

Orzechowski M., Smólczyński S., Kalisz B., Długosz J., Sowiński P. 2020. Chemical and mineralogical composition of the Holocene soil sediments in north-eastern Poland. J. Elem., 25(2): 471-485. DOI: 10.5601/jelem.2019.24.4.1881

RECEIVED: 18 June 2019 ACCEPTED: 14 November 2019

ORIGINAL PAPER

CHEMICAL AND MINERALOGICAL COMPOSITION OF THE HOLOCENE SOIL SEDIMENTS IN NORTH-EASTERN POLAND*

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Abstract

The Holocene sediments in north-eastern Poland are represented by mineral (alluvial and deluvial) and mineral-organic, as well as organic soil formations - peat, mursh and gyttja. The aim of the research was to determine the total content of selected elements and to investigate the mineralogical composition of the clay fraction of various Holocene sediments in north-eastern Poland. For the study, 288 soil samples were collected and total concentrations of Ca, Mg, Na, K, P, Fe, Mn, Zn, Cu after digestion in a mixture of HClO₄ and HNO₃ were analysed. Mineralogical composition of the clay fraction was analysed by the X-ray diffraction method. The highest average content of Fe, Mn and Zn was found in alluvial sediments in river valleys. The lowest average Mg, K, P, Fe, Mn, and Cu content was determined in mineral sediments in the moraine landscape. The content of the elements in sediments of alluvial river valleys was positively correlated with the amount of clay fraction and, except Mn, with the amount of TOC, whereas in deluvial sediments, only the Fe content correlated with the amount of clay fraction. The highest accumulation of Mg, K, Zn and Cu was found in mineral-organic sediments, while the highest Ca was in peat and gyttja. In alluvial formations in the riverine landscape, minerals from the group of mixed-packet minerals of illite-smectite dominated, with the content of smectite packages being in the range of 60-90% S. There were also small amounts of minerals from the group of illite and kaolinite. In the moraine landscape and in the landscape of ice-dammed lake origin, illite minerals dominated in the clay fraction of deluvial sediments. The presence of smectites, illite-smectite mixed-packet minerals and pedogenic chlorites was also stated. The mineralogical composition of the clay fraction of the Holocene deluvial sediments was similar to the composition of the Pleistocene accumulation sediments.

Keywords: alluvial and deluvial deposits, mursh, peat, gyttja, macro- and microelements.

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* The research was financed by University of Warmia and Mazury in Olsztyn, Department of Soil Science and Reclamation (statutory research).

INTRODUCTION

North-eastern Poland, like some other parts of Europe, had started its current development during Vistulian Glaciation (Weichsel Glacial Stage, Vistula Glacial Stage) and now represents young glacial landscape. It stands out among other (older) areas because of its morphogenesis, lithogenesis and soil cover. This landscape was formed by the deposition of material from the glacier during Pleistocene, but the final shape was reached during the Holocene (KONDRACKI 2009).

In northern Europe, during postglacial period, processes of natural and anthropogenic denudations occurred at various intensity levels. They contributed to the mosaic soil cover and heterogeneity of soil formations (FRIELINGHAUS, SCHMIDT 1991). Soil material was washed off, slipped from the slope and deposited in the depressions. Consequently, deluvial soils, mursh-like soils and silted peat-mursh soils were formed during the Holocene. Deluvial soils, due to their location in a relief, between eroded soils and soils of depressions, are the first biogeochemical barrier for chemical compounds flowing along the slope. A similar role is played by alluvial soils which are formed by alluvial sediments in delta and riverine landscapes. Under the influence of natural and anthropogenic processes of denudation and land reclamation, soil cover in young glacial landscape was changed, and the properties and chemical composition of the soils were modified (KALISZ, ŁACHACZ 2009, KALISZ et al. 2010).

