Journal of Elementology ISSN 1644-2296

Orzechowski M., Smólczyński S., Długosz J., Kalisz B., Kobierski M. 2018.
Content and distribution of iron forms in soils formed from glaciolimnic sediments, in NE Poland.
J. Elem., 23(2): 729-744. DOI: 10.5601/jelem.2017.22.4.1413

RECEIVED: 8 February 2017
ACCEPTED: 30 December 2017

ORIGINAL PAPER

CONTENT AND DISTRIBUTION OF IRON FORMS IN SOILS FORMED FROM GLACIOLIMNIC SEDIMENTS, IN NE POLAND*

Mirosław Orzechowski[1], Sławomir Smólczyński[1], Jacek Długosz[2], Barbara Kalisz[1], Mirosław Kobierski[2]

[1]Department of Soil Science and Land Reclamation
University of Warmia and Mazury in Olsztyn, Poland
[2]Department of Soil Science and Soil Protection
University of Technology and Life Sciences in Bydgoszcz, Poland

Abstract

The aim of the study was to determine the influence of lithogenic and pedogenic processes on the distribution of iron forms in soils formed from glaciolimnic sediments, in basins of ice-dammed lakes in north-eastern Poland. The examined soils contained high amounts of clay minerals. However, when they are dry, they shrink and may form large deep cracks, which is unfavourable from the environmental point of view. Therefore, observation and recognition of processes occurring in these soils is crucial. The redox potential and oxygen diffusion rate were measured with a redox potentiometer. The free iron oxides were analysed in sodium citrate and dithionite extract, while amorphous iron oxides were analysed in ammonium oxalate according to the Tamm method. The content of crystalline iron oxides, crystallinity index and weathering index were calculated on the basis of the iron content. Total amounts of iron and manganese were measured after mineralisation in *aqua regia*. Redox potential results suggest anaerobic conditions in the soils studied. Correlation coefficients revealed statistically positive relationships between the content of total iron and manganese (r = 0.295) as well as manganese and redox potential values (r = 0.262). The soil parent material contained considerably more iron silicates, which suggests less intensive weathering, and was also distinguished by lower amounts of free iron. The results of the iron content determinations and calculated indices suggest that the analysed soils are young and the features of soil forming processes are merely marked.

Keywords: ice-dammed lakes, iron activity ratio, Vertisol, weathering index.

---

dr inż. Barbara Kalisz, Department of Soil Science and Land Reclamation, University of Warmia and Mazury in Olsztyn, Plac Łódzki 3, 10-727 Olsztyn, tel. 00485234820, e-mail: barbara.kalisz@uwm.edu.pl

* This research was supported by the Polish Ministry of Scientific Research and Higher Education, grant N N305 2776 33 and research project of University of Warmia and Mazury in Olsztyn No 20.610.007-300.

INTRODUCTION

North-eastern Poland is unlike other regions of the country (Morawski 2005). Its distinguishing feature is the presence of glaciolimnic sediments, whose origin is associated with the deglaciation of ice-dammed lakes originating from the Pomeranian phase of the Vistulian Glaciation. As a result, in front of the ice sheet, local, shallow water bodies of varying duration were formed and clay size limnic material was deposited. Soils formed from these sediments contain more clay fraction (< 0.002 mm) with predomination of illite-smectite and smectite minerals (Dlugosz et al. 2009) than soils formed from glacial till. Soils formed from glaciolimnic sediments have diversified chemical and physical properties, which determine their further transformation. The origin of parent material, its properties and mineralogical composition affect spatial variability of the soil cover, which is associated with various soil factors and overlapping soil-forming processes (Bockheim et al. 2005).

The geological origin of parent material has a decisive influence on the total iron content in soil (Kobierski, Dąbkowska-Naskręt 2012). This metal is subjected to anthropogenic activity, and it is used to assess the degree of accumulation of other metals, as EF – enrichment factor (Bourennane et al. 2010, Kobierski, Dąbkowska-Naskręt 2012). The total amount of iron depends on the parent material, and the content of various iron forms is affected by soil-forming processes. Therefore, this element is used as an indicator of the intensity of geological processes as well as the intensity and duration of pedogenic processes (McFadden, Hendricks 1985, Arduino et al. 1986). Iron in soil occurs in various forms, which are mostly a function of pH, soil moisture, soil temperature and redox potential under anaerobic conditions in particular (Straub et al. 2001, Waychunas et al. 2005). These forms are the result of biochemical transformations, which are particularly intensive in soils rich in organic matter (Wheeler et al. 1999). Changes in the redox potential are responsible for chemical transformations of iron oxides and hydroxides (Davranche, Bollinger 2000). The dissolution of iron oxides has a microbiological background. During this process, microorganisms may acquire energy for oxidation and reduction reactions of Fe (Lack et al. 2002). Microbiological processes are of particular importance in reduction conditions – oxidation of Fe ions may occur only in these conditions, as these processes are catalysed by microorganisms (Waychunas et al. 2005).

The aim of the study was to determine the influence of pedogenic processes on the distribution of iron forms in the profiles of soils formed from glaciolimnic sediments in basins of ice-dammed lakes origin in north-eastern Poland.

