MINERALOGICAL STUDY OF FERRUGINOUS AND MANGANIFEROUS NODULES SEPARATED FROM CHARACTERISTIC PROFILES OF HYDROMORPHIC SOILS IN HUNGARY

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Abstract: Only a few studies have been carried out on the mineralogy of ferruginous and manganiferous nodules in Hungarian hydromorphic soils. Therefore it was decided to enrich the data on these nodules and to make an attempt to interpret them with respect to hydromorphic influences. The brown and black nodules separated from 9 characteristic soil profiles were analysed by X-ray diffraction, thermal analysis, selective dissolution methods and SEM combined with microanalysis. This study confirmed that nodules were formed during the impregnation of the groundmass by iron and manganese compounds. Goethite was common in hydromorphic soils, while lepidocrocite was determined in nodules from horizons with enhanced hydromorphic impacts. Manganese minerals were extremely rare. The nodules contained a considerable amount of amorphous and poorly crystalline compounds; in this context the black nodules contained more of these compounds than the brown ones. The data for selected dissolutions of iron and manganese compounds showed those horizons having different hydromorphic influences. Black nodules with brown coatings were observed in various soil types and in localities which were a considerable distance from each other, and this indicated after accumulation a depletion or inhibited immobilization stage of manganese compounds in the formation processes of the nodules. The mineralogical study of the ferruginous and manganiferous nodules from Hungarian soils contributed to a deeper knowledge of iron and manganese accumulations in the hydromorphic soils of the European prairie ecodivson, as well.

Keywords: amorphous compounds, ferrihydrite, goethite, hydromorphism, lepidocrocite, manganese minerals, nodules, selective dissolutions.

1. INTRODUCTION

More than a century ago the distinguished scientist of Hungarian soil science, Treitz (1905) published a paper on iron nodules.

However, with respect to Hungary only a small amount of data on the mineralogical nature of iron-manganese nodules has been gathered: Pártay (1979), Zentay & Rischák (1983), Pártay et al. (1986), Kapoor et al. (1986, 1988), and Sipos et al., (2009). Sipos et al. (2011) determined an association of 17 trace elements in Fe-rich nodules in a food-plain soil of Ipoly River (North Hungary). Differences of copper (Németh et al. 2010) and of copper and lead contents (Sipos 2010) in brown forest soils (North Hungary) were due to various mineral compositions and organic matter content.

Furthermore, over the years greater knowledge has been gained about the iron and manganese minerals of soils. If only monographs which have added to this knowledge are mentioned the following are significant (since 1990): Dixon et al. (1990), Cornell & Schwertmann (1996), Stucki et al. (1998), Bigham et al. (2002), and Dixon & White (2002).

The aims of the present investigations were to study the mineralogical nature of the iron-manganese nodules of hydromorphic soils and reveal the relationship between the hydromorphic influence and mineralogical characteristics of the nodules.

2. MATERIALS

9 characteristic profiles of hydromorphic soils collected for the micromorphological study of Hungarian soils were selected for investigation. The locations of the sites can be seen in figue 1.

The soil types – according to the Hungarian soil classification system (Szabolcs 1966), their code numbers, sites, and correlation (Michéli et al. 2006, Fuchs et al. 2007, Sisák & Máté 2008) with the World Reference Base for Soil Resources System (FAO/ISRIC/ISSS 1998) are shown in Table 1. Descriptions and sampling of the profiles were performed using standard methods (Szabolcs 1966).

Data on meadow solonetz soil were published in the excursion guide of the symposium on salt-affected soils (Szabolcs 1965), and on meadow soils by Jassó (1964). Stagnant brown forest, peaty meadow soils, soil of swampy forest and of alluvial forest were the profiles selected, described and analysed in the framework of the land evaluations.

Figure 1. Location of the investigated sites in Hungary
Legend: 12 – Lenti, 24 – Hortobágy, 29 – Szarvas, 30 – Besenyszög, 32 – Szeghalom, 37 – Jánkmajtis, 37 –Szíjártóháza

3. METHODS

Size fractions above 1 mm were separated by sieving (this was carried out in the Geological Insti-

tute of Hungary and Hungarian Natural History Museum, Department of Mineralogy and Petrology). Brown and black nodules were separated by hand picking under a stereomicroscope Nikon SMZU.