The lithology and genesis of the Holocene sediments, which deposited from preboreal to subatlantic periods (i.e. during last 10,000 years) are diverse. The Holocene mineral deposits are represented by dune sands, silts of ice-dammed lakes origin, gyttjas, alluvial and deluvial deposits as well as organic formations – peats, detrital gyttjas and muck. These deposits are a record of the Holocene climatic changes, and they play a major role in the circulation of nutrients (ILNICKI, ZEITZ 2003). The Holocene genesis is connected with several issues: (a) translocation of deluvial deposits from the upper slope and its aggradations in the lower parts; (b) sedimentation of alluvial deposits; and (c) accumulation of organic matter in wetlands and water bodies. Deluvial sediments in north-eastern Poland are young. In Central Europe, the onset of deposition of similar sediments is dated to 5,800 years BP (STARKEL 1989). The thickness and growth rate of deluvial deposits do not depend on the time of deposition, but mainly on granular size, slope gradient and local conditions. The scale and time shift of the onset of formation of deluvium was associated with local, selective interception of land for agricultural use (i.e. grazing, plowing) (SMOLSKA, SZWARCZEWSKI 2008).

The purpose of this paper is to describe the chemical and mineralogical composition of sediments and soils developed from the Holocene deposits in north-eastern Poland. Only typical selected sediments in some typical landscapes of young glacial area were included in the research.

MATERIAL AND METHODS

Taking into consideration the topography and lithological characteristics of young glacial landscape, the following zones or types of young glacial landscape can be distinguished: moraine landscape, landscape of ice-dammed lakes origin and riverine landscape (KONDRACKI 2009). In these zones, study sites were located (Figure 1) and 288 soil samples were collected (Table 1). The soil samples were divided into mineral (up to 10% of organic matter),



1 - landscape of ice-dammed lakes origin

2 – moraine landscape

3 - riverine landscape

Fig. 1. Location of the study area

mineral-organic (10-20% of organic matter) and organic (> 20% of organic matter). In the moraine zone, land denivelations range from 5 m to 10 m, and the slope gradient exceeds 7°. Slopes are usually short, with various shapes. Geomorphologically, this type of relief represents rolling ground moraines with numerous hills of frontal moraines and large number of depressions of dead-ice origin filled with lake waters or converted into wetlands. The Holocene deluvial sediments frequently occur in lower parts of slopes and depressions, and they usually cover peat formations. In the zone of ice-dammed lakes origin, land denivelations reach 5 m with a small

Table 1

Holocene sediments	Number of samples					
Riverine landscape						
Mineral alluvial	63					
Mineral-organic	12					
Gyttja	17					
Organic (mursh and peat)	13 and 49					
Moraine landscape						
Mineral deluvial	21					
Mineral-organic	16					
Organic (mursh and peat)	19 and 30					
Landscape of ice-dammed lakes origin						
Mineral deluvial	19					
Mineral-organic	9					
Organic (mursh and peat)	12 and 8					

Number and types of the analysed soil samples

slope gradient of 2° to 7° . The area is a vast lowland basin devoid of welldeveloped moraines and lakes. Geomorphologically, this area represents a flat ground moraine. Processes of denudation are less common than in the morainic area. This zone is characterized by clay sediments rich in swelling clay minerals, which formed soils classified as Vertisols and Gleyic Phaeozems (DŁUGOSZ et al. 2009*a*). In the riverine landscape, alluvial sediments, gyttjas and peats were accumulated. Alluvial deposits found in the deltas of the Vistula and Pasłęka river form a Holocene plain shaped by overflowing river waters. It is the newest genre of landscape, which has been forming for about 5,000 years, and which is distinguished from the previously discussed landscapes by the origin, flat land, low location, and low groundwater table (PIAŚCIK et al. 2001). Holocene deposits of north-eastern Poland were a parent material for alluvial, deluvial, peat and peat-mursh soils.

