Int. Agrophysics, 2002, 16, 1-6

INTERNATIONAL
Agrophysics
www.ipan.lublin.pl/int-agrophysics

Magnetic and mineralogical properties of different granulometric fractions in the soils of the Lublin Upland Region

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Received March 29, 2001; accepted January 7, 2002

A b s t r a c t. The magnetic and mineralogical properties of 5 selected soil granulometric fractions from A and B horizons of Orthic Luvisol, Eutric Cambisol, Haplic Phaeozem and Dystric Cambisol were investigated. The magnetic susceptibilities determined (MS) of consecutive fractions are in the range $5 \cdot 10^{-8}$ - $70 \cdot 10^{-8}$ m^3 kg^{-1}; they vary between $5 \cdot 10^{-8}$ and $30 \cdot 10^{-8}$ m^3 kg^{-1} for brown soils and between $15 \cdot 10^{-8}$ and $70 \cdot 10^{-8}$ m^3 kg^{-1} for degraded chernozem. Differences in the distribution of MS in fractions taken from A and B horizons reflect peculiarities of the soil forming processes and are connected with soil typology. Relationships between chemical and physical properties and transformation of mineral composition of the soil fractions are discussed.

K e y w o r d s: magnetic susceptibility, mineralogical composition, soil granulometric fraction

INTRODUCTION

The magnetic properties of a soil depend of the magnetic properties of minerals and other soil constituents [29]. Quartz, orthoclase, calcium carbonates, water and organic matter exhibit diamagnetic properties. Biotite, iron and manganese carbonate are para-magnetics. Other minerals, as magnetite, are ferro-magnetics, whereas goethite and hematite are anti-ferromagnetic minerals.

Iron oxides are the most abundant metallic soil oxides and are present in the majority of soils from different climatic regions. They play a vital role in soil formation and in the dynamics and fate of nutrients and pollutants in the environment. Pedogenetic environments have a substantial influence on the nature of the iron oxide formed [12,23]. Iron minerals can be used as quantifiable pedogenic indicators [2,5,7,8,10,11,13,20,21].

Studies of the magnetic characteristics of different soil types can give valuable information about iron diagnosis and its depth distribution. In general, the occurrence of iron oxides in different soil environments, and thus the magnetic properties measured, exhibit a high sensitivity to the changes in environment [9,17,24]. It is known that in contemporary soils, magnetic iron minerals respond to soil forming processes in site-specific ways, with a resulting magnetic enhancement or dilution [1,3,4,17]. For example, in very acid or wet soil, dissolution of magnetic oxides on a grain size-specific basis occurs.

Volumetric magnetic susceptibility (MS) is the ratio of induced magnetization in a volume of material to the intensity of the magnetic field applied to that volume. Measurements of MS are reproducible and non-destructive to samples. In general, soil MS is directly related to the concentration of the strongly magnetic minerals present, their grain sizes and to some extent their grain shape. Most MS changes in soils are due to variations in concentrations and grain sizes of magnetite and maghemite.

Measurements of topsoil magnetic susceptibility have been used for assessing levels of pollution in soils [15,22, 26,27]. Strzyszcz *et al*. [26-28] have shown that magnetic susceptibility measurements may be used as an indicator of soil contamination. Arable soils close to steel plants showed a pronounced susceptibility over all ploughed layers. The values of MS decreased along with distance, and due to ploughing their dilution in all ploughed layers took place [28]. Magnetic susceptibility of topsoil is an indicator for assessing levels of industrial pollution in soil, especially in forested areas. Higher values of MS have been found in the

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litter horizon, particularly in the Of/Oh subhorizon which implies their anthropogenic origin [26,27].

Recent studies have shown that magnetic properties of granulometric fractions of soils may contribute to the bulk magnetic signal and thus reflect the processes of weathering and iron oxide formation in soil profiles [4,17,29]. As a rule, for soils developed from the parent material with low magnetic susceptibility, the highest values of MS are correlated with the content of clay fraction (<0.002 mm). However, the magnetic susceptibility progressively decreases in silt and sand fractions. As mentioned above, MS is related to the soil texture. Soil texture classifications used in different countries are not entirely compatible and differ in respect to the definition of the number, as well as the diameters of consecutive soil fractions. It seems that also investigations of the MS of soil fractions exhibiting more pronounced differences in size would allow a more complex analysis of soil formation processes.

