

ACCUMULATION OF TRACE ELEMENTS IN FE-RICH NODULES IN A NEUTRAL-SLIGHTLY ALKALINE FLOODPLAIN SOIL

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Abstract. The nature of soil iron oxides is of great interest from the viewpoints of both pedogenesis and environmental geochemistry as they are sensitive diagnostic indicators of soil hydromorphism on the one hand, and exhibit high sorption capacity for many toxic metal pollutants on the other. In this study, the association of 17 trace elements (Al, Ba, Ca, Cd, Co, Cr, Cu, K, Mg, Mn, Ni, Pb, Si, Sr, Ti, V and Zn) with Fe-rich nodules from a neutral-alkaline floodplain soil using various chemical extractions and dissolution analyses was investigated.

The Fe-rich nodules consist of amorphous phases, probably of ferrihydrite. Other phases in the nodules are corresponding to those forming the soil matrix. Additionally, disordered goethite was found in the pseudomorphs after amphiboles. These amphiboles may have been the source of iron for nodule formation in this soil. Cobalt and Mn showed the highest enrichment in the nodules when compared to their total soil concentrations. Other metals, such as Cd, Ba, Ni, V, Zn, Cu and Pb can be characterized much smaller accumulation similarly to Fe. Additionally, Al, Mg, Si, Ti, K and Cr (e.g. elements bound to silicates and oxides), as well as Ca and Sr (e.g. elements bound to carbonates) also showed similar behavior during the extractions.

At the neutral-slightly alkaline conditions of the studied soil, the effect of pH may overwrite that of hydromorphism on trace metal accumulation in the Fe-rich nodules. Due to the intense sorption on and co-precipitation with oxide phases at these pH conditions, as well as the re-crystallization of oxides during the redox cycles, most of the cationic metals prefer Fe oxides over Mn oxides in their accumulation.

Key words: ferrihydrite, goethite, concretion, aggregate, pseudomorph, oxalate extraction, dithionite extraction, hydromorphism

1. INTRODUCTION

Iron rich nodules are discrete bodies formed in the soil system under alternating reducing and oxidizing conditions. Their nature is of great interest from the viewpoints of both pedogenesis and environmental geochemistry. They are sensitive diagnostic indicators of soil hydromorphism (Zaidelman and Nikiforova, 2010) and are also the catalysts for many chemical reactions, including redox reaction in soils (Huang, 1991). Moreover, besides organic matter (Sipos, 2010) and clay minerals (Németh et al., 2010), iron and manganese oxide phases play the most important role in metal sorption processes (Andráš et al., 2009). They may present in various

forms such as nodules, concretions, spheroids, crusts, coatings etc. in soils. These forms always have inclusions of the soil matrix and contain soil materials and pores cemented together under the influence of iron-manganese oxides. Therefore these concretions are characterized by a higher concentration of iron and manganese oxides, as well as numerous trace metals than the surrounding soil matrix (Zhang and Karathanasis, 1997).

Iron compounds are oxidized at lower redox potential than manganese compounds while manganese compounds are reduced at a higher redox potential than those of iron (Bouma, 1983). Periodic reduction/oxidation during waterlogged conditions and aeration in the soil results in separation of Fe

and Mn phases in these soils (Gasparatos et al., 2005). Aside from the above properties, Mn oxides have a low point of zero charge (PZC), and are poorly crystalline, possessing a high negative charge in most soils. On the contrary, Fe oxides usually had high PZC (between pH 7 and 9), with a positive charge in acid and neutral soils (McKenzie, 1989). This coincides with the results of several studies (e.g. Tan et al., 2006; Neaman et al., 2008) where significant accumulation of cationic and anionic metals associated to Mn and Fe oxides was found, respectively.

According to Bingham et al. (1976), however, the progressive scavenging of bivalent metals occurs during the alternating dissolution and precipitation of Fe oxides resulted by the redox cycles. This seems to be related to specific sorption involving an exchange between reduced Fe(II) ions on the oxides surface with divalent metals in solutions, followed by occlusion during the precipitation of re-oxidized Fe when the soil is drained. Reduction of Fe(III) on oxides surfaces increases their specific surface area thereby increasing temporary their capability of sorption (Brinkman, 1985). The re-precipitation of re-oxidized Fe occludes the sorbed metals within the mineral, virtually forbidding the possibility of interaction with the aqueous phase (Bartlett and James, 1993). In spite of the fact that this process is more pronounced at neutral and alkaline pH conditions, Andr  s et al. (2009) found significant accumulation of cationic trace metals, such as Cu, Zn, Cd, Mg, Mn, Co to poorly crystalline Fe-oxides even at strongly acidic conditions of soils affected by mining activity.