The following laboratory analyses were carried out in the collected soil samples: texture by the Bouyoucos-Cassagrande method modified by Prószyński, loss-on-ignition at 550°C as a measure of organic matter content (only for the identification of mineral, mineral-organic and organic soil formations), total organic carbon (TOC) by the potassium dichromate method, soil pH potentiometrically in H_2O and KCl (1 M dm⁻³). Total content of Ca, Mg, K, P, Na, Fe, Mn, Zn and Cu was measured after digestion in a mixture of HClO₄ and HNO₃ (VAN REEUWIJK 2002). Calcium, potassium and sodium was measured photometrically on a Jenway flame photometer, phosphorous was analysed colorimetrically on a Specol EK 1 spectrocolorimeter, and magnesium was measured on an AAS 1 Zeiss Jena analyzer. The total content of Fe, Mn, Zn and Cu was analysed by atomic absorption spectrometry techniques using a 30 Zeiss Jena analyser.

Analysis of the clay fraction was carried out for: alluvial sediments taken from the Vistula delta (location: Stara Kościelnica - 54°13'58.6"N, 18°59'18.6"E) and which were formed from silt loam (SiL), deluvial sediments in the moraine landscape (location: Prusinowo - 53°42′27.3"N, 21°05′30.3"E) which had loam (L) texture, deluvial sediments and Pleistocene glaciolimnic sediments in the landscape of ice-dammed lakes origin (location: Reszel $-54^{\circ}02'43.7''$ N, 21°18′08.5″E) which had clay (C) texture – according to the USDA classification (2015). The mineralogical composition of clay fraction (< 2 μ m) of alluvial, deluvial and parent materials was determined by X-ray diffractometry using HZG-4 X-ray diffractometer with a CuKα lamp and nickel filter. The clay fraction was isolated on a Buckmann centrifuge after pre-treatment according to the Jackson method (JACKSON 1975) and Na-ionite dispersion (GONET, CIESLA 1988). The samples of the clay fraction were saturated with magnesium ions (Mg^{2+}), which were then solvated with ethylene glycol (Mg + EG), potassium (K^+), which in the next stage was heated at 300°C and 550°C. Based on the diffractograms obtained, a qualitative analysis and analysis of the structure of the illite/smectite mixed-packet minerals were carried out using the method developed by SRODON (1980, 1981, 1984). Interpretation of composite reflections was performed using the Lorenz and Gauss distributions and ORIGIN 7.0 software. Statistical analyses were carried out using Statistica 8.0.

RESULTS AND DISCUSSION

Among mineral sediments, the highest mean content (30.2%) of the clay fraction (< 0.002 mm) was confirmed in deluvial sediments in the landscape of ice-dammed lakes origin and alluvial sediments in riverine landscape 26.1% (Table 2). Alluvial sediments contained over 50% of the silt fraction. Deluvial sediments in the landscape of ice-dammed lakes origin contained twice as much TOC (35.8 g kg⁻¹) as deluvial sediments in moraine landscape. The reaction of the studied Holocene sediments ranged from acidic to neutral. The highest values of pH were found in deluvial sediments in the landscape of ice-dammed lakes origin (pH 5.8-6.9).

Chemical composition

Among the analysed mineral sediments, the highest mean content of Ca – 11.1 g kg⁻¹, Mg – 5.9 g kg⁻¹, K – 6.3 g kg⁻¹, P – 1.3 g kg⁻¹ and Cu – 20.4 mg kg⁻¹ was determined in deluvial sediments in the landscape of ice-dammed lakes origin, whereas alluvial deposits in the riverine landscape had the highest mean amounts of Fe – 31.7 g kg⁻¹, Mn – 694.1 mg kg⁻¹ and Zn – 93.4 mg kg⁻¹ (Table 3). The least amounts of Mg – 4.2 g kg⁻¹, K – 4.2 g kg⁻¹, P – 0.7 g kg⁻¹, Fe – 19.7 g kg⁻¹, Mn – 405.8 mg kg⁻¹ and Cu – 10.1 mg kg⁻¹ were in mineral sediments in the moraine landscape.

