



## ORIGINAL PAPER

# VARIABILITY OF THE CONTENT OF MACROELEMENTS IN SOILS OF A YOUNG GLACIAL RIVER VALLEY - A GEOCHEMICAL LANDSCAPE APPROACH

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## ABSTRACT

The content and relationships between amounts of macroelements (Ca, Mg, K, Na and Fe) and soil properties along three catenas in the young glacial Łyna River valley, NE Poland, are discussed in the paper. The results were presented against the background of four geochemical landscapes distinguished within the study area: eluvial / trans-eluvial, eluvial accumulative, trans-super-aqual and super-aqual. The middle part of the Łyna River valley is covered with Fluvic Phaeozems and Dystric Fluvisols formed from sands, loams and silts. In some parts, Mollic Gleysols (Limnic) formed from peats and gyttja occur. In the areas adjacent to the floodplain, Eutric Umbrisols (Pantocolluvic) and Haplic Umbrisols (Colluvic) formed from loams, silts and clays are located. The upper slope of the valley is covered by Luvic Phaeozems, Luvic Umbrisols, Brunic Dystric Arenosols and Dystric Arenosols. The average content of macroelements reached:  $Ca_t - 6.60 \text{ g kg}^{-1}$ ,  $Ca_{HCl} - 3.17 \text{ g kg}^{-1}$ ,  $Mg_t - 2.79 \text{ g kg}^{-1}$ ,  $Mg_{HCl} - 0.68 \text{ g kg}^{-1}$ ,  $K_t - 7.27 \text{ g kg}^{-1}$ ,  $K_{HCl} - 0.20 \text{ g kg}^{-1}$ ,  $Na_t - 0.84 \text{ g kg}^{-1}$ ,  $Na_{HCl} - 0.22 \text{ g kg}^{-1}$ ,  $Fe_t - 8.72 \text{ g kg}^{-1}$  and  $Fe_{HCl} - 5.48 \text{ g kg}^{-1}$ . The content of macroelements in soils of the analysed area was varied between the four geochemical landscapes. The analysis, supported by PCA ordination, resulted in significant positive relations between the macroelement contents and silt (0.05-0.002 mm) and clay (<0.002 mm) soil fractions,  $CaCO_3$ ,  $pH_{KCl}$  and amounts of organic matter, as well as an inverse relation to the share of sandy (2.0-0.05 mm) soil fraction. Soils in super-aqual geochemical landscape were the most abundant in macroelements (except  $K_{HCl}$  and Na). The most typical sites of macroelement accumulation were the following geochemical landscapes: super-aqual > trans-super-aqual > eluvial accumulative > eluvial / trans-eluvial.

**Keywords:** eluvial, aqual, elements, soil catena.

## INTRODUCTION

Macroelements occur in soils at high concentrations and are taken up by plants in large quantities. They are very important soil components that affect processes of: photosynthesis, respiration, and regulation of water conditions. They also play a role in metabolic processes and are activators in enzymatic reactions. Furthermore, they affect physical properties of soils (GRZEBISZ 2011, KOBIERSKI et al. 2011).

Sources of elements in the soil can be natural – primary and secondary minerals, soil organic matter and anthropogenic – mineral and organic fertilization (KOBIERSKI et al. 2014, VÁCHA et al. 2013).

The soils located in river valleys in young glacial landscape are distinguished by specific toposequences and properties (SMÓLCZYŃSKI et al. 2013, 2015). Various processes (alluvial, colluvial, illuvial etc.) overlap in these soils. The location of soils in land depressions within river valleys (oxbow lakes, floodplain, levees, foot-slopes) makes them a special place in the circulation of elements, which acts as biogeochemical barriers in the landscape (SOWIŃSKI et al. 2004*b*). These soils have higher amounts of organic matter, silt and clay fractions, which affect the sorption capacity. Concave forms located in the relief can prevent the eutrophication and pollution of waters (surface and ground waters) through accumulation of elements in the soil (BEDNAREK et al. 2011, GLIŃSKA-LEWCZUK et al. 2014, ORZECOWSKI, SMÓLCZYŃSKI 2010, SMÓLCZYŃSKI, ORZECOWSKI 2010*a,b*, SOWIŃSKI et al. 2004*a*), bottom sediments (GLIŃSKA-LEWCZUK et al. 2009, OBOLEWSKI et al. 2009, SOROKINA, ZARUBINA 2011, VÁCHA et al. 2013, WALLING et al. 2003) and in plants (OBOLEWSKI et al. 2011).