As cationic trace metals may be associated both to Fe and Mn oxides via several competing immobilization processes at these pH conditions, detailed study of their distribution in Fe-rich nodules

from neutral-alkaline soils may help better understand the metal-oxide interaction. In this study, the distribution and accumulation of 17 cationic trace metals (Al, Ba, Ca, Cd, Co, Cr, Cu, K, Mg, Mn, Ni, Pb, Si, Sr, Ti, V and Zn) in Fe-rich nodules from a neutral-slightly alkaline floodplain soil was studied. Our goal was to find whether what trace metals prefer to associate to Fe or Mn oxides at the studied pH conditions. We also aimed at studying the effect of increasing pH downwards on the trace metal distribution between Fe and Mn oxides.

2. MATERIALS AND METHODS

The studied profile was sampled on a meadow with grass vegetation on the floodplain of the Ipoly River, 200 m away from the river near the village Ipolysz  g, North Hungary. The soil-sediment profile was sampled down to 250 cm, its most important physico-chemical properties are shown in Table 1. The Fe-rich nodules of macroscopic size appear between 20 and 180 cm. Down to 60 cm depth, they are present as reddish brown, loose aggregates of 1-1.5 mm size with increasing amounts downwards. The highest amount of nodules can be found in the layer between 60 and 90 cm, where brown-black concretions and geode-like nodules are present with the size up to 2-3 mm. In this layer, pseudomorphs after amphiboles also appear.

Below 90 cm, the amount of nodules significantly decreases, and they probably occur gravitationally only below 120 cm. Also reddish brown coatings on other soil minerals appear in the layer between 20 and 120 cm. The main zone of the in situ formation of nodules can be found between 20 and 120 cm with the highest hydromorphism between 60 and 90 cm (Sipos et al., 2009a).

Table 1. Some physico-chemical properties of the studied soil profile and samples.

Layer (cm)	TOC (%)	pH (H ₂ O)	Loam (g/kg)	Clay (g/kg)	Fe (%)	Fe _o (%)	Fe _d (%)	Type of Fe-rich nodules	Clay mineralogy
0-15	3.14	6.32	323	644	5.17			-	
15-40	1.55	6.68	327	628	5.25	1.70	1.56	Agg + Coa	
40-60	1.41	7.16	249	712	5.41			Agg + Coa	
60-90	0.98	7.46	196	699	5.39	1.17	1.00	Nod + Con + Pse + Agg + Coa	smectite,
90-120	0.47	7.95	215	710	5.26			Con + Nod (+ Agg + Pse)	illite, kaolin-
120-150	0.29	7.78	219	676	5.05	0.84	0.81	Fra (+ Con + Nod)	ite
150-180	0.17	7.91	162	609	4.39			Fra	
180-230	0.21	7.67	147	713	5.93	0.81	1.00	-	
230-250	0.22	7.70	320	554	5.09			-	

Fe_d = sodium-dithionite extractable iron, Fe_o = ammonium-oxalate extractable iron, n.d. = no data, Agg = aggregates, Coa = coatings, Nod = nodules, Con = concretions, Pse = pseudomorphs, Fra = fragments

Also lime-spots with the size of a few mm appear from 90 cm downwards. The soil carbonate phases are made up primarily of calcite. The soil pH slightly increases downwards: it is neutral (between pH 6.68 and 7.16) in the upper part and slightly alkaline (between pH 7.46 and 7.91) in the lower part of the profile where Fe-rich nodules appear. The total organic carbon content of the samples decreases downwards from the maximum value of 3.14%. The soil texture is clay with relatively steady and high clay content in the whole profile (661 ± 56 g/kg clay). The major clay minerals of the profile are smectite, illite and kaolinite in the order of dominance. The total Fe content of the samples is $5.2 \pm 0.4\%$ with a slight enrichment in the layers between 40 and 60 (5.4%), as well as 180 and 230 cm (5.9%).

The samples were air dried, gently crushed and passed through a 2 mm sieve before analyses. Iron-rich nodules were separated manually from the sand fraction after wet sieving of the samples. Soil pH was analyzed in 1:2.5 soil:distilled water suspension. The total organic carbon of the samples was determined by a Tekmar-Dohrmann Apollo 9000N TOC instrument. Particle size distributions of the samples were determined by Fritsch Analysette Microtech A22 laser diffraction analyzer. The soil samples and clay fractions were characterized for mineralogical composition using a Philips PW 1710 X-ray diffractometer (XRD). Clay minerals were identified from the clay fractions of bulk samples by XRD diagrams obtained from parallel-oriented specimens. Separation of the clay fractions ($< 2\mu\text{m}$) were performed by sedimentation in aqueous suspension. The total Fe and Mn content of the samples were analyzed by a Philips PW 1410 X-ray fluorescence spectrometer (XRF) from pressed powder samples. The average relative standard deviations of the XRF analyses for Fe and Mn are 0.6% and 2%, respectively.