		Alluvial sediments	Deluvial sediments		
Specification	Value	riverine landscape	moraine landscape	landscape of ice-dammed lakes origin	
% fraction (mm)	mean	17.6	58.8	27.6	
2.0-0.05	SD	10.14	17.05	8.27	
Sand	CV (%)	57.7	29.0	30.0	
	mean	56.3	33.6	42.2	
0.05-0.002	SD	10.64	7.80	7.28	
Silt	CV (%)	18.9	23.2	17.3	
	mean	26.1	7.6	30.2	
< 0.002	SD	14.64	6.60	13.95	
Clay	CV (%)	56.1	86.9	46,2	
	mean	18.7	18.0	35.8	
TOC (g kg ⁻¹)	SD	9.45	13.71	25.07	
	CV (%)	50.6	76.2	70.1	
	mean	5.3	5.7	6.2	
pH (KCl)	min	4.8	4.5	5.8	
	max	6.8	7.1	6.9	

Basic properties of the analysed Holocene sediments

 $\mathrm{SD}-\mathrm{standard}$ deviation, $\mathrm{CV}-\mathrm{coefficient}$ of variation

The content of these elements in alluvial sediments was positively correlated with the content of the clay fraction and, beside Mn, also with the content of TOC (Table 4). In deluvial sediments, only the amount of Fe was correlated with the amount of the clay fraction, whereas Ca and Cu correlated with TOC. The total amount of iron, manganese and zinc in alluvial sediments was much higher than in deluvial sediments, and it exceeded geochemical background for Polish soils stated by CZARNOWSKA (1996). The high concentration of the mentioned elements in alluvial sediments was related to the high groundwater level and changeable oxidation-reduction conditions. Excessive soil moisture may lead to increased solubility and mobility of such elements as iron and manganese. Higher accumulation of Fe, Mn and Zn in alluvial sediments, in addition to variable aerobic conditions, was favoured by a high content of allochthonous minerals deposited by river waters from anthropogenically converted areas. The research by ORZECHOWSKI and SMÓLCZYŃSKI (2010) as well as SOWIŃSKI et al. (2016) also demonstrate higher concentrations of these elements in alluvial soils than in soils outside river valleys.

Sediments accumulated in river valleys show changes that have occurred and take place in the catchment. In the analysed river valleys, apart from mineral sediments, there are mineral-organic formation, peat, mursh and

Table	3
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		Alluvial sediments	Deluvial sediments			
Specification	Value	riverine landscape	moraine landscape	landscape of ice-dammed lakes origin		
	mean	7.5	7.1	11.1		
Ca (g kg ⁻¹)	SD	1.25	4.65	4.85		
	CV (%)	16.7	65.5	43.7		
	mean	5.1	4.2	5.9		
Mg	SD	1.12	0.90	0.78		
	CV (%)	22.0	21.5	13.2		
	mean	4.6	4.2	6.3		
К	SD	1.21	0.89	3.26		
	CV (%)	26,3	21.2	51.8		
D	mean	0.9	0.7	1.3		
Г	SD	0.25	0.28	0.92		
	CV (%)	27.8	40.0	70.7		
	mean	0.3	0.4	0.2		
Na	SD	0.11	0.08	0.06		
	CV (%)	36,7	20.0	30.0		
	mean	31.7	19.7	27.9		
Fe	SD	10.54	3.45	3.56		
	CV (%)	33.2	17.6	12.8		
	mean	694.1	405.8	422.4		
Mn (mg kg ⁻¹)	SD	224.42	201.89	94.82		
	CV (%)	32.4	49.8	22.5		
Zn	mean	93.4	52.1	52.8		
	SD	32.20	8.96	11.11		
	CV (%)	34.5	17.2	21.1		
	mean	16.7	10.1	20.4		
Cu	SD	8.01	1.82	4.81		
	CV (%)	48.0	18.1	23.6		

Total content of Ca, Mg, Na, K, P, Fe, Mn, Zn, Cu in alluvial and deluvial sediments