MATERIAL AND METHODS

The studied sites were formed during the Pomeranian phase of Vistula Glaciation, and represent areas of ice-dammed lake origin. Five glaciolimnic basins of various area, relief, hypsometry (from 40.0 m a.s.l. to 120.0 m a.s.l.) and soil cover were studied. The basins are located in Sępopol Lowland and northern part of Mazurian Lakeland, NE Poland. The basins are near the following towns: Reszel, Kętrzyn (2 basins), Sępopol and Lidzbark Warmiński (Figure 1). At the Reszel and Kętrzyn sites, Verisol (Mollic and Eutric), Gleyic Chernozem and Haplic Luvisol prevailed. At the Sępopol and Lidzbark Warmiński sites, Gleyic Chernozem, Haplic Gleysol, Vertic Eutric Cambisol, and Vertisol (Dystric) prevailed. Genetic horizons of eighteen soil profiles (in catenal and random sequences) were examined and the soils were classified according to the World Reference Base for Soil Resources (IUSS Working Group 2015). In 75 soil samples taken for analysis, the following properties were examined:

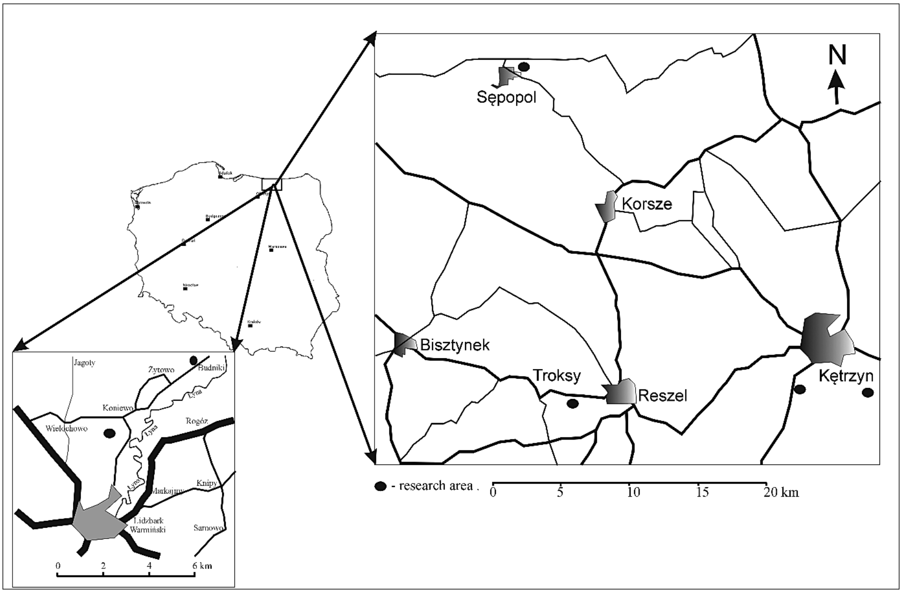

Fig. 1. Location of the soil sites

- soil texture by the pipette method, with an Eijkelkamp pipette apparatus of NEN 5753 and ISO 11277 standards;
- content of exchangeable cations in a solution of ammonium acetate (1 M CH_3COONH_4 dm^{-3}) at pH 7.0, using a spectrometer SOLAAR 969 Pye Unicam (Ca and Mg) and FLAPHO 4 (K and Na);
- hydrolytic acidity by the Kappen method in a solution of sodium acetate (1 M CH_3COONa dm^{-3});

- content of calcium carbonate by the Scheibler method (van Reeuwijk 2002);
- content of organic carbon using a CN Analyser VARIO MAX CUBE Elementar;
- redox potential (Eh) and oxygen diffusion rate (ODR) using a redox potentiometer of the Agrophysics Institute of Polish Academy of Sciences, Lublin, Poland (Gliński et al. 2000).

The content of free iron oxides (Fe_d) was determined in sodium citrate and dithionite extract (Mehra, Jackson 1960), and amorphous iron oxides (Fe_o) were determined in ammonium oxalate according to the Tamm method (Schwertmann 1964). The amounts of iron in the extracts mentioned above were measured with a spectrophotometer PU 9100X Philips. The content of crystalline iron oxides (Fe_c) was calculated as the sum of Fe_d and Fe_o. The iron activity ratio (Fe_o/Fe_d) and weathering index of iron (Fe_d/Fe_t) were also determined.The content of Fe_s silicate forms was calculated from the difference between the total iron content (Fe_t) and free iron (Fe_d) – Fe oxides. Total amounts of iron (Fe_t) and manganese (Mn_t) after mineralisation in *aqua regia* (a mixture of HCl and HNO_3 acids in a 3:1 ratio) were measured with a Carl Zeiss AAS 30.

All analyses were carried out in duplicate. Statistical analyses were conducted using Statistica 10.0 software (StatSoft Inc.).

RESULTS

Vertisols are typical for areas of ice-dammed lake origin, glaciolimnic basins. These soils do not stretch over vast areas but are found in mosaic-like patterns with other soils, e.g. Gleyic Chernozems, Haplic Luvisols, Haplic Gleysols and Vertic Cambisols (Eutric). For Vertisols to appear, vertic horizons with well-formed slickensides are required. These soils had a stable, sharp-edged and coarse prismatic structure.

The studied soils had the texture of clay (C), loam (L), clay loam (CL) and heavy clay (HC). The soils did not contain any coarse fraction with a diameter of > 2.0 mm, the content of sand fraction (2.0-0.05 mm) was low, and ranged from 7.0% to 44.3% and the clay fraction (diameter of < 0.002 mm) prevailed (up to 73.7%) – Table 1.

The mineralogical studies of clay minerals revealed substantial amounts of swelling, mixed packet minerals of illite/smectite type (I/S) and homogenous smectite in vertic horizons (Długosz et al. 2009). The thickness of the mollic horizon in Haplic Gleysol, Vertic Cambisol, Vertisol (Mollic and Eutric) ranged from 30 cm to 46 cm, whereas in Gleyic Chernozem it reached 72 cm. In Haplic Luvisol and Vertisol (Dystric), the thickness of the umbric horizon was smaller and ranged from 18 cm to 27 cm.