Total soil samples collected from the layers 15-40 cm, 60-90 cm and 120-150 cm were subjected to sodium-dithionite and ammonium-oxalate dissolution according to the methods of USDA (Burt et al., 2004). Additionally, aqua regia digestion was performed on these total soil samples as well as on nodules separated from the sand fraction of the layer between 120 and 150 cm. Concentrations of Fe and 17 trace elements (Al, Ba, Ca, Cd, Co, Cr, Cu, K, Mg, Mn, Ni, Pb, Si, Sr, Ti, V and Zn) in the solutions were analyzed by ICP-OES method (Spectro Genesis simultaneous spectrometer). The average relative standard deviations of the analyses were $<1\%$ for major and $<5\%$ for trace elements for the aqua regia dissolutions, and $<10\%$ for the oxalate and dithionite extractions. Multivariate cluster analysis was applied to the chemical extraction data of the studied samples.

3. RESULTS

3.1. Mineralogical analyses

Significant changes in soil mineralogy with depth were not found in the profile. Dominant mineral species in the samples are smectite (35-55%) and quartz (30-45%). Additionally, kaolinite (5-13%), plagioclase (3-7%) and illite (2-5%) also appear in the samples subordinately. Smectite shows its highest amount in the layer between 60 and 230 cm, while kaolinite and illite can be characterized by slight decrease in their amount with depth. Calcite also appears in the layer between 90 and 180 cm with increasing amount downwards (up to 10%).

X-ray peaks characteristic of crystalline Fe-oxide phases could not be detected both in bulk soil samples, soil sand fractions and separated nodule samples (Figure 1). However, the high background of X-ray patterns and their humping with a maximum at $25^\circ 2\theta$ suggest the presence of iron and amorphous material, respectively. Broad peaks at around 35° and $62^\circ 2\theta$ may be characteristic both of clay minerals and ferrihydrite. In contrast to the nodules, crystalline goethite was found in the pseudomorphs. According to the X-ray analyses, this phase seems to be poorly crystalline. Other mineral phases in nodules are the same as those can be found in the bulk soil. However, smectites are poorly crystallized and contain illite interstratifications in the nodules. The amounts of clay minerals are higher in the loose aggregates than in the concretions and geode-like nodules. In the latter ones, clay minerals are much more poorly crystalline than in the previous ones, which are supported by the lack of smectite's base reflection in the nodule samples from the layer between 60 and 120 cm.

Sodium-dithionite and ammonium-oxalate extractions can be also used for the characterization of iron-oxide phases in soils, as the previous one is considered to extract both crystalline and non-crystalline iron-oxides (Mehra and Jackson, 1960) while the latter one dissolve only the amorphous and poorly crystalline iron-oxide phases, primarily ferrihydrite (Schwertmann, 1959).

In this case, the highest extractable iron amount was found in the layer between 20 and 40 cm (1.56% of dithionite and 1.70% of oxalate extractable Fe) with decreasing amounts downwards (see Table 3 and 4). The extractable amounts do not correlate with the total iron content of the samples, their amounts measure up to 30% of total iron in the upper and 15% in the lower layers. Coincidentally to X-ray diffractometry analyses, the ratio of oxalate and dithionite ex-

tractable iron is around 1 in each studied sample (1.03 ± 0.15) suggesting that iron-oxides are primarily poorly crystalline or amorphous in the studied samples.