Selective dissolution methods were carried out according to Mehra & Jackson (1960), Schwertmann (1964) and Bascomb (1968). (The practical work was done in the Geological Institute of Hungary and Research Institute for Soil Science and Agrochemistry of the Hungarian Academy of Sciences as well as in the Institute for Soil and Plant Protection of Fejér County). Thermal analyses were carried out in a Derivatograph-PC controlled and evaluated by computer, with simultaneous TG, DTG and DTA recordings. Corundum crucibles, Al_2O_3 inert material and 10 ^{o}C/min. heating velocity (up to 1000 ^{o}C) were also used.

X-ray diffractograms were prepared by a Phillips PW 1730 Diffractometer controlled and evaluated by computer. The parameters of the investigations were: Cu-anticathode, 40 kV high voltages, 30 mA intensity of currents, graphite monocromator, and 2°/min. goniometer speed. The mineralogical composition was calculated by taking into account the relative intensity ratios of the characteristic reflexions of minerals and applying the literary or experimental corundum factors on minerals. The amount of the amorphous phase was estimated by the method of Rischák (1989). In order to determine manganese minerals with minor quantities differential X-ray diffraction was performed: diffractograms prepared after selective dissolution were subtracted from the diffractograms of untreated sample (Schulze 1981, Schwertmann et al. 1982, Wells et al. 1992). (These works were performed in the Geological Institute of Hungary: Földvári et al. 1998a, b, c, 2001; Kovács-Pálffy & Baráth 1998, 1999a, b).

Nodules were investigated by AMRAY 1830 I/T6 SEM equipped with an EDAX PV9800 energy dispersive spectrometer using 20KeV accelerating potential and 1-2 nA beam current.

Table 1. Codes of soil types, soil types according to the Hungarian soil classification and correlations with WRB system (FAO/ISRIC/ISSS, 1998), locations of sites

Codes	Soil types according to the Hungarian soil classification	Correlations with the WRB	Location of sites
12	Stagnant brown forest soil	Stagnic Luvisol	Lenti 115, 209
24	Meadow solonetz soil	Solonetz	Hortobágy
29	Solonetzic meadow soils	Sodic Vertisol	Szarvas
30	Meadow soil	Haplic Vertisol	Besenyszög 22, 29
32	Peaty meadow soil	Humic Gleysol	Szeghalom
37	Soils of swampy forest	Gleysol	Jánkmajtis
37	Soils of alluvial forest	Gleysol	Szíjártóháza

The evaluations of ED spectra were made by ZAF-correction (avoid the matrix effects) using standardless program of the instrument. The results were normalized to 100%. (The measurements were carried out at the Eötvös University, Department of Petrology and Geochemistry).

4. RESULTS AND DISCUSSION

First the nodules that had been separated from the profiles were characterised, and then the soils were divided according to various degree of water logging. A few typical nodules can be seen in Fig. 2.
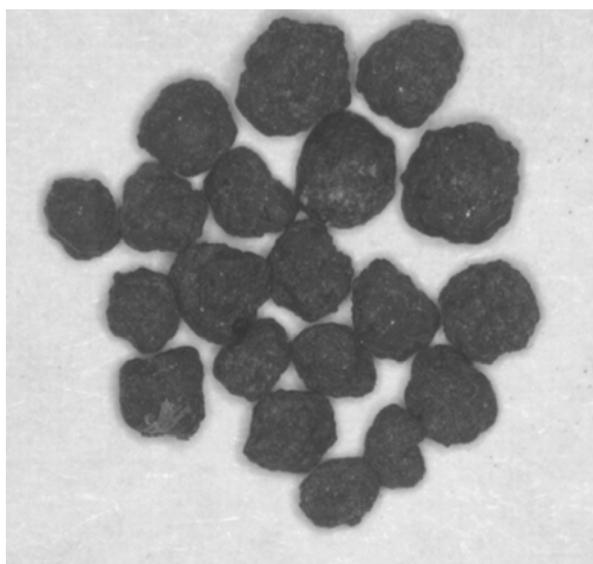

Figure 2. Nodules separated from B_2-horizon of solonetzic meadow soil. Width of picture: 17 mm

4.1. Crystalline phases

Earlier micromorphological studies of the investigated profiles (Szendrei 2001) proved that the ferruginous and manganiferous nodules were formed impregnating the soil groundmass (e.g. coarse and fine materials, micropores) by iron and manganese compounds. The observations on polished thin sections (prepared from stagnant brown forest, meadow, solonetz-like meadow soils and soils of swampy and alluvial forests for scanning electron microscopy) also