Table 1

Selected basic properties of the soils studied

Soil	Horizon	Value	OC	% content of particle size fractions (mm)			Eh	ODR
			(g kg^{-1})	2.0-0.05	0.05-0.002	<0.002	(mV)	(µg m^{-2} s^{-1})
1	2	3	4	5	6	7	8	9
Vertisol (Mollic)	mollic	*X*	29.3	30.2	36.4	33.4	295	53.1
		SD	20.7	8.90	7.02	11.4	23.7	4.07
		CV (%)	70.7	29.5	19.3	34.2	8.00	7.70
	vertic	*X*	-	9.30	17.0	73.7	245	37.4
		SD	-	2.87	6.97	4.92	43.0	1.22
		CV (%)	-	30.9	41.0	6.70	17.6	3.30
	parent material	*X*	-	10.5	28.0	61.5	186	30.9
		SD	-	5.44	20.81	17.6	28.4	1.81
		CV (%)	-	51.8	74.3	28.6	15.2	5.90
Statistically significant differences				mollic > parent material, vertic	mollic > vertic	mollic > parent material, vertic	mollic > parent material	mollic > parent material, vertic
Vertisol (Eutric)	mollic	*X*	25.8	24.3	40.3	35.4	338.8	60.1
		SD	14.7	4.43	10.7	14.5	14.9	4.98
		CV (%)	57.1	18.2	26.5	40.9	4.40	8.30
	vertic	*X*	-	9.8	16.5	73.7	305.0	49.2
		SD	-	5.25	5.80	5.91	5.77	4.41
		CV (%)	-	53.4	35.2	8.00	1.90	9.00
	parent material	*X*	-	7.00	29.3	63.7	265.0	44.7
		SD	-	4.76	14.5	15.9	15.8	6.39
		CV (%)	-	68.0	49.5	24.9	6.00	14.3
Statistically significant differences				mollic > vertic, parent material	mollic > vertic	mollic < vertic, parent material	mollic > vertic, parent material	mollic > vertic, parent material
Vertisol (Dystric)	umbric	*X*	29.6	43.5	40.0	16.5	342	65.8
		SD	25.2	2.12	9.90	7.78	17.7	11.9
		CV (%)	85.0	4.90	24.8	47.2	5.20	18.1

cont. Table 1

1	2	3	4	5	6	7	8	9
Vertisol (Dystric)	vertic	*X*	-	29.0	28.5	42.5	285	48.6
		SD	-	12.7	9.19	3.54	42.4	7.21
		CV (%)	-	43.9	32.2	8.30	14.9	14.8
	parent material	*X*	-	15.7	28.3	56.0	223	35.8
		SD	-	12.5	12.0	21.7	69.0	12.9
		CV (%)	-	79.8	42.4	38.8	30.9	36.2
Statistically significant differences				umbric > parent material		umbric < vertic, parent material		umbric > parent material
Gleyic Chernozem	mollic	*X*	26.7	27.4	46.1	26.5	246	42.9
		SD	13.3	11.2	7.98	7.09	40.6	6.44
		CV (%)	49.8	40.8	17.3	26.8	16.5	15.0
	parent material 1	*X*	-	19.7	34.0	46.3	165	29.7
		SD	-	14.7	8.76	18.8	39.4	10.1
		CV (%)	-	74.5	25.8	40.6	23.9	34.1
	parent material 2	*X*	-	22.8	33.0	44.2	119	22.6
		SD	-	21.3	6.36	21.7	22.2	7.15
		CV (%)	-	93.6	19.3	49.2	18.6	31.6
Statistically significant differences					mollic > parent material 1, 2	mollic < parent material 1	mollic > parent material 1, 2	mollic > parent material 1, 2
Haplic Luvisol	umbric	*X*	28.5	39.5	38.5	22.0	352	66.9
		SD	21.0	2.12	3.53	5.65	38.9	4.10
		CV (%)	73.8	5.40	9.20	25.7	11.0	6.10
	luvic	*X*	-	43.0	41.0	16.0	327.5	57.7
		SD	-	1.41	1.41	0.32	3.54	0.14
		CV (%)	-	3.30	3.40	2.00	1.10	0.20
	argic	*X*	-	27.0	38.5	34.5	277	49.9
		SD	-	2.83	10.6	7.78	46.0	1.91
		CV (%)	-	10.5	27.5	22.6	16.6	3.80
	parent material	*X*	-	44.3	30.5	25.2	241	38.2
		SD	-	9.29	9.26	5.19	30.1	7.62
		CV (%)	-	21.0	30.4	20.6	12.5	12.1

cont. Table 1

1	2	3	4	5	6	7	8	9
Statistically significant differences				argic < umbric, luvic, parent material			parent material < umbric, luvic	umbric, luvic > argic, parent material
Vertic Eutric Cambisol	mollic		14.2	25.0	38.0	37.0	330	63.8
	cambic		-	15.0	46.0	39.0	285	51.2
	parent material		-	130.	59.0	28.0	245	43.4
Haplic Gleysol	mollic		15.7	38.0	48.0	14.0	265	46.0
	gleyic horizon 1		-	30.0	41.0	29.0	210	39.5
	gleyic horizon 2		-	7.00	60.0	33.0	170	33.2

x – mean, SD – standard deviation, CV – coefficient of variation

The highest amount of calcium carbonates in parent material was observed in Vertic Cambisol (16.9%). The mean content of calcium carbonate in Eutric Vertisol ranged from 1.2% in epipedons to 11.2% in parent materials, whereas in Vertisol (Mollic) it was lower: 0.6-7.6% (Figure 2). The epipedons of Vertisol (Dystric), Haplic Luvisol, Gleyic Chernozem and Haplic Gleysol did not contain calcium carbonates, whereas the parent materials contained only small amounts of calcium carbonates. In Mollic Vertisol, Gleyic Chernozem and Haplic Gleysol, gleyic processes (redoximorphic features) occurred just under the epipedons.