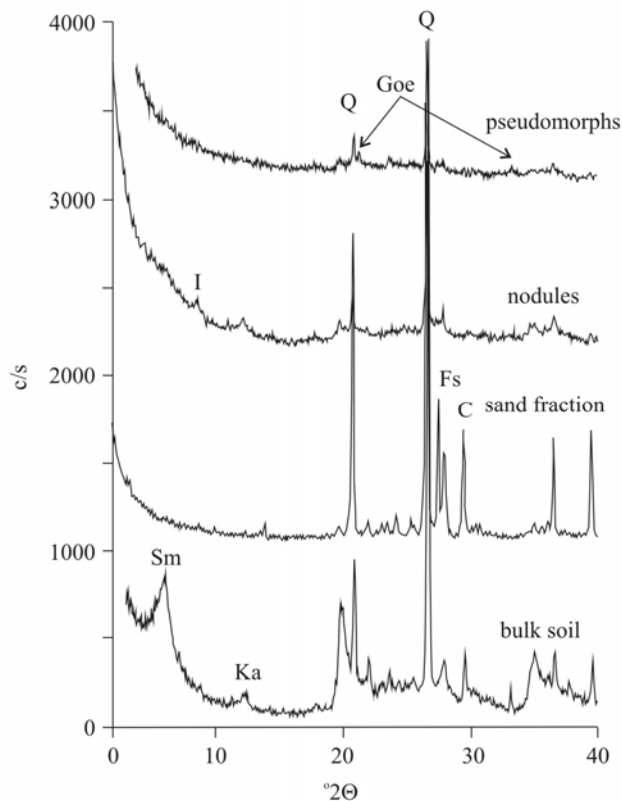


Figure 1. XRD patterns of the bulk soil, separated nodules and pseudomorphs from the sample collected in the layer between 60 and 90 cm. Q=quartz, Goe=goethite, Fs=feldspar, C=Calcite, Sm=smectite, I=illite, Ka=kaolinite.

3.2. Chemical extractions

The results of the chemical extraction and dissolution studies are shown in tables 2-5. Enrichment factors (EF) were calculated for the characterization of metal accumulation in iron oxides as follows. In the case of dithionite and oxalate extractions, extracted and total metal concentrations were normalized to Ti, which is known as an immobile element in soil conditions (Egri and Fitze, 2000). After normalization, EF values were calculated by dividing the extractable metal concentration by the total metal concentration. For aqua regia dissolution of nodules, no normalization was performed. In this case, metal concentration in nodules was divided by total metal concentrations in bulk soil samples.

In the case of dithionite extraction, each studied metal showed higher accumulation than Ti (see Tables 2 and 3). Generally, the enrichment factors increase downwards for each studied elements. Ex-

tremely strong enrichment for Co was found with EF values between 127 and 483. Still strong enrichment in decreasing order was found for Mn, Ca, Sr, Cd, Ba and Ni with EF values between 31 and 245. Other metals, such as V, Cu, Zn, Mg, Fe and K can be characterized much smaller accumulation (EF values between 14 and 97). However, only slight enrichment was observed for Al and Si, their EF values were between 1.9 and 11.

Slightly different metal behavior was observed for the ammonium-oxalate extractions (see Tables 2 and 4). There are some elements, such as K, Pb, Si, Sr and Ca which does not show any enrichment in this extraction. Their enrichment factors are below 1. Similarly to the results of dithionite extraction, Co shows the highest enrichment again along with Mn and Ni (EF values are above 10). Immediate enrichment is characteristic of Cd, V, Mg, Fe, Ba and Cu with EF values between 5 and 10. Zinc, Cr and Al can be characterized by slight enrichment in this extraction, their EF values are between 1 and 5.

The results of the dithionite and oxalate extractions can be effectively compared when the respective enrichment factor values are plotted against the soil pH (Figure 2). Cobalt and Mn show the highest enrichment in both extractions with increasing EF values with soil pH. The increase in EF values is much more characteristics for the dithionite extractions. Barium, Cd, Cu, Fe, Ni, V and Zn can be characterized lower but still significant enrichment in both extractions. Their EF values also increase with soil pH for the dithionite extraction. However, those for the oxalate extraction show quite diverse behavior. These EF values for metals may show slight increase (Ni, Ba and V), slight decrease (Cd, Fe, Zn) or no relation to pH (Cu). Calcium and Sr show high enrichment only in the dithionite extraction.

At least, there are metals, such as Al, K, Mg and Si which can be characterized by only a slight enrichment both in dithionite and oxalate extracted phases with increasing EF values with soil pH. Much more exact difference for metal behavior can be observed when the aqua regia dissolution of nodules and bulk soil samples are compared (see Tables 2 and 5).

However, this was performed in nodules from only one layer (between 120 and 150 cm). Metals, such as Mg, Sr, Ca, Cr, Al, Ti, K and Si does not enrich in the nodules when compared to the bulk soil. On the contrary, Co and Mn can be characterized by strong accumulation with 20-30 times higher concentrations in the nodules when compared to their total soil concentrations.