 $\mathrm{SD}-\mathrm{standard}$ deviation, $\mathrm{CV}-\mathrm{coefficient}$ of variation

gyttja. The soil formations which contain from 10% to 20% of mineral sediments contain the highest amounts of: Mg - 4.7 g kg⁻¹, K - 5.5 g kg⁻¹, Na - 1.6 g kg⁻¹, Fe - 39.7 g kg⁻¹, Mn - 930.9 mg kg⁻¹, Zn - 116.8 g kg⁻¹ and Cu - 37.2 mg kg⁻¹ (Table 5). Such a high content of the studied macroand microelements was caused by their elution from soils located along river valleys and their accumulation in sediments of the ecotone zone between mineral and organic soils. The fine-grained alluvial silts of river valleys form a permanent connection with organic matter and, in comparison with the

Table 4

Properties	Ca	Mø	K	р	Na	Fe	Mn	Zn	Cu
Troperties	οu	1115	11 · 1 · 1	· / D	1	1		211	ou
Alluvial sediments - Riverine landscape									
Clay (fraction < 0.002 mm)	0.404**	0.809**	0.677**	0.232*	0.458**	0.692**	0.516**	0.530**	0.733**
Silt (0.05-0.002 mm)	-0.507**	-0.698**	-0.648**	-0.286**	-0.390**	-0.647**	-0.440**	-0.488**	-0.691**
TOC (g kg ⁻¹)	0.598**	0.291**	0.356**	0.409**	0.381**	0.404**	0.167	0.354**	0.697**
		D	eluvial sed	liments - N	Ioraine lar	ndscape			
Clay (fraction < 0.00 2mm)	0.450	0.627*	0.519	0.027	-0.540	0.778**	-0.514	0.461	0.512
Silt (0.05-0.002 mm)	0.208	-0.107	-0.01	-0.106	-0.04	-0.06	0.723**	-0.445	-0.559*
TOC (g kg ⁻¹)	0.593*	0.467	0.088	0.658*	-0.318	-0.057	-0.546	0.412	0.845**
	Ι	Deluvial se	diments - l	Landscape	of ice-dam	med lakes	origin		
Clay (fraction < 0.002 mm)	0.277	0.250	-0.070	0.639**	0.423	0.541*	-0.323	-0.130	-0.013
Silt (0.05-0.002 mm)	-0.015	-0.064	0.146	-0.716**	-0.339	-0.258	0.560*	0.072	-0.061
TOC (g kg ⁻¹)	0.511*	0.313	0.369	0.126	0.553*	-0.133	-0.415	0.524*	0.862**

Pearson's correlation coefficients between silt (0.05-0.002 mm), clay (<0.002 mm) and total organic carbon

* correlations significant at $p \le 0.05$; ** correlations significant at $p \le 0.01$

mineral-organic sediments of deluvial origin, they contain more Ca, Na, Fe, Mn, Zn and Cu (Tables 5, 6). The higher content of Mn, Cu and Zn in the soils of the transition zone between mineral and organic soils was stated by SMÓLCZYŃSKI et al. (2004) as well as SMÓLCZYŃSKI and ORZECHOWSKI (2010). The highest content of calcium was found in gyttjas, in which these quantities were 1.5-fold higher than in peat and mursh, and twice as high as in mineral-organic sediments. Peat formations were characterised by the lowest content of Mg, K, P, Fe, Mn, Zn and Cu. The amounts of these elements were 2- to 3-fold lower than in mineral-organic sediments, murshes and gyttjas.