confirmed this conclusion. The forms of the iron and manganese compounds observed by SEM also suggested an impregnation process (Table 2). As an example, the infilling of manganese compounds and manganese mapping are shown on figure 3.
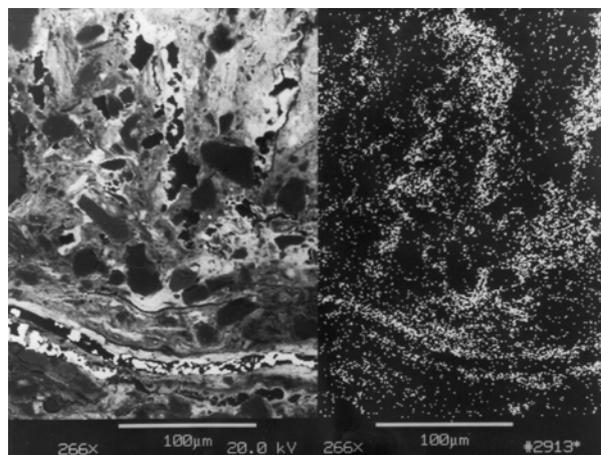

Figure 3. Infillings and mapping of manganese compounds in black nodules from the BC-horizons of meadow solonetz soil. Left: BSE-image, right: Mn- X-ray image.

Large parts of ferruginous and manganiferous nodules consisted of minerals other than iron-manganese, such as skeleton minerals (quartz, feldspars, micas, etc.) and minerals of fine-materials (clay and carbonate minerals, etc.). (Table 3.)

The amounts of iron and manganese minerals determined by XRD are given in Table 4. The most common iron mineral was goethite (57 samples out of 62), lepidocrocite was less frequent (15 samples), hematite and siderite were rare (1-1 sample), and manganese minerals were very scarce. In last case the average amounts show very low percentages. Differences were found between brown and black nodules: the average respective amounts of goethite were higher in brown nodules compared to black ones.

Muscovite was not present in the black nodules but more than 30 wt% illite was determined in the black nodules separated from B_3- and C-horizons of stagnant brown forest soils (in contrast with brown nodules having only muscovite).

Table 2. Forms of iron and manganese impregnations studied by SEM

Soil types, site	Horizon	Colour of nodule	Tube	Crust	Mottle	Quasi-coating	Hypo-coating	Infilling
Stagnant brown forest soil, Lenti	A_{pl}, B_1	brown	+		+	+		
	A_{pl}, B_1	black	+		+	+	+	
Meadow solonetz, Hortobágy	B_3	brown		+	+		+	+
	B_3	black		+	+	+		
Soil of swampy forest, Jánkmajtis	C_1	brown		+	+			
	C_1	black		+		+		

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Table 3. Non-iron and non-manganese minerals of nodules determined by X-ray diffraction (wt%)

Colour of nodule		Quartz	Plagio-clase	K-feld-spar	Musco-vite	Chlorite	Calcite	Dolomite	Amphi-bole
Black	average/ ranges	37.3/19-55	12.4/6-19	2.1/0-5	7.6/0-39	10.0/4-22	1.4/0-13	<1	<1
Brown		42.1/29-60	11.8/6-24	2.1/0-6	12.2/0-29	8.1/tr-12	1.6/ 0-28	<1	<1
	Gypsum	Parago-nite	Zeolite	Römerite	Montmo-rillonite	Illite/ montmo-rillonite	Illite	Kaolinite	Palygors-kite
Black	<1	<1	<1	<1	4.7/ 0-15	6.9/ 0-21	11.7/ 0-32	<1	<1
Brown	<1	<1	<1	<1	5.1/ 0-12	3.3/ 0-15	3.9/ 0-20	<1	

20 analyses of both brown and black nodules were made from the same horizons. The sum of the wt% iron- and manganese minerals (in nodules from the same horizon) was more in black nodules (42% of nodules) versus in brown nodules (32%), and in 26% of nodules were equal amount. Goethite was more frequent in brown nodules (45%) compared to black nodules (15%). The frequency of lepidocrocite was 1:5 in brown and black nodules, respectively.

Regarding earlier data with respect to Hungarian soils, goethite was identified by Pártay (1979), and Pártay et al. (1986) in the iron concentrations of B_2- and B_3-horizons of salt-affected soil (Hortobágy), and by Kapoor et al. (1986, 1988) in meadow soils (Karcag). Zentay & Rischák (1983) determined limonite aggregates and concretions in sandy soils (Danube and Tisza Interfluve).