The soils developed from the Holocene alluvial and colluvial materials, as well as organic materials (peat, gyttja, muds) have varied macroelement content. Soils occurring in young glacial river valleys are modified by the processes of translocation of soil material down the slope due to anthropogenic denudation. In upper parts of the slope, there is a decrease in the content of easily dissolved elements (e.g. Ca and Mg), which are accumulated in lower parts of the slope or in depressions (CHODAK et al. 2005, ORZECOWSKI, SMÓLCZYŃSKI 2010, SMÓLCZYŃSKI, ORZECOWSKI 2010*a, b*, SOWIŃSKI et al. 2004*a*, SOWIŃSKI, LEMKOWSKA 2010). The impact of land use on the content of nutrients is also important (LI et al. 2011). Transformation of organic matter in drained organic soils is another process of great importance. Mursh soils contain more macroelements than peats or muds in the accumulation stage (KALISZ, ŁACHACZ 2009).

The geochemical variability of concentrations of macroelements in soils of young glacial river valleys is conditioned by topographical and hydrological factors. The migration of nutrients in soils provide the basis for geochemical landscape classification developed by Russian pedologists such as Glazovskaya and Perelman (WICIK, OSTASZEWSKA 2012).

The aim of this paper was to determine the content of Ca, Mg, K, Na and Fe and their relationships with soil properties. Vertical and horizontal distribution of macroelements in soils occurring in four geochemical landscapes in a young glacial river valley, NE Poland, was discussed. Multivariate techniques of PCA were used for the analysis of relationship between the content of macroelements and soil properties.

## MATERIAL AND METHODS

The study was carried out at three soil catenas in the middle course of the Lyna River (Figure 1). The study area is a typical young glacial land-