The aim of our study was the investigation of the magnetic and mineralogical properties of various textural fractions of soils and relating these properties to soil formation.

MATERIALS AND METHODS

Materials for the experiment were taken from A and B horizons of different soils formed from loess and sand of the Lublin Upland Region. They included brown podzolic soil, leached brown soil, degraded chernozem and acid brown soil. According to the FAO classification scheme the above listed soils are Orthic Luvisol, Eutric Cambisol, Haplic Phaeozem and Dystric Cambisol, respectively. The selected properties of the soils investigated are given in Table 1.

Granulometric fractions 1-0.05, 0.05-0.02, 0.02-0.06, 0.06-0.002, <0.002 mm were prepared from soils as follows. The dispersion of soil suspensions was produced by ultrasonic vibration. Soil fractions were obtained by a few cycles of sedimentation and siphoning, using the Cassagrande-Prószyński method. The suspensions of soil fractions were centrifuged, air dried and gently powdered in a mortar.

The measurements of magnetic susceptibility (MS) were performed with Kappabridge KLY-2 (Geofyzika Brno) apparatus.

The mineralogical composition of fractions was determined by X-ray diffractometry with Ni filtered CuKα radiation and with DRON-3.0 diffractometer. Quantitative evaluation of the relative abundance of major clay minerals groups was performed by the Biscay method. The identification of clay minerals was based on the spectra for Mg forms, ethylene glycol saturated, and 350 and 550°C heated clays. The samples were step-scanned between 2° and 65° 2θ, using 0.1° 2θ increments with a 3 s counting time per increment. A semi-quantitative estimation of mineral concentrations was carried out.

RESULTS AND DISCUSSION

The mineralogical composition of the soil fractions investigated is collected in Table 2 and selected XRD patterns are show on Fig. 1. The magnetic susceptibilities MS of these soils is presented in Fig. 2.

The soil formation processes are reflected by mineralogical characteristics of soil fractions. Quartz appears always; its lowest concentration (up to 20%) is in the fraction < 0.002 mm. However, its concentration is several times higher in the fractions 1-0.05, 0.05-0.02, 0.02-0.06 mm (up to 70%). Feldspar and plagioclase occur in all fractions in equivalent portions (almost 20%) with some decrease observed for the fraction < 0.002. Calcite is present mostly in the fractions 1-0.05, 0.05-0.02 and 0.02-0.06 mm

T a b l e 1. Some selected characteristics of genetic horizons of soils

Type	Depth (cm)	pH[a]		C_{org}[b] (%)	Percentage of fractions (mm)[c]			Specific surface[d] ($m^2 g^{-1}$)	Total porosity[e] (%)
		H_2O	KCl		1-0.02	0.02-0.002	<0.002		
Orthic	0-20	6.1	4.9	1.38	57	36	7	15.0	32.5
Luvisol	40-60	5.2	3.9	0.11	53	26	12	34.4	26.9
Eutric	0-20	6.1	5.0	1.38	53	21	36	68.0	22.1
Cambisol	30-60	6.2	4.8	0.28	34	16	50	121.4	27.5
Haplic	0-20	6.1	5.2	2.53	66	24	10	42.8	26.9
Phaeozem	65-95	7.7	6.9	2.02	57	26	17	34.1	20.8
Dystric	0-20	5.3	4.1	0.66	91	7	2	7.8	13.8
Cambisol	30-50	5.4	4.6	0.18	94	4	2	4.1	7.2

[a] - 1:2.5 soil solution ratio, [b] - Tiurin method, [c] - Cassagrande-Pruszyński method, [d] - from water vapour desorption, BET, [e] - from mercury porosimetry.