The location of Holocene sediments in a relief is an important factor differentiating the content of macro- and microelements in soils. Calcium is a labile component that easily migrates from the soils located higher to mid-moraine depressions filled with organic matter. In the landscape

4	7	9

Table 5

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Specification	Value	Mineral- -organic formation	Mursh	Peat	Gyttja
Ca (g kg ⁻¹)	mean SD CV (%)	16.9 6.90 40.8	22.2 6.71 30.2	26.0 9.37 36.0	$33.6 \\ 36.9 \\ 110.1$
Mg	mean SD CV (%)	4.7 0.48 10.3	3.4 0.72 21.2	$1.9 \\ 1.09 \\ 57.1$	$3.7 \\ 1.04 \\ 28.1$
К	mean SD CV (%)	$5.5 \\ 0.92 \\ 16.8$	3.9 0.42 10.8	$1.9 \\ 1.55 \\ 80.2$	4.0 0.78 29.5
Р	mean SD CV (%)	$1.4 \\ 0.20 \\ 14.3$	$1.6 \\ 0.51 \\ 31.9$	$0.7 \\ 0.30 \\ 44.6$	$1.6 \\ 0.57 \\ 37.5$
Na	mean SD CV (%)	$1.6 \\ 0.36 \\ 22.5$	1.3 0.30 23.1	$1.2 \\ 0.47 \\ 38.1$	1.3 0.39 30.0
Fe	mean SD CV (%)	39.7 3.20 8.1	32.7 8.21 25.1	15.6 11.24 72.0	32.3 7.58 23.5
Mn (mg kg ⁻¹)	mean SD CV (%)	930.9 128.31 13.8	745.8 265.44 35.6	$315.3 \\ 194.54 \\ 61.7$	$649.0 \\ 166.10 \\ 25.7$
Zn	mean SD CV (%)	116.8 24.07 20.6	69.8 20.32 29.2	23.4 26.27 112.3	57.8 18.05 31.3
Cu	mean SD CV (%)	37.2 9.10 24.4	22.8 7.68 33.7	14.4 12.15 84.4	23.9 7.53 31.5

Total content of Ca, Mg, Na, K, P, Fe, Mn, Zn, Cu in riverine landscape

 $\mathrm{SD}-\mathrm{standard}$ deviation, $\mathrm{CV}-\mathrm{coefficient}$ of variation

of ice-dammed lakes origin and moraine landscape, the highest content of calcium was in organic formations (peat and mursh), and its amount was almost 3-fold higher than in mineral-organic sediments and 4-5-fold higher than in mineral sediments (Tables 3, 6). Mineral and organic sediments were the place of the highest accumulation of Mg, K, Cu and Zn, while the content of Fe and Mn was similar in mineral-organic sediments and murshes.

Mineralogical composition

The analysed clay fraction of alluvial sediments in riverine landscape (Vistula delta) was dominated by minerals from the illite-smectite group of mixed-packet minerals which was confirmed by 1.66 nm reflexes and very wide reflexes in the range of 0.560-0.500 nm at the diffractograms for the samples saturated with Mg²⁺ and solvated with ethylene glycol (Mg²⁺ + GE) – Figure 2. This was also confirmed by a wide reflex of 1.2-1.0 nm at the