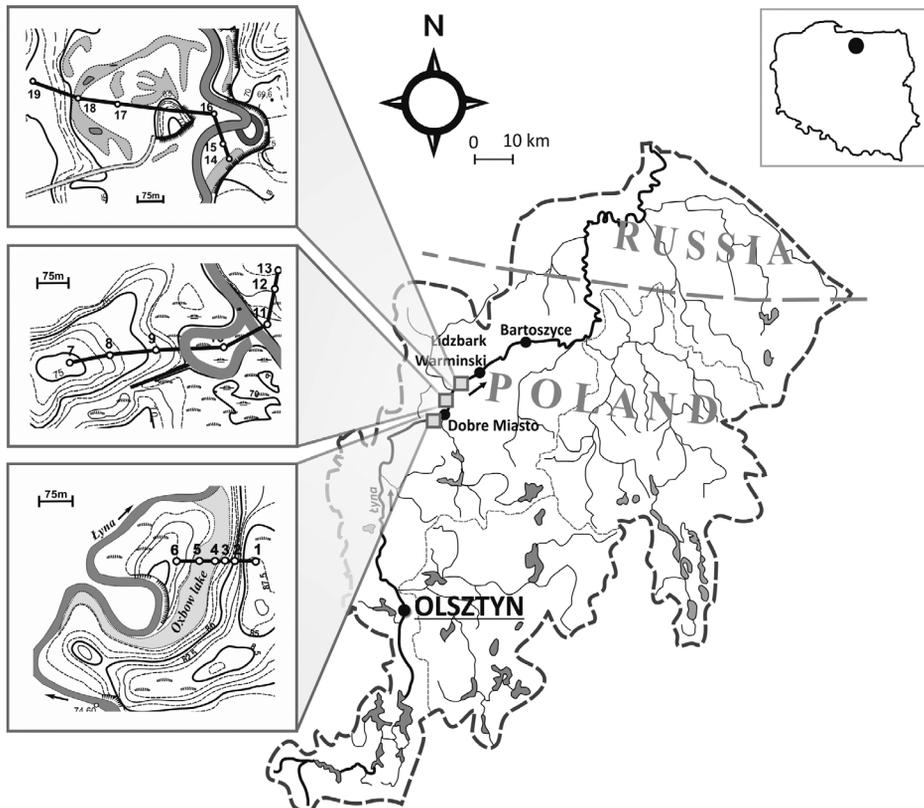


Fig. 1. Location of soil profiles in catenas

scape of north-eastern Poland. The origin of this landscape is related to the glacier activity in the Pomeranian Phase of Vistula glaciation (Pleistocene) as well as the processes (meltwaters and fluvial) which took place in Holocene.

For the analysis of macroelements, the catenas located at: Knopin (catena I – soil profiles 1-6), Smolajny (catena II – soil profiles 7-13) and Łaniewo (catena III – soil profiles 14-19) – Figure 1 were chosen. More detailed description of the sites was presented in previous papers (GLIŃSKA-LEWCZUK, BURANDT 2011, GLIŃSKA-LEWCZUK et al. 2014).

According to the Typology of Geochemical Integration by Glazovskaya (WICIK, OSTASZEWSKA 2012), four types of geochemical landscapes were distinguished: (1) eluvial / trans-eluvial, (2) eluvial accumulative, (3) trans-super-aqual and (4) super-aqual.

Fifty-seven soil samples were collected from genetic horizons. The following properties were analysed: particle size distribution, organic matter content (OM), soil reaction and content of  $\text{CaCO}_3$ . The methods of physical-chemical analyses have been described in previous paper (GLIŃSKA-LEWCZUK et al. 2014, SOWIŃSKI et al. 2016).

The pseudo-total content of Ca, Mg, K, Na and Fe was measured after digestion in *aqua regia* (3:1 mixture of hydrochloric and nitric acid).  $\text{Ca}_t$ ,  $\text{Mg}_t$  and  $\text{Fe}_t$  were determined using AAS technique on a SOLAAR 969 Pye Unicam,  $\text{K}_t$  and  $\text{Na}_t$  were measured using the AES method on a FLAPHO 4 (GAŚSIOR et al. 2012, SAPEK, SAPEK 1997).

Potentially labile forms of macroelements were analysed in 1M HCl (mineral soil samples) or 0.5 M HCl (organic soil samples) using SOLAAR 969 Pye Unicam analyser ( $\text{Ca}_{\text{HCl}}$ ,  $\text{Mg}_{\text{HCl}}$ ,  $\text{Fe}_{\text{HCl}}$ ) and FLAPHO 4 analyser –  $\text{K}_{\text{HCl}}$  and  $\text{Na}_{\text{HCl}}$  (GAŚSIOR et al. 2012, SAPEK, SAPEK 1997). The results of the macroelement content were calculated in relation to dry matter (105°C).

The local geochemical background of macroelements in soils was calculated on the basis of average contents in the parent material at depths of > 90 cm according to CZARNOWSKA (1996).

Soils were classified according to the WRB system (IUSS Working Group WRB 2015), and horizon symbols were given according to Polish Soil Classification System (2011).

Non-parametric analysis of variance using the Kruskal-Wallis test (K-W;  $p \leq 0.05$ ) was applied to assess the general differences among the content of the studied forms of macroelements and soil properties. The precise statistical significance of differences in the analysed element content among the sites was determined with the Dunn's test ( $p \leq 0.05$ ). Except the Dunn's test, all other statistical analyses were performed using Statistica 10.0 PL for Windows.

For the identification of primary environmental gradients affecting the content of macroelements in soils, multivariate statistical analyses involving a linear indirect method of Principal Component Analysis (PCA) were applied using default (standard) options. The data (excluding pH) were transformed to logarithms  $\log(n+1)$  to meet conditions of normality. For the ordination analysis, CANOCO 4.5 software was used (TER BRAAK, ŠMILAUER 2002).