Lepidocrocite was found in stagnant brown forest soils, and also in horizons of other studied soils close to the groundwater table. Lepidocrocite is one of the typical minerals of reductomorf soils; this has been noted by many authors, e.g. Fitzpatrick (1988), Schwertmann (1988), Rogobete & Grozav (2007). Lepidocrocite generally occurred in non-calcareous horizons. However, it was also found in the B- and C-horizons of solonetz-like meadow soils, which were calcareous. Earlier studies also stated that lepidocrocite was characteristic for hydromorphic, non-calcareous soils (Blume 1988, Schwertmann 1988). There is only sparse data on its occurrence in calcareous soils (Ross & Wang, 1982).

Besides goethite and lepidocrocite, hematite was determined in one horizon (B_2-horizon, stagnant brown forest soils, Lenti 115). This association was also rare at other sites (Schwertmann 1988, Stolt et al. 1994). Siderite also occurred in one horizon (B_2-horizon, solonetz-like meadow soil).

Sets of lamellae were observed by SEM (Fig. 4) in the black nodules from the C-horizon of the solonetz-like meadow soils. These were microana-lysed in two separate spots: the manganese contents were 81.1 wt% and 82.6 wt%, respectively (other elements detected: Al, Ba, Ca, Mg, Si). The quantity of iron was below the detection limit. Traces of manganite and 1 wt% pyrolusite were determined by XRD.
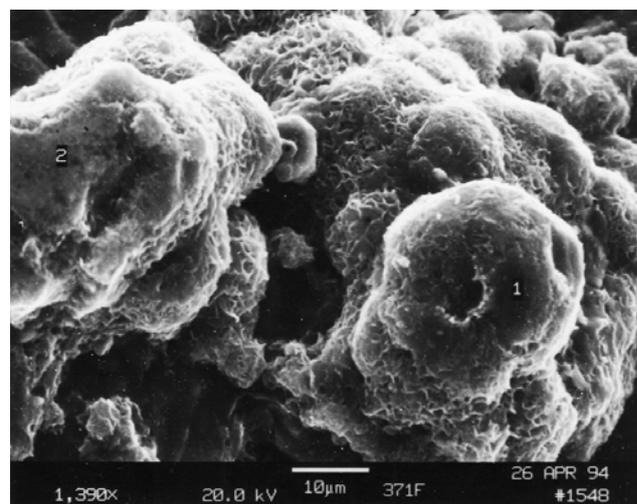

Figure 4. Sets of lamellae of manganese minerals in black nodules. C-horizon of solonetz-like meadow soil

In order to detect minor amounts of crystalline phases, XRD analyses were performed on residues – i.e. after selective dissolution, nodules from the C-horizon of peaty meadow, meadow solonetz and solonetzic meadow soil. To determine minor quantities of phyllo- and tectomanganates, which can be found in soils, differential X-ray diffraction (DXRD) analyses were carried out on 12 samples.

The XRD-s of samples treated with Schwertmann's method was substracted from the XRD-s of the untreated samples (Schulze 1981, Schwertmann et al. 1982, Wells et al. 1992).

Apart from the above mentioned minerals (Table 4), new crystalline manganese phases were not determined.

Table 4. Iron and manganese minerals and amorphous materials determined by X-ray diffraction, wt%

Soil type, site	Horizon	Brown nodules						Black nodules					
		goethite	lepidocrocite	manganite	pyrolusite	todorokite	amorphous material	goethite	hematite	lepidocrocite	siderite	todorokite	amorphous material
Stagnant brown forest soils Lenti 209	A_pl	tr					5			3			10
	B_1	tr	1?				4	tr		2			5
	B_2	1?, tr	3					1		3			
	B_3	tr	2				4			4			1
	C	tr	2				4	1?, tr		2			3
Lenti 115	B_2	5					3	4	3	2		tr	5
	B_3	5				tr	5	3					4
Meadow solonetz Hortobágy	B_2						5						5
	B_3							4					5
	BC	tr					7	tr			4		4
	C	2, 5					3	4, 5					4, 3
Solonetzic meadow soil Szarvas	A_pl							tr					
	A	3						tr					
	B_1	tr						tr					
	B_2							tr		4			
	BC	6						tr					
	C	tr, 4	2	tr	1			tr, 4					
Meadow soils Besenyszög 22	Apl							3					9
	B							4					4
	B_g							4					9
	BC							tr					7
	C							1					5
Besenyszög 29	A							2, 5					8
	B							3					8
	BC							3					0
	C							1					13
Peaty meadow soil Szeghalom	C_1	15											
Soil of alluvial forest Szíjártóháza	A	5						5					
	B_1	4						4					
	B_2	5						4					
	C	3, 5				3		3, 3					
Soil of swampy forest Jánkmajtis	A_pl	tr						tr		3			
	C_1									3			
	C_2	tr	5										
Average		2,8	0,7					1,8		0,85			

A possible reason should be that phyllomanganates and Mn-goethite are generally poorly crystalline and only a few wide reflections were observed (Manceau et al. 1992) The detection limit of ferrihydrite by DXRD was 15 wt% (Schulze 1981, Schwertmann et al. 1982; Childs 1992).