C		Mo	raine landsc	ape	L. of ice-dammed lakes origin			
cation Value		mineral- -organic	mursh	peat	mineral- -organic	mursh	peat	
Ca	mean	12.9	31.6	37.9	12.7	40.2	40.1	
$(a k a^{-1})$	SD	2.85	25.92	14.78	4.40	30.51	15.73	
(g Kg)	CV (%)	22.1	82.1	3.0	34.7	75.9	39.3	
	mean	5.5	3.7	2.1	6.4	4.5	2.1	
Mg	SD	1.22	1.27	1.26	0.96	1.45	0.91	
	CV (%)	22.2	33.4	60.0	15.0	32.3	43.4	
	mean	4.7	2.8	1.6	8.2	4.6	1.4	
K	SD	1.72	1.37	1.04	1.63	2.48	0.88	
	CV (%)	36.6	49.0	65.0	19.9	54.0	62.9	
	mean	1.2	1.5	0.9	1.2	2.0	1.2	
Р	SD	0.45	0.95	0.61	0.40	0.81	0.64	
	CV (%)	37.5	63.4	67.8	33.4	40.5	53.4	
	mean	0.4	0.3	0.4	0.7	0.6	0.6	
Na	SD	0.08	0.07	0.06	0.34	0.31	0.21	
	CV (%)	20.0	23.4	15.0	48.7	51.7	35.1	
	mean	25.2	19.4	11.3	21.9	18.8	8.9	
Fe	SD	5.87	6.35	8.10	6.06	8.04	8.73	
	CV (%)	23.3	32.8	71.7	27.8	42.7	97.9	
Mn	mean	510.0	530.7	236.4	485.9	471.2	216.9	
(mg kg ⁻¹)	SD	142.91	236.74	194.51	101.53	101.17	99.18	
(ing kg)	CV (%)	28.1	44.6	82.3	20.9	21.4	45.7	
	mean	59.5	43.2	19.2	67.2	41.7	14.9	
Zn	SD	11.32	19.01	23.00	10.56	13.78	7.24	
	CV (%)	19.1	44.0	119.8	15.7	33.0	48.5	
	mean	18.1	13.7	13.5	22.6	16.1	6.2	
Cu	SD	7.65	4.99	10.84	2.82	3.35	5.29	
	CV (%)	42.3	36.5	80.3	12.5	20.8	85.3	

Total content of Ca, Mg, Na, K, P, Fe, Mn, Zn, Cu in moraine landscape and landscape of ice-dammed lakes origin

SD - standard deviation, CV - coefficient of variation

diffractograms for potassium-saturated samples (K⁺). Analysis of illite-smectite minerals showed that it is a mixture of minerals with a 60-90% content of smectite packets. In addition to these minerals, there were also minerals from the group of illite (reflexes 1.0, 0.499, 0.334 nm) and kaolinite (0.712, 0.356 nm). The analysed sediments did not contain minerals from the chlorite group which was proven by the shift of 1.45 nm reflexes in Mg²⁺ diffractograms to 1.2 nm in K⁺ diffractograms and to 1.0 nm after heating at 300°C. The studies of DABKOWSKA-NASKRET and DŁUGOSZ (1996) also showed a dominant share of mixed-packet smectite minerals (of illite/smectite type) in the clay fraction of alluvial sediments in Vistula river valley. Moreover, in the sediments of Vistula and Pasłęka rivers, significant quantities of mixedpacket minerals of illite/smectite with a disordered structure, containing 60-70% of smectite packets (DŁUGOSZ et al. 2009b), were found.



Fig. 2. X-ray diffractograms of clay fraction of alluvial sediments in riverine landscape (location: Stara Kościelnica – the Vistula Delta)

In the moraine landscape, illite minerals dominated in the clay fraction of deluvial sediments, which was proven by reflexes of 1.01, 0.500 and 0.334 nm occurring in the diffractograms of samples saturated with K⁺ and Mg²⁺ and solvated with ethylene glycol (Mg²⁺ + GE) – Figure 3. These samples also contained minerals from the chlorite group, as indicated by reflexes of 1.45 nm, 0.723 nm and a reflex of 0.475 nm in Mg²⁺ + GE diffractograms.



Fig. 3. X-ray diffractograms of clay fraction of deluvial sediments in moraine landscape (location: Prusinowo)

The presence of chlorites was indicated by a strong reflex of 1.45 nm in the diffractogram of Mg^{2+} saturated samples and a small 1.4 nm reflex in the diffractogram of K⁺ saturated samples. The chlorites belonged to the so-called pedogenic chlorites because the mentioned reflex disappeared in the diffractograms of K⁺ saturated samples and heated at 550°C. The occurrence of smectite minerals was proven by a wide reflex of 1.7 nm in the diffractograms of Mg^{2+} + GE samples. Smectite minerals apparently occur in a pure form as well as in the form of mixed-packet minerals, e.g. illite/smectite. This is suggested by a wide reflex of 1.7 nm in the Mg^{2+} + GE diffractogram and reflexes of 1.4-1.0 nm in the diffractograms for K⁺ samples. A high amount of smectite can be a sign of the smectitization process. Kaolinite and quartz were accessory minerals.