The soil reaction in the humus horizon of these soils ranged from strongly acidic in Vertisol (Dystric) – pH_{KCl} 3.5 to neutral in Vertisol (Mollic) – pH_{KCl} 6.7. Vertically (in a soil profile) pH values were increasing with the depth, which was due to the presence of calcium carbonates in the parent material and overlying horizons. (Figure 2). The highest cation exchange capacity (CEC) amounting to 28.0 cmol(+) kg^{-1} and the sum of base (calcium, magnesium, sodium, potassium) cations (SBC) amounting to 26.5 cmol(+) kg^{-1} were stated in humus horizons of Vertisol (Mollic and Eutric) and in the Vertic Cambisol profile. Base saturation (BS) in these soils exceeded 94.9%. In humus horizons of Vertisol (Dystric), the values of CEC, BS and SBC were considerably lower (CEC – 14.0 cmol(+) kg^{-1}, SBC – 5.1 cmol(+) kg^{-1}, BS – 37.0%). In all the studied soils, CEC and BS values were increasing with the depth (Figure 2).

As a result of high amounts of swelling minerals in the clay fraction and high soil moisture, the soils had distinctive redoximorphic features. The analyses of the redox potential (Eh) and oxygen diffusion rate (ODR) were low, which suggests anaerobic conditions in these soils (Table 1). The mean ODR

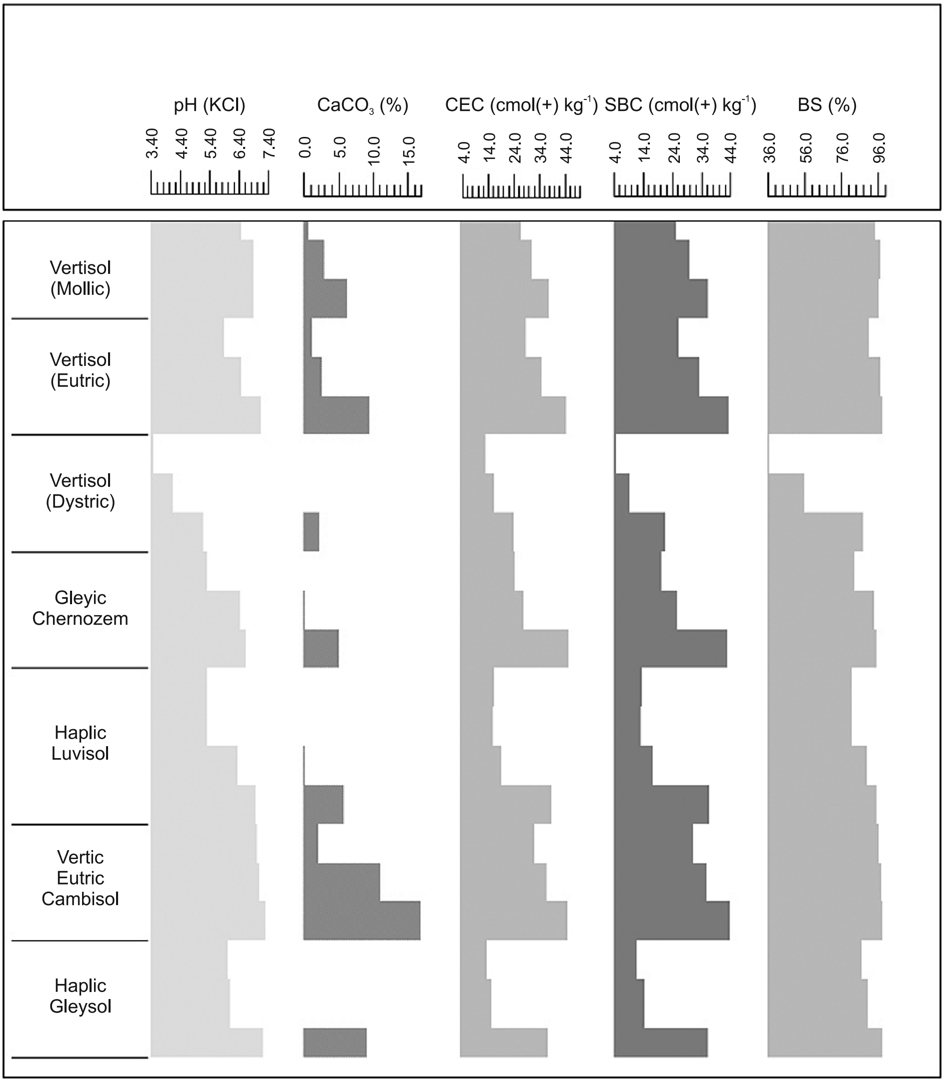

Fig. 2. Sorptive properties of the soils

value was the highest (66.9 μg m^{-2} s^{-1}) in the humus horizon of Haplic Luvisol, and the lowest (42.9 μg m^{-2} s^{-1}) in Gleyic Chernozem. In the subsurface horizons of Gleyic Chernozem, the value of ODR was up to 35.0 μg m^{-2} s^{-1}. The values of Eh and ODR were decreasing vertically, with the depth of a soil profile.