Table 2. Concentrations of the studied metals in the bulk soil samples (mg/kg)

Layer	Al	Ba	Ca	Cd	Co	Cr	Cu	Fe	K
15-40 cm	93344	518	11444	4	8	102	53	51149	4239
60-90 cm	96523	544	16323	3	5	77	107	51530	3799
120-150 cm	92159	554	26362	4	7	103	53	51442	3475
	Mg	Mn	Ni	Pb	Si	Sr	Ti	V	Zn
15-40 cm	11098	1350	25	55	257569	115	4021	108	90
60-90 cm	10565	1144	25	53	266893	107	3641	107	92
120-150 cm	11401	1692	28	60	259268	118	3451	105	90

Table 3. Sodium-dithionite extractable metal content of the bulk soil samples (mg/kg)

Layer	Al	Ba	Ca	Cd	Co	Cr	Cu	Fe	K
15-40 cm	3172	164	5431	2	10	<3	21	15597	613
60-90 cm	3493	179	6301	1	6	<3	18	9977	474
120-150 cm	2720	195	19011	<0.5	9	<3	17	8089	349
	Mg	Mn	Ni	Pb	Si	Sr	Ti	V	Zn
15-40 cm	1705	995	13	<13	4834	53	41	30	26
60-90 cm	1850	803	14	<13	4764	50	14	29	24
120-150 cm	2166	1172	<13	<13	4697	55	9	25	17

Table 4. Ammonium-oxalate extractable metal content of the bulk soil samples (mg/kg)

Layer	Al	Ba	Ca	Cd	Co	Cr	Cu	Fe	K
15-40 cm	6007	78	14	1.7	10	7.7	10	17053	100
60-90 cm	7089	85	16	1.1	7.2	7.7	10	11699	87
120-150 cm	5639	106	10	0.76	9.2	5.9	8.6	8446	74
	Mg	Mn	Ni	Pb	Si	Sr	Ti	V	Zn
15-40 cm	2424	1099	14	2.3	4730	1.3	211	28	13
60-90 cm	2587	911	14	1.8	5263	1.1	142	29	11
120-150 cm	2762	1216	16	0.0	4592	0.21	115	28	5.9

Table 5. Concentrations of the studied metals in the nodules from the layer 120-150 cm (mg/kg)

Layer	Al	Ba	Ca	Cd	Co	Cr	Cu	Fe	K
Nodules 1	21097	3156	7353	124	265	29	155	164905	264
Nodules 2	20583	3155	7460	129	269	27	189	161013	131
Nodules 3	20971	3144	7520	26	268	21	178	161399	423
	Mg	Mn	Ni	Pb	Si	Sr	Ti	V	Zn
Nodules 1	4422	32682	154	117	698	35	411	488	317
Nodules 2	4368	32561	157	192	900	35	435	484	394
Nodules 3	4420	32613	152	158	773	33	447	500	352

Other metals, such as Cd, Ba, Ni, V, Zn, Cu and Pb can be characterized by 3-6 fold enrichment similarly to Fe. Trace metal concentrations in nodules can be as high as 3156 mg/kg for Ba, 129 mg/kg for Cd, 269 mg/kg for Co, 189 mg/kg for Cu, 154 mg/kg for Ni, 192 mg/kg for Pb, 488 mg/kg for V and 394 mg/kg for Zn. Their Fe content is above 16%, while that of Mn exceeds 3% with Fe/Mn ratio around 5.

3.3. Statistical analyses

Hierarchical cluster analysis was performed on the chemical extraction and dissolution data of metals to help the comparison of these significantly different chemical methods. Its result shows that two major element groups can be distinguished (Figure 3).