T a b l e 2. Mineralogical composition of investigated soil granulometric fractions

Type	Depth (cm)	Soil fraction (mm)	Quartz	Feld-spars	Cal-cite	Mag-nesite	Smec-tite	Illite	Kaoli-nite	Chlo-rite	Vermi-culite
Orthic Luvisol	A 0 - 20	< 0.002	+	(+)	-	-	-	+	++	(+)	++
		0.002 - 0.006	++	+	(+)	-	-	+	+	(+)	+
		0.006 - 0.02	no.	+	+	-	-	-	-	-	-
		0.02 - 0.05	+++	(+)	-	+	-	-	-	-	-
		0.05 - 1	+++								
	B 40 - 60	< 0.002	+	(+)	-	-	-	+	++	(+)	++
		0.002 - 0.006	++	(+)	-	-	-	+	+	-	+
		0.006 - 0.02	++	(+)	-	-	-	+	+	-	+
		0.02 - 0.05	+++	+	(+)	-	-	(+)	(+)	-	(+)
		0.05 - 1	+++	(+)	-	(+)	-	-	-	-	-
Eutric Cambisol	A 0 - 20	< 0.002	+	-	-	-	+++	+	+	-	-
		0.002-0.006	+	-	-	-	+++	+	+	-	-
		0.006 - 0.02	+	-	-	-	++	(+)	+	-	-
		0.02 - 0.05	++	+	-	-	+	(+)	(+)	-	-
		0.05 - 1	no.								
	B 30 - 60	< 0.002	+	-	-	-	+++	+	+	-	-
		0.002 - 0.006	++	(+)	-	-	+++	+	+	-	-
		0.006 - 0.02	++	(+)	-	-	++	(+)	+	-	-
		0.02 - 0.05	++	+	-	-	-	-	-	-	-
		0.05-1	+++	+	-	-	-	-	-	-	-
Haplic Phaeozem	A 0 - 20	< 0.002	+	(+)	-	-	+	++	+	(+)	-
		0.002 - 0.006	++	(+)	-	-	+	+	+	(+)	-
		0.006 - 0.02	++	+	(+)	-	-	(+)	(+)	-	-
		0.02 - 0.05	+++	+	(+)	-	-	-	-	-	-
		0.05 - 1	+++	+	(+)	-	-	-	-	-	-
	B 65 - 95	< 0.002	+	(+)	-	-	++	+	+	(+)	-
		0.002 - 0.006	++	(+)	-	-	++	+	+	(+)	-
		0.006 - 0.02	++	+	-	-	+	+	+	-	-
		0.02 - 0.05	+++	+	+	-	-	-	-	-	-
		0.05 - 1	+++	+	(+)	+	-	-	-	-	-
Dystric Cambisol	A 0 - 20	< 0.002	+	(+)	-	-	-	(+)	+	(+)	++
		0.002 - 0.006	++	+	-	-	-	(+)	+	-	+
		0.006 - 0.02	+++	+	-	-	-	(+)	(+)	-	(+)
		0.02 - 0.05	+++	+	-	-	-	-	(+)	-	(+)
		0.05 - 1	+++	(+)	-	+	-	-	-	-	-
	B 30 - 50	< 0.002	+	(+)	-	-	-	(+)	+	-	++
		0.002 - 0.006	+++	+	-	-	-	(+)	(+)	-	(+)
		0.006 - 0.02	+++	+	-	-	-	(+)	(+)	-	(+)
		0.02 - 0.05	+++	+	-	-	-	(+)	-	-	-
		0.05 - 1	+++	(+)	-	+	-	-	-	-	-

+++ - ≈80%, ++ - ≈50%, + - ≈20%, (+) - ≈5%, - - absence, no. - not evaluated.