Haplic Luvisols contained similar amounts of total iron in soil horizons, which was revealed by low values of the coefficient of variance (CV). Similar relations were observed in Vertisol (Eutric). The most variable amounts of iron occurred in the umbric horizons of Vertisol (Dystric) – CV from 52.2%

for Fe_c to 73.6% for Fe_s. Variation was observed within the soil profile and between the soil types. The content of total iron in the humus horizons of the soils ranged from 18.85 g kg^{-1} in Haplic Gleysol to 39.75 g kg^{-1} in Vertisol (Mollic), whereas the total content of manganese was 50- to 90-fold lower than that of iron. The content of manganese in the soils ranged from 0.20 g kg^{-1} in Haplic Gleysol to 0.52 g kg^{-1} in Vertisol Eutric (Table 2). The vertical distribution of Mn_t, in the soils, except for Vertisol (Dystric) and Haplic Gleysol, was similar. Correlation coefficients revealed statistically significant positive relationships between the content of total iron and manganese ($r = 0.295$) as well as manganese and Eh values ($r = 0.262$) – Table 3.

Table 2

Total manganese and forms of iron in the soils

Soil	Horizon	Value	Mn_t	Fe_t	Fe_d	Fe_o	Fe_c	Fe_s	Fe_o/Fe_d	Fe_d/Fe_t
			(g kg^{-1})							
1	2	3	4	5	6	7	8	9	10	11
Vertisol (Mollic)	mollic	X	0.49	39.7	7.65	3.24	4.41	32.19	0.43	0.20
		SD	0.08	12.7	1.80	1.23	2.34	12.0	0.19	0.05
		CV (%)	16.3	31.8	23.5	38.0	53.1	37.4	44.2	25.0
	vertic	X	0.58	44.9	10.2	2.94	7.28	34.6	0.28	0.23
		SD	0.24	7.29	1.03	2.35	1.45	6.28	0.20	0.01
		CV (%)	41.4	16.2	10.1	79.9	19.9	18.1	71.4	4.3
	parent material	X	0.46	42.5	7.76	2.04	5.72	34.7	0.26	0.18
		SD	0.10	3.42	3.49	1.55	2.13	3.50	0.08	0.07
		CV (%)	21.7	8.10	45.0	76.0	37.2	10.1	30.8	38.9
Statistically significant differences					vertic > mollic					
Vertisol (Eutric)	mollic	X	0.52	34.1	7.54	3.01	4.52	26.5	0.40	0.23
		SD	0.13	8.00	0.01	1.09	0.96	7.93	0.11	0.07
		CV (%)	25.0	23.5	0.10	36.2	21.2	29.9	27.5	30.4
	vertic	X	0.51	43.6	7.85	1.94	5.91	35.8	0.25	0.18
		SD	0.04	6.37	0.74	0.61	1.16	7.02	0.09	0.04
		CV (%)	7.8	14.6	9.40	31.4	19.6	19.6	36.0	22.2
	parent material	X	0.46	42.6	6.84	1.35	5.49	35.7	0.20	0.16
		SD	0.05	4.78	1.43	0.22	1.32	3.46	0.04	0.02
		CV (%)	10.9	11.2	20.9	16.3	24.0	9.70	20.0	12.5

cont. Table 2

1	2	3	4	5	6	7	8	9	10	11
Statistically significant differences						mollic > parent material			mollic > parent material	
Vertisol (Dystric)	umbric	X	0.44	31.7	3.52	2.18	1.34	28.2	0.61	0.12
		SD	0.43	23.0	2.21	1.51	0.70	20.8	0.05	0.01
		CV (%)	97.7	72.3	62.8	69.3	52.2	73.6	8.20	8.30
	vertic	X	0.19	37.5	7.29	2.71	4.58	30.2	0.37	0.19
		SD	0.08	5.65	0.27	0.23	0.50	5.39	0.04	0.02
		CV (%)	42.1	15.1	3.70	8.50	10.9	17.8	10.8	10.5
	parent material	X	0.51	44.2	8.49	1.97	6.53	35.7	0.24	0.19
		SD	0.23	8.38	3.07	0.32	3.15	6.15	0.09	0.04
		CV (%)	45.1	19.0	36.2	16.2	48.2	17.2	7.5	21.1
Statistically significant differences							umbric < vertic, parent material		umbric > vertic, parent material	
Gleyic Chernozem	mollic	X	0.51	31.8	7.93	4.32	3.61	23.9	0.55	0.25
		SD	0.30	6.22	2.31	1.20	1.38	4.94	0.08	0.05
		CV (%)	58.8	19.6	29.1	27.8	38.2	20.7	14.5	20.0
	parent material 1	X	0.30	40.0	7.03	2.49	4.54	32.9	0.37	0.18
		SD	0.14	8.95	1.32	0.52	1.63	8.70	0.11	0.05
		CV (%)	46.7	22.4	18.8	20.9	35.9	26.4	29.7	27.8
	parent material 2	X	0.31	34.3	5.82	1.60	4.22	28.5	0.32	0.16
		SD	0.15	13.12	2.85	0.53	2.51	10.95	0.11	0.05
		CV (%)	48.4	38.3	49.0	33.1	59.5	38.5	34.4	31.3
Statistically significant differences						mollic > parent material 1, 2			mollic > parent material 1, 2	mollic > parent material 2