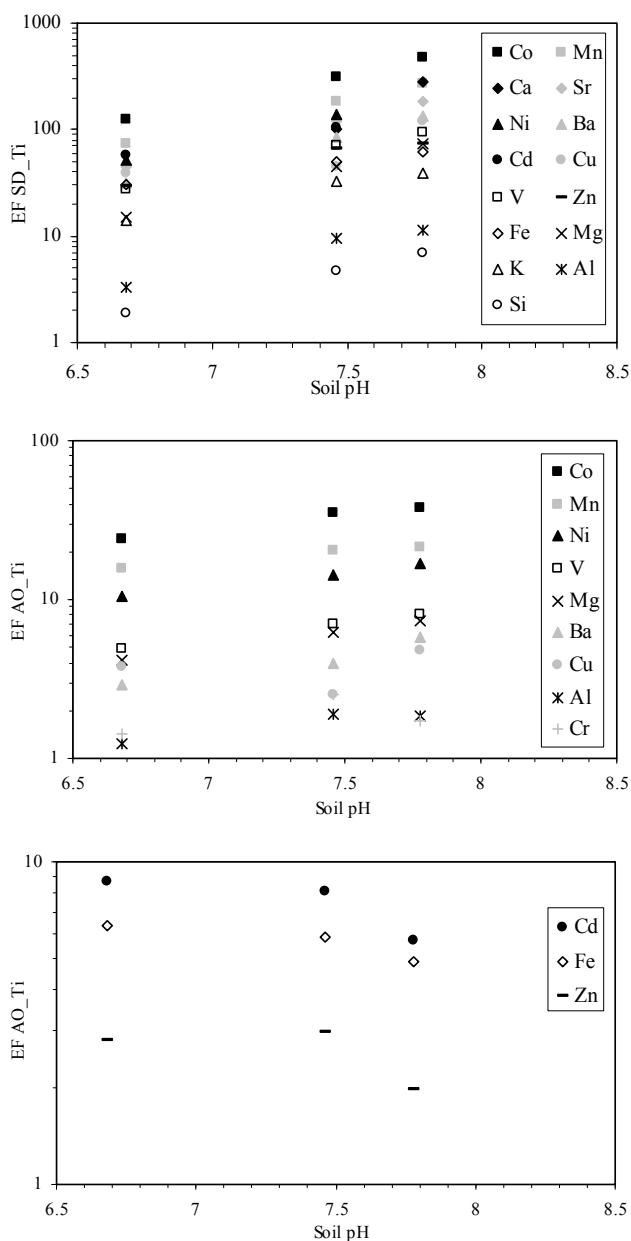


Figure 2. Ti-normalized enrichment factor values (EF) in the dithionite (SD) and oxalate (AO) extractions for the studied metals as related to pH.

Elements showing enrichment in nodules, such as Ba, Cd, Co, Cu, Fe, Mn, Ni, Pb, V and Zn make up one of the groups. Within this group, Co and Mn forms a subgroup with the lowest dissimilarity. Barium, Cd, Fe, Ni, Pb, V and Zn can be also grouped together while Cu significantly differentiates within its major group. The other major group consists of elements showing no enrichment in the nodules, such as Al, Ca, Cr, K, Mg, Si, Sr and Ti. Aluminum, K, Mg, Si and Ti show very similar behavior within the group, while Cr, Sr and Ca show slight and increasing dissimilarity from other metals in this major group.

4. DISCUSSION

Mineralogical and extraction studies show that the iron-oxide phases in the studied nodules consist primarily of X-ray amorphous, short range ordered ferrihydrite. The iron oxides in the Fe-rich nodules have been reported to appear as X-ray amorphous (Childs, 1975; Sidhu et al., 1977) or very poorly crystalline (White and Dixon, 1996). Nevertheless, in several studies goethite (Rhoton et al., 1993; Zhang and Karathanasis, 1997) was identified in Fe-Mn concretions of temperate regions' soils. Ferrihydrite, a phase of low crystallographic order and high surface area, is in most cases the first scale precipitate of the Fe oxide sequence (Schwertmann and Taylor, 1989). According to their micro-morphological, mineralogical and chemical characteristics, the Fe-rich nodules are young precipitations formed in situ in the studied soil (Sipos et al., 2009a). The main source of iron and other trace metals is the weathering of amphiboles. They are present in form of pseudomorphs in the studied soil and can be characterized by more crystallized phases, such as goethite, as they transformation to Fe-oxides started before the nodule formation.

However, its crystallization is rather inhibited at the neutral-alkaline pH conditions of the studied soil (Schwertmann and Murad, 1983). Amphiboles are common source of iron and trace metals in soils due to their diverse composition and low resistance to weathering (Huang, 1989). The primarily in situ precipitation of iron after release from amphibole is shown by the joint presence of the largest concretions and pseudomorphs in the same layer (between 60 and 90 cm). However, iron also precipitated both in lower and higher depth due to the fluctuation of groundwater table, capillary or gravitational pore water migration.

Chemical extractions are mostly operationally defined so they not only dissolve the target phases but also other metal pools. For example both the dithionite and oxalate extraction also partly dissolve organically complexed metals and amorphous aluminosilicates (Burt, 2004). Additionally, Bartley (1989) found that dithionite attack Fe-rich layer silicate at similar rates as with well crystallized Fe oxides. That is why metals generally found in aluminosilicates and oxides (Al, Cr, K, Mg, Si, Ti) were also extracted with both extraction methods. These elements may have released through the partial dissolution of poorly crystallized aluminosilicates. Additionally, Ca and Sr can be also characterized by high accumulation in the dithionite extractable fraction but they were not mobilized after oxalate extraction.