In the clay fraction of the landscape originating from ice-dammed lakes, minerals from the group of illites prevailed, as evidenced by strong reflexes of 1.01, 0.500 and 0.334 nm occurring in diffractograms of samples saturated with both K⁺ and Mg²⁺ ions, and in the samples solvated with magnesium ethylene glycol (Mg²⁺ + GE) – Figure 4. In addition to the illites, smectite minerals were found, as evidenced by 1.68 nm reflexes in the Mg²⁺ + GE diffractograms. The group of these minerals was represented mainly by the illite-smectite mixed-packet minerals with a content of 90% S smectite packets, as evidenced by reflexes of 0.550-0.500 nm (Mg²⁺ + GE diffractogram). In addition to these minerals, the presence of chlorite minerals was also detected. Kaolinite (reflexes 0.72, 0.357 nm), quartz (0.427 nm reflex), feldspar (0.303-0.33 nm reflections) and chlorites were accessory minerals.



Fig. 4. X-ray diffractograms of clay fraction of deluvial sediments in the landscape of ice-dammed lakes origin (location: Reszel)

The presence of chlorites was confirmed by a reflex of 1.4 nm in K⁺ diffractograms. These are most likely vermiculited chlorites. Illite minerals prevailed in the clay fraction of Pleistocene glaciolimnic sediment in the landscape of ice-dammed lakes origin, which was proven by reflexes of 1.00, 0,500, 0.334 nm, in addition to mixed-packet minerals with swelling illite-smectite packets containing 70-90% S smectite packets (Figure 5). Chlorite minerals,



Fig. 5. X-ray diffractograms of clay fraction of Pleistocene glaciolimnic sediments in the landscape of ice- dammed lakes origin (location: Reszel)

in the form of pedogenic chlorites, (1.45, 0.719, 0.475 nm) were also found. Kaolinite was an accessory mineral. The study of the mineralogical composition of the clay fraction of glacial and glaciolimnic sediments carried out by DŁUGOSZ et al. (2009*a*) in Sępopolska Plain also proved the prevalence of illite minerals being a mixture of illites and illite/smectite mixed-packet minerals (with a content of smectite packets up to 10%). Significant amounts of swelling minerals of the illite-smectite structure (I/S), containing 80-90% of smectite packets and vermiculite-chlorite mixed-packet minerals, were also found. The most important factor determining the mineralogical and geochemical composition of the clay fraction is the composition of the parent material and the conditions under which it is weathering (PEURANIEMI et al. 1997). The similar mineralogical composition of clay fraction of Holocene sediments and sedimentary rocks of Pleistocene suggests their Pleistocene origin and short period of transformation.

CONCLUSIONS

1. Holocene sediments in north-eastern Poland were represented by mineral alluvial and deluvial sediments, mineral-organic sediments, and organic formations – peat, mursh and gyttja.

2. Among the analysed mineral sediments, the highest mean content of Ca, Mg, K, P and Cu were found in deluvial sediments in the landscape of ice-dammed lakes origin, whereas the alluvial sediments in the riverine landscape had the highest mean amounts of Fe, Mn and Zn.

3. Mineral-organic sediments were the site of the highest accumulation of Mg, K, Zn and Cu, while Ca was accumulated in peat and gyttja.

4. In the clay fraction of riverine landscape, illite-smectite mixed-packet minerals with the content of 60-90% of smectite packets prevailed. Kaolinite and illite minerals also occurred but in minor amounts.

5. In the moraine landscape and in the landscape of ice-dammed lakes origin, illite minerals dominated in the clay fraction of deluvial deposits. The presence of smectite minerals in the pure form and in the form of illite-smectite mix-packet minerals as well as minerals from the group of pedogenic chlorites was determined. The mineralogical composition of Holocene deluvial sediments was similar to the composition of Pleistocene sediments.

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