4.2. Amorphous and poorly crystalline compounds

The thermoanalytical investigations were useful first of all in point of view of amorphous phases.

Three groups of characteristic curves of ferrihydrites may be separated.

1st group: only one great peak asymmetric to higher temperatures due to the water loss was recognized. Average peak temperature was 95 °C (e.g. Fig. 5a, Meadow solonetz, B_1-horizon, black nodules, 4 of total samples). Similar peak was observed earlier in case of gel of iron compounds precipitated from spring water. 2nd group: the water loss consisted of 3 separate stages: 99, 185, 274 °C average peak temperatures (Fig. 5b, Meadow solonetz, A-horizon, black nodules, 24 samples).
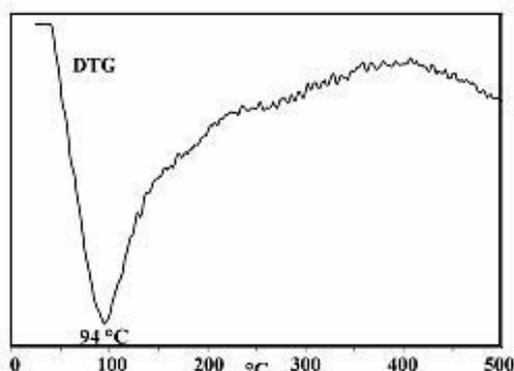
Figure 5a. DTG curve of ferrihydrite. Meadow solonetz, B_1-horizon, black nodules (No. 1803)
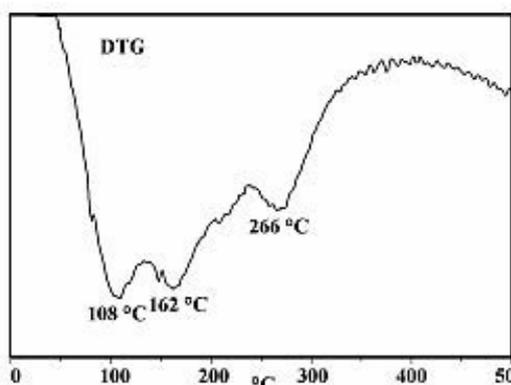

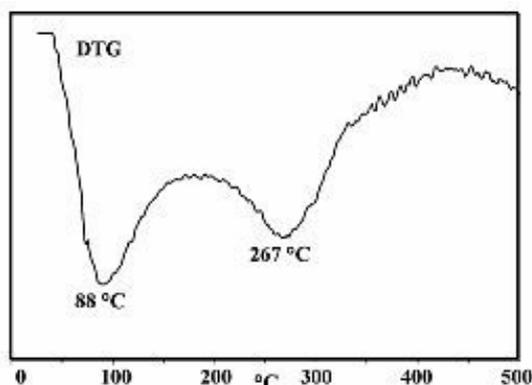Figure 5b. DTG curves of ferrihydrite. Meadow solonetz, A-horizon, black nodules (No. 1802)

Figure 5c. DTG curves of ferrihydrite. Stagnant brown forest soil, A_{pl}-horizon, brown nodules (No. 1675).

3rd group: only the first and third reaction can be observed at 88 and 267 °C average peak temperature (Fig.5c, Stagnant brown forest soil, A_{pl} –horizon, brown nodules, 16 samples). It is supposed the 3 groups indicate 3 different degree of crystallinity. The first two peaks may be attributed to the water content model of Manceau & Gates (1995), third may be interpreted as a dehydroxilation process, similar to goethite, but the peak temperature are lower with about 50-75 °C.

The elemental Fe_2O_3-content was 12.29 wt% and 19.46 wt% in the nodules from C-horizons of solonetz-like meadow and peaty meadow soils, respectively. In contrast to this, 6 wt% and 15 wt% FeOOH minerals were determined by XRD, which corresponds only to 5.4 wt% and 13.5 wt% Fe_2O_3, respectively. The total amounts of MnO were, respectively, 4.33 wt% and 1.35 wt%; only traces (i.e. up to a maximum of 1 wt%) of manganese minerals were detected by XRD. This indicates that a considerable quantity of amorphous and poorly crystalline material was present in the nodules. The amounts of the amorphous and poorly crystalline materials determined by XRD were between 0-13 wt% (Table 4).

