. L., LUCCHESE, M., CIRILLO, R., DOTTA, L., ZANETTE, ML. & ORIO, A.A. (1985): Heavy metal speciation in the sediments of Northern Adriatic Sea. A new approach for environmental toxicity determination.– Heavy metal in the environment, 2, 454–456.

PEKEČ, S., VRBEK, B., ORLOVIĆ, S. & BALLIAN, D. (2013) Water dynamics and Physical characteristics of hydromorphic soils in southern Bačka.– Periodicum biologorum, 115/3.

PIPER, C.S. (1931): The Availability of Manganese in the Soil.– The Journal of Agricultural Science, 21, 762–779.

PRICA, M. (2011): Correlation between different approaches for metal availability Assessment.– Romanian Journal of Aquatic Ecology 1.1., 1–18.

PUEYO, M., MATEU, J., RIGOL, A., VIDAL, M., LO´PEZ-SA´NCHEZ, J.F. & RAURET G. (2008): Use of the modified BCR three-step sequential extraction procedure for the study of trace element dynamics in contaminated soils.– Environmental Pollution, 152, 330–341.

RAMIREZ, M., MASSOLO, S., FRAICHE, R. & CORREA, J. (2005): Metal speciation and environmental impact on sandy beaches due to El Salvador Coppermine, Chile.– Marine Pollution Bull, 50, 62–71.

RESULOVIĆ, H. (1997): Pedologija sa geologijom.– Federacija BiH Ministarstvo obrazovanja, nauke, kulture i sporta. Sarajevo-Publishing, Sarajevo.

RESULOVIC, H. & ČUSTOVIĆ, H. (2002): Pedologija.– Univerzitet u Sarajevu.

ROUHOLLAH, K. & FARZANEH, S. (2010): Determination of Trace Levels of Nickel and Manganese in Soil, Vegetable, and Water.– Clean Soil, Air, Water, 38, 177–1183.

ROBBINS, J.M., LYLE, M., HEATH, G.R. (1984): A sequential extraction procedure for partitioning elements among co-existing phases in marine sediments.– College of Oceanography, Oregon State University, 84–3, 64.

RUTTEN, A. & GERT, J. (2003): Sequential extraction of iron, manganese and related elements in S1 sapropel sediments, eastern Mediterranean.– Palaeogeography, Palaeoclimatology, Palaeoecology, 190, 79–101.

SALETOVIC, M., HODZIC, Z., BANJANIN, B. & KESIC, A. (2011): Bioavailability of microelements (Cu, Zn, Mn) in medicinal plants.– HealthMED, 5/5, 1358–1364.

SAHUQUILLO, A., RIGOL, A. & RAURET, G. (2003): Overview of the use of leaching/extraction tests for risk assessment of trace metals in contaminated soils and sediments.– Trends in Analytical Chemistry, 22, 152–159.

SCHWERTMANN, U. (1991): Solubility and dissolution of iron oxides.– Plant Soil, 130, 1–25.

SILVEIRA, M.L., ALLEONI, L.R.F., O'CONNOR, G.A. & CHANG, A.C. (2006): Heavy metal sequential extraction methods – A modification for tropical soils.– Chemosphere, 64, 1929–1938.

SUTHERLAND, R.A., TACK, F.M.G., TOLOSA, C.A. & VERLOO, M.G. (2000): Operationallydefined metal fractions in road deposited sediment, Honolulu, Hawaii.– J. Environ. Qual., 29, 1431–1439.

TESSIER, A. & CAMPBELL, P.G.C. (1987): Partitioning of trace metals in sediments: relationship with bioavailability.– Hydrobiologia, 149, 43–52.

TESSIER, A., CAMPBELL, P.G.C. & BISON, M. (1979): Sequential extraction procedure for the speciation of particulate trace metals.– Analitica Chemica, 5, 844–851.

TRUDINGER, P.A. & SWAINE, D.J. (1979): Biogeochemical cycline of mineral – forming elements.– Elsevier Scientific Publ., 253 p.

VUKADINOVIĆ, V. & LONČARIĆ, Z. (1998): Ishrana bilja, poljoprivredni fakultet u Osijeku, Osijek.

WARREN, R.S. & BIRCH, P. (1987): Heavy metal levels in atmospheric particles, roadside dust and soil along a major urban highway.– Sci. Total. Environ., 59, 253–256. doi: 10.1016/0048-9697(87) 90446-3.

WUANA, R.A., OKIEIMEN, F.E. & IMBORVUNGU, J.A. (2010): Removal of heavy metals from a contaminated soil using organic chelating acids.– Int. J. Environ. Sci. Tech., 7/3, 485–496.

ZAKIR, H.M. & SHIKAZAONO, N. (2011): Environmental mobility and geochemical partitioning of Fe, Mn, Co, Ni and Mo in sediments of an urban river.– Journal of Environmental Chemistry and Ecotoxicology, 3/5, 116–126.

ZEMBERYOVA, M., BARTEKOVA, J. & HAGAROVA, I. (2006): The utilization of modified BCR three-step sequential extraction procedure for the fractionation of Cd, Cr, Cu, Ni, Pb and Zn in soil reference materials of different origins.– Talanta, 70, 973–978.

ZHANG, Y., CAI, Y., WANG, C. & XUE, G. (2012): Characters and Influencing Factors of the Distribution of Cultivated Available Soil Fe, Mn, Cu and Zn in Xichang City, Sichuan Province, China.– Journal of Geography and Geology, 4, 2.

ZOUMIS, T., SCHIMDT, A., GRIGOROVA, L. & CALMANO, W. (2001): Contaminants in sediments: remobilisation and demobilisation.– The Science of the Total Environment, 266, 195–202.

Manuscript received August 12, 2012
Revised manuscript accepted February 18, 2014
Available online March 21, 2014

.