cont. Table 2

1	2	3	4	5	6	7	8	9	10	11
Haplic Luvisol	umbric	X	0.45	22.0	5.30	2.50	2.80	16.7	0.48	0.24
		SD	0.02	1.98	0.75	0.24	0.51	1.23	0.03	0.02
		CV (%)	4.4	9.00	14.2	9.60	18.2	7.40	6.30	8.30
	luvic	X	0.42	21.5	5.16	2.38	2.78	16.0	0.45	0.17
		SD	0.03	2.41	0.46	0.10	0.55	1.55	0.08	0.06
		CV (%)	7.1	11.2	8.90	4.20	19.8	9.70	17.8	35.3
	argic	X	0.37	47.1	5.99	3.44	2.56	41.2	0.58	0.12
		SD	0.09	0.57	0.34	0.92	1.25	1.33	0.18	0.01
		CV (%)	24.3	1.20	5.70	26.7	48.8	3.20	31.0	8.30
	parent material	X	0.38	27.1	3.89	1.14	2.75	23.1	0.29	0.15
		SD	0.02	7.18	0.41	0.38	0.43	6.80	0.10	0.02
		CV (%)	5.3	26.5	10.5	33.3	15.6	29.4	34.5	13.3
Statistically significant differences				argic >umbric, luvic, parent material	parent material < umbric, luvic, argic	parent material < umbric, luvic, argic		argic > umbric, luvic, parent material		umbric > argic, parent material
Vertic Eutric Cambisol	mollic		0.56	35.2	6.92	1.81	5.11	28.3	0.26	0.20
	cambic		0.57	28.1	7.52	1.46	6.06	20.6	0.19	0.27
	parent material		0.51	42.9	7.51	1.29	6.22	35.4	0.17	0.17
Haplic Gleysol	mollic		0.20	18.8	6.19	2.42	3.77	12.7	0.39	0.33
	gleyic horizon 1		0.15	34.1	6.38	2.74	3.64	27.7	0.43	0.19
	gleyic horizon 2		0.56	44.2	10.2	1.04	9.16	34.0	0.10	0.23

Fet, Mnt – total content of Fe and Mn, Fed – free iron oxides, Feo – amorphous iron oxides, Fec – crystalline iron content, Fes – silicate forms, Feo/Fed – activity index of iron compound, Fed/Fet – mobility index of iron compounds

The content of free iron oxides (Fe_d) in humus horizons was similar and ranged from 5.30 to 7.93 g kg^{-1}, and it was lower only in the umbric horizon of Vertisol Dystric, where it equalled 3.52 g kg^{-1} (Table 2). The highest amounts of Fed were recorded in the horizons rich in the clay fraction (argic,

Table 3

Distribution indices of Fe_t, Fe_d and Fe_o

Soil type	Fe_t		Fe_d		Fe_o	
Vertisols	vertic /mollic[#]	parent material / mollic	vertic /mollic	parent material / mollic	vertic / mollic	parent material /mollic
Mollic	1.13	1.07	1.34	1.02	0,91	0.63
Eutric	1.28	1.25	1.05	0.91	0.65	0.45
Vertisol Dystric	vertic /umbric	parent material /umbric	vertic /umbric	parent material /umbric	veritc /umbric	parent material / umbric
	1.19	1.40	2.08	2.42	1.25	0.91
Gleyic Chernozem	parent material1 / mollic	parent material2 / mollic	parent material1 / mollic	parent material2 / mollic	parent material1 / mollic	parent material2 / mollic
	1.26	1.08	0.89	0.74	0.58	0.37
Haplic Luvisols	argic / umbric	parent material / umbric	argic / umbric	parent material / umbric	argic / umbric	parent material / umbric
	2.14	1.24	1.13	0.74	1.38	0.46
Vertic Eutric Cambisol	cambic / mollic	parent material / mollic	cambic / mollic	parent material / mollic	cambic / mollic	parent material / mollic
	0.80	1.22	1.09	1.09	0.81	0.72
Haplic Gleysol	gleyic1 / mollic	gleyic2 / mollic	gleyic1 / mollic	gleyic2 / mollic	gleyic1 / mollic	gleyic2 / mollic
	1.81	2.35	1.03	1.65	1.14	0.43

[#] ratio in horizons

vertic) in Haplic Luvisol, Vertisol (Mollic and Eutric). Beside the Fed content, the intensity of weathering can be described by the Fe_d/Fe_t, ratio (the weathering index), which ranged between 0.12 and 0.33 in the soils. The highest values of this ratio were noted in the humus horizons of Vertisol (Eutric), Gleyic Chernozem, Haplic Luvisol and Haplic Gleysol.

The content of Fe_o varied and ranged from 1.14 g kg^{-1} in the soil parent material of Haplic Luvisol to 4.32 g kg^{-1} in the humus horizon of Gleyic Chernozem. In the profiles of Vertisol (Mollic), Vertisol (Eutric), Gleyic Chernozem and Vertic Eutric Cambisol, the highest amounts of Fe_o were noted in the humus horizons (from 1.81 g kg^{-1} to 4.32 g kg^{-1}). The iron activity ratio Fe_o/Fe_d varied from 0.10 to 0.61 in the soils (Table 2). In the humus horizons, the share of silicate iron (Fe_s) in total iron (Fe_t) ranged from 0.67 in Haplic Gleysol to 0.88 in Vertisol (Dystric). The soil parent materials contained considerably more silicate iron.