The amorphous and poorly crystalline iron compounds (Fe_o) were analysed in acidic ammonium-oxalate extracts (Schwertmann 1964), pedogenic iron oxides and oxihydroxides (Fe_d) in dithionite-citrate-bicarbonate (DCB) extracts (Mehra & Jackson 1960) were examined. The organic-iron compounds were determined using Bascomb's method (1968), their amount exceeded 1 wt% only in the nodules separated from the A_{pl}-horizon of stagnant brown forest soil.

The strong hydromorphic impact produces a long period of reducing conditions in soils (or in some of their horizons). This can lead to the mobilization of the iron and manganese compounds and, as a consequence, they can be leached out under suitable conditions. Clear evidence of this process could be recognized in pale, depleted zones in thin sections using a polarizing microscope (Veneman et al. 1976, Bouma et al. 1990, Vepraskas et al. 1994). It was observed in stagnant brown forest soils and meadow solonetz soils in Hungary (Szendrei 2001). Further evidence was demonstrated by low Mn_o-, Fe_o-, Fe_d-contents (Table 5). The diminution of the iron and manganese content due to a hydromorphic impact has been illustrated by Blume (1988) and others.

Elless & Rabenhorst (1994) reported that Fe_d- and Mn_d-values were lower in pale zones that in redox concentrations. Mn_o/Fe_o-values diminished with increasing hydromorphic influences (i.e. shallower water tables) in the studied soils (Table 6). Our results were in accordance with earlier studies; these reported that Mn/Fe-ratios determined by selective dissolutions were interpreted as the indicators of Eh-pH gradient (McDaniels & Buol 1991, Zaidel'man & Nikiforova 1991). The accumulation of amorphous and poorly crystalline iron compounds (Fe_o/Fe_d-values) was also interpreted as an indicator of hydromorphic influence by Blume & Schwertmann (1969), Vorobyeva & Sing Dalzchit (1995), and others. Willett & Higgins (1980) reported that the Fe_o/Fe_d-ratios of alternating-reduced and oxidized horizons were in the range of 0.2-0.4, and were between 0.4-0.6 in active, redoximorph soils (Cornell & Schwertmann 1996).

Table 5. Horizons with the strongest hydromorphic influences, as indicated by the figures determined by selective dissolutions

Soil types	Ground-water depth, m	Brown nodules					Black nodules				
		minimum				maximum	minimum				maximum
		Mn_o	Fe_d	Fe_o	Mn_o/Fe_o	Fe_o/Fe_d	Mn_o	Fe_d	Fe_o	Mn_o/Fe_o	Fe_o/Fe_d
Soils of swampy forest	0.0-0.8	C_2	C	C_1	C_2	C	C_1	C_1	C_2	C_1	C_1
Soils of alluvial forest	0.0-0.8	B/B_g	C	C	B_g	A					
Solonetzic meadow soil	1.5-2.5	B_1	B_2	B_1	B_1	B_2	C	B_2	B_1	B_2	B_2
Meadow soils	1.5-3.5						C	B	C	A_{pl}	A_{pl}
							C	-	C	B	B-C
Meadow solonetz	1.5-3.5	A/C	BC	C	A	B_2	C	B_1	C	B_2	B_1
Stagnant brown forest		B_1	B_1	C	B_1	B_1	B_1	B_3	B_3	B_1/A_{pl}	B_1

Table 6. Relationship between hydromorphic impact (depth of groundwater table) and Fe_o/Fe_d-, and Mn_o/Fe_o ratios in brown nodules

Soil type	Site	Depth of groundwater table, m	Fe_o/Fe_d average	Fe_o/Fe_d extreme values	Mn_o/Fe_o average	Mn_o/Fe_o extreme values
Soil of swampy forest	Jánkmajtis	0.0-0.8	0.75	0.68-0.83	0.07	0.06-0.08
Soil of alluvial forest	Szíjártóháza	0.0-0.8	0.59	0.36-0.78	0.02	0.003-0.06
Meadow solonetz	Hortobágy	1.5-3.5	0.50	0.30-0.84	0.94	0.65-1.35
Solonetzic meadow soil	Szarvas 4	1.5-2.5	0.39	0.25-0.64	1.09	0.34-1.41
Stagnant brown forest soil	Lenti		0.47	0.05-1.36	0.22	0.04-0.57

This value was close to that was published by Willett & Walker (1982). 54% of the investigated samples had Fe_o/Fe_d-values above 0.4.