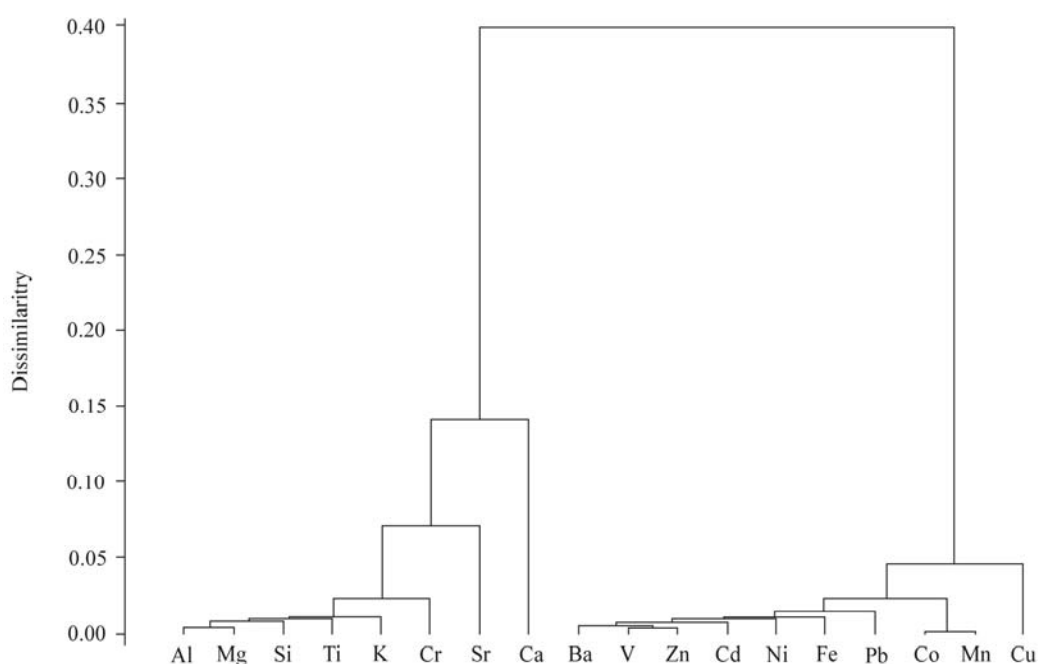


Figure 3. Results of the cluster analyses based on dithionite and oxalate extractions, as well as aqua regia dissolution.

This is due to the formation of Ca and Sr oxalate after carbonate dissolution which was also mentioned by Bartley (1989). In spite of the fact that these metals showed also accumulation in the oxalate and dithionite extractable pools, they could be distinguished effectively from those associated with Fe oxides in the studied soil.

The very strong accumulation of Co in Mn-oxide phases is suggested by all three chemical extractions used. This phenomenon was also found by other studied using both chemical extractions (Cornu et al., 2005) and direct analyses (Neaman et al., 2008). The high affinity of Co for Mn oxides has been explained by the oxidation of soluble divalent Co to insoluble trivalent Co by $\text{Mn}^{3+}/\text{Mn}^{4+}$ transition (Murray and Dillard, 1979). After its oxidation, Co migrates to the vacancy sites of phyllosilicate layer or substitute Mn in the crystal structure of Mn oxide (Manceau et al., 1997). Other studied metals, such as Ba, Cu, Cd, Ni, Pb, V and Zn show much lower enrichment in the nodules and they seem to be associated to Fe-oxides according to their behavior in extraction used in our case. Many studies showed that these cationic metals accumulate in Mn oxide rather than Fe oxide phases in soils (e.g. Tan et al., 2006; Neaman et al., 2008). These results coincide with the fact that Mn oxides possess a negative charge in most soils adsorbing primarily cationic metals while its reverse is true for Fe oxides (McKenzie, 1989). Among these metals, only V may present in anionic form in soils. However, periodic precipitation of the oxidized Fe results in occlusion

of cationic metals within Fe oxides, as well (Bartlett and James, 1993). This phenomenon is more pronouncing in neutral and mainly in alkaline soils as the amount of negative surface charge of Fe oxides increases with pH. That is why enrichment of cationic metals in Fe oxides was found in the studied soil. Similarly, Cornu et al. (2005) also observed that Cu, Pb and Zn could be associated with iron oxides in their slightly alkaline soils. Additionally, element that form carbonate and hydroxide complexes (e.g. Pb) were reported as preferentially bound to the slightly positively charged Fe oxide surface. The neutral-slightly alkaline pH conditions favor the association of large complexes with low charge densities to Fe oxide surfaces (Palumbo et al., 2001). According to Manceau et al. (2000), Ni can be partly incorporated in the structure of natural Fe oxides via Ni-Fe substitution. The incorporation of Cd, Cu and Zn in the structure of natural Fe oxides is, however, more surprising because these elements have a lower geochemical affinity for Fe oxides and higher affinity for Mn oxides and phyllosilicates. As their ionic radii is much larger than that of Fe, their substitutional incorporation in the Fe oxide structure result in a displacement of higher shells relative to the Ni-Fe substitution. According to the EXAFS study by Manceau et al. (2000) these variations in interatomic distances can be compensated simultaneously by a displacement of nearest atomic shells and a modification of interpolyhedral angles between corner-linked octahedra in adjacent chains. On the other hand, the close association of Fe oxides with clay

minerals by particle interaction may result in increased metal sorption in these phases (Zachara et al., 1992; Sipos et al., 2009b). The high surface area of the poorly crystalline smectites may prefer their association with Fe oxides in the studied nodules. However, the exact process of metal accumulation in the associated soil phases needs further analyses.