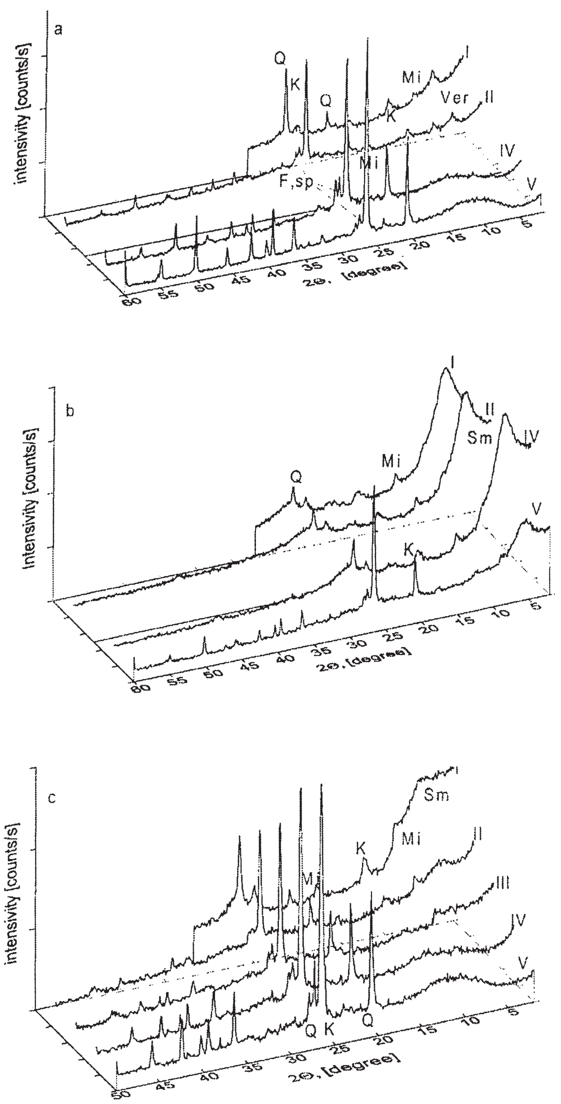

Fig. 1. XRD patterns of the selected granulometric fraction from A horizon for investigated soils: a) Orthic Luvisol, b) Eutric Cambisol, c) Haplic Phaeozem. Granulometric fractions: I - <0.002, II - 0.002-0.006, III - 0.006-0.02, IV - 0.02-0.05, V - 0.05-1.0 mm.

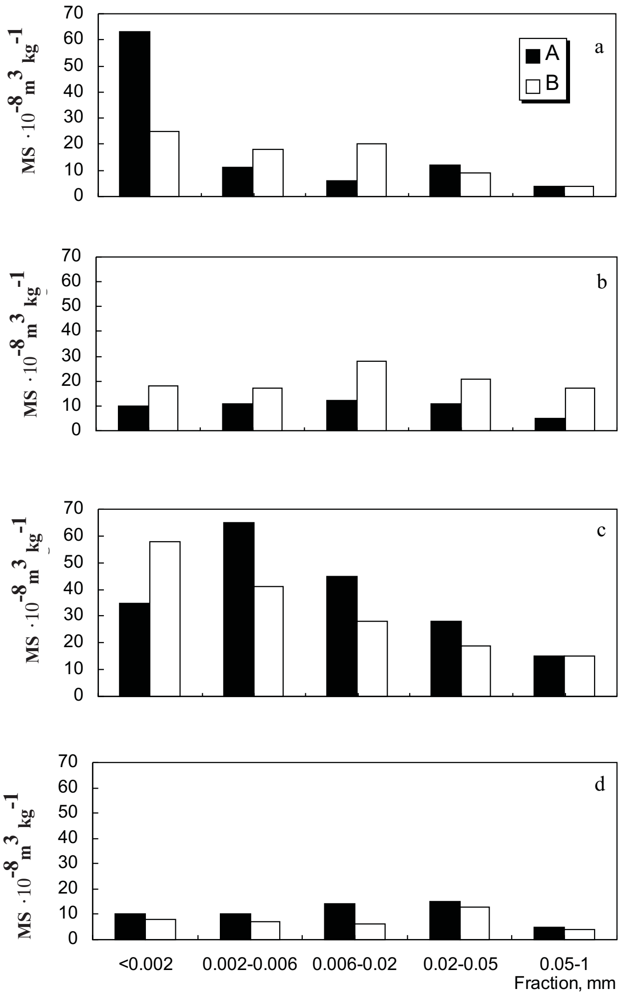

Fig. 2. Magnetic susceptibility (MS) of the granulometric fractions from horizon A and B of the investigated soils: a) Orthic Luvisols, b) Eutric Cambisol, c) Haplic Phaeozem, d) Dystric Cambisol. A, B - genetic horizon.