The difference between brown and black nodules was that in black ones there were more amorphous and poorly crystalline materials, higher Fe_o/Fe_d-ratios were more frequent (Fig. 6).
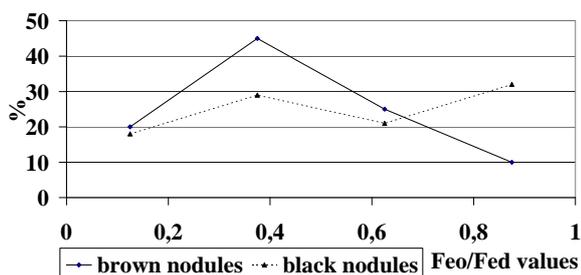

Figure 6. Frequency of Fe_o/Fe_d ratios in brown and black nodules

The highest average Fe_o/Fe_d-ratios were in the soils with the strongest hydromorphic impact and with the shallowest groundwater table (Table 6). Fe_o/Fe_d-ratios were generally highest in the humus horizons due to the inhibiting influence of organic matter on the crystallization of iron oxides and oxihydroxides (Cornell & Schwertmann 1996). As an example, Fe_o/Fe_d-values grow towards the surface in stagnogley soils in Great-Britain (Thomasson & Bullock 1975). In our case it was only in the soil of alluvial forest and in a meadow soil. The horizons with minimum Mn_o/Fe_o-ratios, maximum Fe_o/Fe_d-values, andminimum Mn_o-, Fe_o and Fe_d-values were expected to be horizons with the strongest hydromorphic influences.

Furthermore, in soils with a shallower groundwater table (i.e. soils of alluvial and swampy forest) the majority of these data actually met the expectation. In salt-affected soils (solonetz-like meadow and meadow solonetz) and in one of the meadow soils, the above mentioned data indicated B-horizons with the strongest hydromorphic impact.

This can be explained by the presence of stagnant water above the B-horizons with considerable clay accumulation (Table 7).

In horizons with a weaker hydromophic influence, reduced and oxidized periods alternate and as a consequence the accumulation of amorphous and poorly crystalline iron compounds (Fe_o) can occur. The sequence of horizons with minimum and with

maximum Fe_o-contents indicates a gradient of changing (decreasing) hydromorphic influence, increasing distance from the groundwater table (Table 8).

Table 7. Distribution of clay fractions, wt%

Horizon	Stagnant brown forest soils	Solonetz like meadow soil	Soil of swampy forest	Meadow solonetz
Clay fraction mm	0,002>	0,002>	0,002>	0,001>
A_{pl}	20	28	29	19
B_1	21	35		30
B_2	28	43		38
B_3	28			
BC		38		
C_1	20	21	34	
C_2			49	

Table 8. Horizons with extreme amounts of amorphous and poorly crystalline iron compounds (Fe_o) indicating the gradient of changes of hydromorphic influence

Soil type	Groundwater depth, m	Extremes	Brown nodules	Black nodules
			horizons	
Soil of swampy forest	0.0-0.8	max	A_{pl}	A_{pl}
		min	C_1	C_2
Soil of alluvial forest	0.0-0.8	max	B_g	
		min	C	
Solonetzic meadow soil	1.5-2.5	max	B_2	A_{pl}
		min	B_1	B_1
Meadow soils	1.5-3.5	max		B_g
		min		C
	1.5-3.5	max		A_{sz}
		min		C
Meadow solonetz	1.5-3.5	max	B_2	B_1
		min	C	C

Black nodules with brown coatings were observed in polished thin sections of rather different soil types (stagnant brown forest soil, meadow solonetz, solonetz-like meadow, meadow and soil of swampy forest). These soils were taken from sites long distance away from each other (Lenti, Hortobágy, Szarvas, Besenyszög and Jánkmajtis). Such nodules were also taken from soils which had undergone various formation processes (stagno- and groundwater gleys). Thus it can be assumed that the formation process of the brown coatings is a quite common one.

Such Fe-Mn-nodules had earlier been described by others (Cescas & Tyner 1967, Quereshi et al. 1969, Gallaher et al. 1973, Schwertmann & Fanning 1976). Different explanations for the forming processes were proposed as summarized below.

On the one hand, it was suggested that the manganese ion concentration diminished in the last period of the nodule formation. (Cescas & Tyner 1967). On the other hand, when the soils were wetted the soil solution was reduced for Mn^{4+}-ions, while the surface of the Fe-Mn nodules was still oxidized. Therefore the manganese ions diffused from the nodule surface to the solution, and in this way the surface of nodules became rich in iron compounds (White & Dixon 1996). In the case of an enhanced hydromorphic influence and diminishing redox potential, manganese nodules form first according to the model of Bouma et al. (1990) and White & Dixon (1996). In the preceding processes there would have been a range of redox potentials when iron ions were mobilised and, with increasing redox potential, the iron compounds were precipitated while manganese ions remained in the solution in a reduced state.