The increasing enrichment of most of the studied metals in dithionite and partly in oxalate extraction with depth may be related to the increasing hydromorphism. Its maximum, however, does not overlap with the largest metal enrichments. Our results show that the effect of pH may overwrite that of hydromorphism on trace metal accumulation in nodules. Palumbo et al. (2001) found that trace metal partitioning is much more pronounced in nodules which are characterized by a well-developed Fe-Mn banded structure when compared to those with lack of this structure. This study does not confirm this observation as there is no significant difference between the fractionation of the studied metals in the upper and lower layers where loose aggregates as well as well-developed concretions and geode-like nodules prevail, respectively. The neutral and slightly alkaline conditions in the soil (the pH is 6.68 in the upper and increases up to 7.78 in the lower layers containing nodules) results in preferable conditions for cationic metal sorption on and co-precipitation with Fe oxides, as well. Benjamin and Leckie (1981) showed that cationic metal sorption on Fe oxides increases with increasing pH. They found that metals with high affinity such as Pb and Cu show complete retention on Fe oxides above pH 6 even at high metal concentrations while those with low affinity such as Zn and Cd only at alkaline conditions. The total Fe content of the samples does not show significant changes with depth. However, dithionite and oxalate extractable iron decrease nearly by its half downwards. Contrarily, enrichment of trace metals significantly increases with depth: from 3 to 6 fold increase in enrichment factor values can be found in the case of the dithionite extraction while that for oxalate extraction may be as high as 2. This suggests the higher enrichment of trace metals in the well-developed nodules when compared to aggregates in the upper layers. This higher enrichment can be due to the lower amounts of aluminosilicates inherited from the surrounding soil in the well-developed nodules than in the aggregates. Additionally, the more alkaline conditions in the deeper layers may also favor the higher enrichment of metals. Evidence exists for incorporation of cationic metals into poorly crystalline Fe oxides by co-precipitation which is more significant at alkaline conditions similarly to metals sorption (Ford et al., 1997). These authors also found that cationic metals

show gradual incorporation into the re-crystallizing oxide structure with ageing. This observation can be probably referred to the nodule development, as well. Both absolute and relative decrease in oxalate extractable iron and some other metals (such as Cd, Zn) with depth also correspond to the more developed nodule structures in the lower layers. This supports the observation that certain cationic metals may prefer Fe oxides over Mn oxides at slightly alkaline conditions. Moreover, more intense weathering may inhibit the structure development of nodules and crystallization of oxide phases in the upper layers more effectively. Weathering may also increase the re-mobilization of trace metals from the Fe-rich nodules. This potential remobilization, however, did not result in significant differences in partition of trace metals between Fe and Mn oxides in our case.

5. CONCLUSIONS

Iron-rich nodules accumulate trace metals strongly. According to their geochemical behavior shown by the chemical extractions used, Co accumulates in Mn oxides, while Ba, Cd, Ni, Pb and Zn enrich preferably in Fe oxide phases. Chemical extractions and dissolution used in this study were all suitable to study the association of trace metals with Fe and Mn oxides separately. With their common use, however, trace metal mobilization occurring not from the target phases could be more effectively recognized

At the neutral-slightly alkaline conditions of the studied soil, the effect of pH may overwrite that of hydromorphism on trace metal accumulation in the Fe-rich nodules. Due to the intense sorption on and co-precipitation with oxide phases at these pH conditions, as well as the oxide re-crystallization during the redox cycles, most of the cationic metals studied prefer Fe oxides over Mn oxides for their accumulation. In spite of the mineralogical and micro-morphological changes observed, the increase of pH with depth characteristic of the studied profile (from 6.5 to 8) does not seem to be large enough to find changes in trace metal partitioning between Fe and Mn oxides.

Acknowledgements

The financial support of Hungarian Scientific Research Fund is thanked (OTKA PD 75740).

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Received at: 08. 06. 2010

Revised at: 18. 08. 2010

Accepted for publication at: 06. 09. 2010

Published online at: 08. 09. 2010