of the Haplic Phaeozem and of the Orthic Luvisol. The dominant clay minerals (Table 2) in fractions finer than 0.02 mm are as follows: mica, smectite, kaolinite, chlorite (Haplic Phaeozem); smectite, mica, kaolinite (Eutric Cambisol); mica, kaolinite, vermiculite, chlorite (Orthic Luvisol) and kaolinite, vermiculite, mica, chlorite (Dystric Cambisol). Transformation of fine-grained matter in Orthic Luvisol consists in the destruction of particular mineral phases. One of those predominant phases is mica; however the lessivage process can also occur in this case.

The main component of granulometric fractions from A and B horizons of Eutric Cambisol is smectite (50-80%). The content of hydromica and kaolinite is low (below 20%). The influence of the soil processes on the clay minerals seems to be rather weak. This soil profile is situated at the bottom of a hill and thus it can be concluded that the lower part of the hill contains less transformed material. The existence of relationships between chemical and physical properties and the transformation of mineral composition of the clay fraction by gleic processes in heavy soils has been discussed by Biesiacki and Zagórski [5].

The surface area for the soils investigated is connected with the content of organic matter and clay, and also with the mineralogical composition (Tables 1 and 2). The highest values of surface area exhibit Eutric Cambisol and Haplic Phaeozem. Both soils have a high amount of clay minerals, especially smectite. Other soils, i.e., Orthic Luvisol and Dystric Cambisol are characterized by rather low values of the surface area. These soils contain a lot of quartz and their values of the surface area are probably the result of a quantity of vermiculite.

The distribution of iron oxides among consecutive granulometric fractions of Orthic Luvisol and the values of MS for A horizon increase with a decrease of fraction sizes and exhibit a maximum for the clay fraction <0.002 mm (Fig. 2a). The values of MS for the fraction <0.002 mm, taken from A horizon are two times higher ($63 \cdot 10^{-8} \pm 3.89$ m^3 kg^{-1}) than those evaluated for the B horizon ($25 \cdot 10^{-8} \pm 2.05$ m^3 kg^{-1}). In the A horizon a higher part of crystalline iron occurs in clay fraction. Differences between the distributions of MS in consecutive fractions from A and B horizons reflect the peculiarities of soil formation processes and are connected with soil typology. The intensity of weathering is the highest in A horizon. In comparison with the parent material, we can observe the breakdown of smectite [2]. During weathering the iron releases from mineral lattices and then crystallizes into iron oxide phases. Any visible distribution of MS in fine granulometric fractions (<0.02 and <0.002 mm), taken from B-horizon is practically not observed.

The distribution of relative bulk Fe content within Haplic Phaeozem profile (Fig. 2c) indicates some accumulation of iron in the B horizon and exhibits a maximum ($58 \cdot 10^{-8} \pm 4.25$ m^3 kg^{-1}) of MS for < 0.002 mm fraction. The MS values for 0.06 - 0.002 mm fraction taken from A horizons are about two times higher ($65 \cdot 10^{-8} \pm 3.27$ m^3 kg^{-1}) than the relevant values of MS for the fraction < 0.002 mm ($35 \cdot 10^{-8} \pm 1.98$ m^3 kg^{-1}). The distribution of MS for granulometric fractions indicates that crystalline iron occurs mostly in fractions coarser than clay. The MS values for B horizon increase with a decrease of the fraction size and exhibit a maximum for the clay fraction. Similar results are found in our previous paper [2]. For the chernozem profile the distribution of the relative bulk clay Fe content (from Mossbauer spectra) within the profile indicates also some accumulation of iron in clay in the B horizon. Thus, the distribution of crystalline iron forms in granulometric fractions is connected with the mineralogical peculiarities of the parent material and with the soil forming processes in the horizons. The Feng and Johnson's [9] study demonstrates that 40% of the variation in bulk magnetic susceptibility is due to clay fraction magnetic susceptibility and 56% of the variation - due to silt and clay fraction magnetic susceptibility together. After adding the sand fraction, 66% variation of magnetic susceptibility is accounted for.