The data gathered during this present study do not provide a chance to choose among the above-mentioned processes.

Brown nodules with black coatings were observed very rarely (C_1-horizon, soil of swampy forest), and concentric nodule was also very uncommon (B_1-horizon, stagnant brown forest soil).

4.3. Grouping of investigated soils according to hydromorphic influences

The investigated soils can be divided into the following groups according to hydromorphic impacts, and subdivided on the basis of their calcium carbonate content:

A/ Groundwater gleys

Aa/ Calcium carbonate-free soil types with a very shallow groundwater table (<1 m): alluvial and marshy alluvial forest soils.

In these soils there were only brown nodules or these nodules were dominant (67-67.6 pcs/cm^2 of brown nodules versus 3.3-3.4 pcs/cm^2 of black nodules in soil of swampy forest).

Goethite was present in both profile and lepidocrocite in soil of swampy forest. The mangnese content was the lowest in brown nodules and was relatively low in black nodules. In these soils could be found the lowest Mn_o/Fe_o (<0.08) and the highest Fe_o/Fe_d values (Table 6). The characteristic values were determined by selective dissolutions and these

indicated a strong hydromorphic impact on the subsoils (Table 5).

The sequences of horizons with minimum and maximum values of amorphous and poorly crystalline iron compounds (Fe_o) showed a decreasing hydromorphic influence toward the surface (Table 8).

Ab/ Calcium carbonate-free soils with a high groundwater level (1.5-3.5 m): meadow soils. Only black nodules could be separated. Among iron oxi-hydroxide and hydroxide minerals goethite was identified.

70 % of Fe_o/Fe_d values were above 0.4, which is the limit for redoximorf soils. 50 % of characteristic values of selective dissolutions indicating the strongest hydomorphic impact were found in the C-horizons (Table 5). The gradient of diminishing hydromorphic influence was towards the surface (Table 8).

Ac/ Calcareous soils with high groundwater table (1.5-3.5 m): meadow solonetz and solonetz-like meadow soil.

Goethite was found in both profiles, while lepidocrocite occurred in a few horizons of solonetzic meadow soils. The selective dissolution analyses showed that the B-horizon had been subjected to stronger hydromorphic influences; this is feasible due to the stagnant water above the horizon with high amounts of clay (Table 7).

Horizon with minimum and overlying horizon with maximum values of selective dissolutions (with a single exception), denoted decreasing hydromorphic influences towards the surface (meadow solonetz soils).

B/ Stagnant brown forest soil

The figures for selective dissolutions showed the B-horizons which had been subjected to the strongest hydromorphic influences (Table 5).

The distributions (with depths) of the Fe_d/clay (A_{pl}-horizon: 0.03, B_1: 0.04, B_2: 0.07, B_3: 0.08, C: 0.07) provided evidence of a synchronous mobilization of these compounds in B_2-C-horizons, this had been mentioned earlier (Blume & Schwertmann 1969, Richardson & Hole 1979, Khan & Fenton 1994), and in the case of illuviated brown forest soils in Hungary (Stefanovits 1971).

5. CONCLUSIONS

The ferruginous and manganiferous nodules were formed during the impregnation and cementation of the groundmass (coarse and fine grains and micropores) by iron and manganese compounds.

The nodules consist of a large amount of amorphous and poorly crystalline iron and manganese compounds. Black nodules contained more amorphous and poorly crystalline materials than brown ones. In the nodules, goethite and lepidocrocite were common but manganese minerals were very rare. The presence of lepidocrocite indicated an enhanced hydromorphic impact on the soils.

The selected dissolution methods helped to show the horizons with strongest hydromorphic impacts; these were subsoil horizons in the groundwater gleys and B-horizons in the salt-affected and stagnant brown forest soils. It can be supposed that stagnant water in the B-horizons (with a high clay content) of salt-affected soils also contributed to the hydromorphic impact.

Black nodules with brown coatings were common and indicated after accumulation of manganese constituents a period of depletion or inhibited immobilization of manganese compounds, and also couple with the factors causing such changes.

The investigations on the ferruginous and manganiferous nodules of selected soils from Hungary were consistent with earlier worldwide studies. The mineralogical characteristics of the nodules also represented a useful tool for acquiring more knowledge on the hydromorhic influences of soils in the European prairie ecodivison.

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