DISCUSSION

Soils with high content of clay minerals are very fertile, but shrink and swell as their moisture content changes. Clay minerals adsorb water and increase in volume when they are wet, but as they become dry, they shrink and cause cracks (sometimes large and deep). As a result of pedogenic processes, in the basins of ice-dammed lake origin studied here, typical soil types were formed. They do not form vast complexes but occur in various geomorphological configurations in association with other soil types.

The results of Eh and ODR determinations suggest anaerobic conditions in the soils studied. The Eh values exceeded 300 mV only in the humus horizons of Vertisol (Eutric), Vertisol (Dystric), Haplic Luvic and Vertic Cambisol. This is a conventional threshold value between the oxygenated state and reduction conditions in soil. Below this value, intensive reduction of iron and manganese occurs. Under more iron reducing conditions, soils simultaneously undergo acidification and present decreasing Eh values. However, pH values are of greater importance than Eh values (Atta et al. 1996). An ODR value which is no higher than 35.0 mg m^{-2} s^{-1} suggests a possibly insufficient oxygen supply for the root system of cultivated plants, as this is the boundary value of oxygenation (Gliński et al. 2000). Such values were stated in some subsurface horizons. A high water content in soil and the presence of swelling clay minerals with a small volume of aeration pores favour gleyic processes, which is also confirmed by the redoximorphic features.

No differences in the content of total iron and total manganese were noted between the sites studied. However, such differences occurred between the soil types. Beside the total content of iron, the vertical distribution of various iron forms in a soil profile is also of great importance. Transformations of iron compounds occur under soil-forming processes.

High amounts of Fe_d in soil horizons are not a result of weathering but are caused by illuviation. Since hydrous Fe oxides have very small particle sizes and are often associated with clay minerals (Kämpf et al. 2000), the Fe_d concentration in the analysed soils correlated well with the clay fraction content ($r = 0.528$). Contents of Fe_t, Fe_s, Fe_c and Fe_d were significantly positively correlated with the clay content (Table 3). The higher content of Fe_d in the surface horizons as compared to the parent material was the results of more intensive weathering. In the surface horizons of Vertisol (Mollic and Eutric), amounts of free iron were 2-fold higher than in Vertisol (Dystric), which suggests a more favourable influence of soil reaction (pH_{KCl} 6.0-6.7) on the intensity of Fe transformations (Table 2). The content of Fed in the parent material varied. The lowest Fe_d content was stated in the parent material containing $CaCO_3$. This proves the influence of geochemical conditions on the form of iron oxides in the soils studied (Mocek1988).

The values of the weathering index (Fe_d/Fe_t) were low, which suggests that the soils are young. According to Arduino et al. (1986), the intensity of the weathering of soils formed in similar climatic and soil conditions is correlated with their age.

Free iron may occur in soil in the crystalline (Fe_c) or amorphous oxides (Fe_o), which are most labile and active forms of irons (Schwertmann 1964). Increased amounts of Fe_o in soil horizons may be a result of the organic matter content and temporary anaerobic conditions, which inhibit crystallisation of iron oxides (Alamdari et al. 2010). The majority of free iron compounds in the soils studied was in the crystalline form (Fe_c). The subsurface horizons and soil parent material contained more Fe_c than the surface humus horizons, which suggests that the conditions for crystallisation of iron oxides are unfavourable in humus horizons.

The transformations of Fe compounds can also be studied on the basis of the iron activity ratio Feo/Fed, which determines the relation between most active forms of iron and its non-silicate forms (Schwertmann 1964). High mean values of Fe_o/Fe_d ratio in humus horizons (0.40-0.61) suggest predominance of iron oxides with poorly ordered structure and a slow rate of iron crystallisation. The Fe_o/Fe_d ratio tends to decrease with the soil age (Moody, Graham 1995). The absence of a clear time trend of the Fe_o/Fe_d ratio can be explained by other factors (in this case, redox processes and organic matter content) having greater impact on the Fe_o/Fe_d ratio than the time factor. Distribution of iron in Haplic Luvisols is a result of pedogenesis, as higher

Table 4

Correlation coefficients between the soil properties studied (* significant at $\alpha = 0.05$)

Specification	Mn_t	Fe_t	Fe_d	Fe_o	Fe_c	Fe_s
OC	-0.492*	0.175	0.248	0.352	0.059	0.134
2.0-0.05	-0.295*	-0.692*	-0.581*	0.121	-0.685*	-0.631*
0.05-0.02	-0.164	-0.458*	-0.315*	0.269*	-0.495*	-0.437*
0.02-0.002	0.089	-0.036	-0.046	-0.086	0.010	-0.028
0.05-0.002	0.025	-0.204	-0.161	0.017	-0.173	-0.189
<0.002	0.192	0.637*	0.528*	-0.098	0.611*	0.584*
Eh	0.262*	-0.179	-0.153	0.171	-0.272*	-0.163
ODR	0.207	-0.196	-0.187	0.223	-0.335*	-0.173
Mn_t	1.000	0.295*	0.321*	0.081	0.289*	0.248*
Fe_t	-	1.000	0.613	0.161	0.552*	0.975*
Fe_d	-	-	1.000	0.373*	0.832*	0.424
Fe_o	-	-	-	1.000	-0.196	0.081
Fe_k	-	-	-	-	1.000	0.400*
Fe_s	-	-	-	-	-	1.000

values of the distribution index in argic/umbric horizon in comparison to the values of the distribution index in the parent material/umbric horizon indicate accumulation of iron in the illuvial horizon, typical of this type of soils (Table 4). Lithogenic accumulation of iron occurred in Haplic Gleysol and Gleyic Chernozem, which may be associated with groundwater gleyic processes. The study of Mocek (1988) also proved strong influence of air-water conditions on the content of various iron forms in Vetisols.