The granulometric fractions of Haplic Phaeozem are characterized by high values of MS (from $20 \cdot 10^{-8} \pm 1.58$ to $65 \cdot 10^{-8} \pm 4.26$ m^3 kg^{-1}), compared with other investigated soils (Fig. 2). The fractions of latter soils exhibit much lower values of MS - about $20 \cdot 10^{-8} \pm 1.63$ m^3 kg^{-1}. The Eutric Cambisol (Fig. 2b) and the Dystric Cambisol (Fig. 2d) have not revealed any visible distribution of MS within the granulometric fractions. The high values of MS observed for Haplic Phaeozem indicate some accumulation of crystalline iron compounds that predominantly appear in a superdispersive form [2]. The content of organic carbon in A and B horizons of the Haplic Phaeozem is 2.5 and 2.0%, respectively (see Table 1). Organic matter via its interaction with surface of iron compounds inhibits the formation of goethite [16, 24]. The ratio of oxalate extractable Fe_o to dithionite extractable Fe_d is higher in horizons richer in organic carbon [6].

Low values of magnetic susceptibility for granulometric fractions of Eutric and Dystric Cambisol may be the result of acid reaction (Table 1) or mineralogical composition (Table 2). Józefaciuk [14] has shown that during acidification processes, clay minerals and soils undergo some transformation; their MS values decrease with acidity increase. Several clay minerals, as, for example, smectite contain iron [7]. However, smectite is absent in Orthic Luvisol and Dystric Cambisol (Table 2) and there must exist other reasons for the low magnetic susceptibility of these soils.

As noted in the Introduction, measurements of topsoil magnetic susceptibility are a very rapid, convenient and useful method for assessing levels of anthropoid pollution in soils. MS values exceeding $500 \cdot 10^{-8}$ m^3 kg^{-1} are characteristic for areas with a large industrial emission, whereas the values of MS in the range of $200 \cdot 10^{-8}$ m^3 kg^{-1} - for areas with moderate and low level of industrial emission [26]. However, magnetic susceptibilities of the investigated soil fraction are in the range $5 \cdot 10^{-8}$ - $70 \cdot 10^{-8}$ m^3 kg^{-1}. Such low values of MS provide proof of the lack of industrial pollution in those soils.

CONCLUSIONS

The soil forming processes modify the mineralogical composition of soil fractions. We found that the lowest concentration of quartz (up to 20%) is in the fraction < 0.002; in all the remaining fractions its concentration is much higher and attains a level of 70% in the coarser fractions. Among clay minerals present in the fractions finer than 0.02 mm, we found: mica, smectite, kaolinite, chlorite (for Haplic Phaeozem); smectite, mica, kaolinite (for Eutric Cambisol); mica, kaolinite, vermiculite, chlorite (Orthic Luvisol) and kaolinite, vermiculite, mica and chlorite (for Dystric Cambisol).

The magnetic susceptibility of the investigated soil fractions are within the range $5 \cdot 10^{-8}$ - $70 \cdot 10^{-8}$ m^3 kg^{-1}; they vary between $5\cdot10^{-8}$ and $30\cdot10^{-8}$ m^3 kg^{-1} for the Eutric Cambisol, Orthic Luvisols and Dystric Cambisol, and between $15\cdot10^{-8}$ and $70\cdot10^{-8}$ m^3 kg^{-1} for the Haplic Phaeozem. High MS values obtained for the Haplic Phaeozem indicate some accumulation of crystalline iron forms, occurring predominantly in super-dispersive forms. For different horizons of Dystric Cambisol the values of MS are similar. For the Orthic Luvisol and Eutric Cambisol a higher value of MS is observed for B horizon. The behaviour of MS in fractions taken from A and B horizons reflects the peculiarities of the soil formation processes and is connected with soil typology. For all soils, crystalline iron forms occur mainly in a granulometric fraction coarser than clay.

Data on the granulometric composition and surface areas agrees well with the mineralogy of the soils investigated. Soil formation processes are expressed in the character of mineralogical and physicochemical profile characterizations.

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