CONCLUSIONS

1. Soils formed from glaciolimnic sediments of ice-dammed lake origin in north-eastern Poland are Vertisol (Mollic, Eutric and Dystric), Gleyic Chernozem, Haplic Luvisol, Vertic Eutric Cambisol and Haplic Gleysol.
2. Relatively low values of the Fe_d/Fe_t ratio suggest that the soils studied are young and the features of soil forming processes are merely marked.
3. Higher values of the Fe_o/Fe_d ratio suggest higher activity of soil forming processes and younger age of soil material in humus horizons.
4. Lower values of the Fe_o/Fe_d ratio in the parent material than in overlying soil horizons suggest higher crystallisation of iron oxides.
5. In Vertisol (Dystric) and Haplic Gleysol, lithogenic accumulation of iron was observed; whereas in Haplic Luvisol pedogenic iron was accumulated.

REFERENCES

Alamdari P., Jafarzadeh A.A., Oustan S., Toomanian N. 2010. *Iron oxide forms and distribution in a transect of Dasht-e-Tabriz soils, northwest Iran*. J. Food Agric. Environ., 8: 976-979.

Arduino E., Berberis E., Marsan F.A., Zanini E., Franchini M. 1986. *Iron oxides and clay minerals within profiles as indicators of soil age in Northern Italy*. Geoderma, 37: 45-55.

Atta S.K.H., Mohammed S.A., Van Cleemput O., Zayed A. 1996. *Transformations of iron and manganese under controlled Eh, Eh-pH conditions and addition of organic matter*. Soil Technol., 9: 223-237.

Bockheim J.G., Gennadiyev A.N., Hammer R.D., Tandarich J.P. 2005. *Historical development of key concepts in pedology*. Geoderma, 124: 23-36.

Bourennane H., Douay F., Sterckeman T., Villanneau E., Ciesielski H., King D., Baize D. 2010. *Mapping of anthropogenic trace elements inputs in agricultural topsoil from Northern France using enrichment factors*. Geoderma, 157: 165-174.

Davranche M., Bollinger J.C. 2000. *Release of metals from iron oxyhydroxides under reductive conditions: Effect of metal/solid interactions*. J. Colloid Interf. Sci., 232: 165-173.

Długosz J., Orzechowski M., Kobierski M., Smólczyński S., Zamorski R. 2009. *Clay minerals from Weichselian glaciolimnic sediments of the Sępopolska Plain (NE Poland)*. Geol. Carpath., 60: 263-267.

Gliński J., Stępniewski W., Stępniewska Z., Ostrowski J., Włodarczyk T., Brzezińska M. 2000. *Agroecological apects of aerobic conditions of arable soils*. Acta Agroph., 32: 1-87. (in Polish)

IUSS Working Group WRB. 2015. *International soil classification system for naming soils and creating legends for soil maps*. World Reference Base for Soil Resources 2014, update 2015. World Soil Resources Reports No. 106.

Kämpf N., Scheinost A.C., Schulze D.G. 2000. *Oxide minerals*. In: *Handbook of soil science*. Sumner M.E. (Ed). CRC Press, Boca Raton, FL.

Kobierski M., Dąbkowska-Naskręt H. 2012. *Local background concentration of heavy metals in various soil types formed from glacial till of the Inowrocławska Plain*. J. Elem., 17: 560-585.

Lack J.G., Chaudhuri S.K., Chakraborty R., Achenbach L.A., Coates J.D. 2002. *Anaerobic biooxidation of Fe(II) by Dechlorosoma Suillum*. Microb. Ecol., 43(4): 424-431.

McFadden L.D., Hndricks D.M. 1985. *Changes in the content and composition of pedogenic iron oxyhydoxides in a chronosequence of soils in southern California*. Quaternary Res., 23: 189-204.

Mehra O.P., Jackson M.L. 1960. *Iron oxide removal from soils and clays by a dithionate citrate system with sodium bicarbonate*. Clay Miner, 7: 313-327.

Mocek A. 1988. *Iron in Vertisols and Mollisols from Shahrazoor and Raniya in north-eastern Iraq*. Rocz. Glebozn. (Soil Sci. Annu.), 39(3): 45-55. (in Polish)

Moody L.E., Graham R.C. 1995. *Geomorphic and pedogenic evolution in coastal sediments, central California*. Geoderma, 67: 181-201.

Morawski W. 2005. *Warmia paleogeographic province of Pleistocene (north-eastern Poland)*. Prz. Geogr., 53: 477-488. (in Polish)

Schwertmann U. 1964. *Differenzierung der Eisenoxide des Bodens durch Extraktion mit Ammoniumoxalat-Lösung*. J. Plant Nutr. Soil Sci., 105(3): 194-202.

Straub K., Benz M., Schink B. 2001. *Iron metabolism in anoxic environments at near neutral pH*. FEMS Microbiol. Ecol., 34: 181-186.

van Reeuwijk L.P. 2002. *Procedures for Soil Analysis*. 6th ed. ISRIC, Wageningen, Netherlands.

Waychunas G.A., Kim C.S., Banfield J.F. 2005. *Nanoparticulate iron oxide minerals in soils and sediments: unique properties and contaminant scavenging mechanisms*. J. Nanopart. Res., 7: 409-433.

Wheeler D.B., Thompson J.A., Bell J.C. 1999. *Laboratory comparison of soil redox conditions between red soils and brown in Minnesota, USA*. Wetlands, 19: 607-616.