## RESULTS AND DISCUSSION

The middle part of the Łyna River valley is covered with Fluvic Phaeozems and Dystric Fluvisols formed from sands, loams and silts (super-aqual and trans super-aqual landscapes). In some parts, Mollic Gleysols (Limnic) (super-aqual landscape) formed from peats and gyttja occur. In the areas adjacent to the floodplain, Eutric Umbrisols (Pantocolluvic) and Haplic Umbrisols (Colluvic) formed from loams, silts and clays (eluvial accumulative landscape) are located. The upper slope of the valley is covered by Luvic Phaeozems, Luvic Umbrisols, Brunic Dystric Arenosols and Dystric Arenosols (eluvial / trans-eluvial landscape) – Table 1. The description of the soil properties was presented previously (GLIŃSKA-LEWCZUK et al. 2014, Sowiński et al. 2016).

The highest macroelement content was stated in Eutric Umbrisol (Pantocolluvic;  $\text{Ca}_t$ ,  $\text{Mg}_t$  and  $\text{Na}_t$ ) in 2C horizon (profile 6), Luvic Phaeozem ( $\text{K}_t$ ) in C horizon (profile 7) and Fluvic Phaeozem ( $\text{Fe}_t$ ) in A2 horizon (profile 11) – Table 1.

The highest values of potentially labile macroelements were determined in the parent material of Eutric Umbrisol (Pantocolluvic; profile 6) for  $\text{Ca}_{\text{HCl}}$  and  $\text{Na}_{\text{HCl}}$ , Fluvic Phaeozem (profile 10) for  $\text{Mg}_{\text{HCl}}$ , Luvic Phaeozem (profile 7) for  $\text{K}_{\text{HCl}}$  and in the humus horizon (A2) of Fluvic Phaeozem (profile 11) for  $\text{Fe}_{\text{HCl}}$  (Table 1).

Significant positive correlation between the analysed macroelements was determined ( $n = 57$ , at  $p \leq 0.01$ ) for Ca ( $r = 0.778$ ), Mg ( $r = 0.587$ ), K ( $r = 0.788$ ), Na ( $r = 0.705$ ) and Fe ( $r = 0.890$ ) – Figure 2.

In order to distinguish natural and anthropogenic origins of macroelements (pseudo-total contents) in the Łyna River valley, the local geochemical background of the parent material was analysed. Mean values of pseudo-total macroelements in the parent material amounted to  $11.35 \text{ g Ca}_t \text{ kg}^{-1}$ ,  $3.35 \text{ g Mg}_t \text{ kg}^{-1}$ ,  $8.38 \text{ g K}_t \text{ kg}^{-1}$ ,  $1.03 \text{ g Na}_t \text{ kg}^{-1}$ ,  $8.08 \text{ g Fe}_t \text{ kg}^{-1}$ . The differences among investigated parent materials were noted (Table 2). The highest amounts of macroelements were found in Pleistocene loams and clays, whereas the lowest amounts occurred in fluvio-glacial sands.

Of all the elements, only  $\text{Ca}_t$ ,  $\text{K}_t$  and  $\text{Fe}_t$  showed statistically significant correlations with soil properties (Table 3).  $\text{Ca}_t$  was significantly correlated with  $\text{CaCO}_3$  ( $r = 0.643$ ,  $p \leq 0.05$ ) and pH values ( $r = 0.664$ ). The content of  $\text{K}_t$  and  $\text{Fe}_t$  was significantly correlated with clay ( $r = 0.819$ ;  $r = 0.851$ , respectively). Potentially labile forms of macroelements were significantly positively correlated with pH values ( $\text{Ca}_{\text{HCl}}$ ,  $\text{Mg}_{\text{HCl}}$ ,  $\text{Na}_{\text{HCl}}$ ,  $\text{Fe}_{\text{HCl}}$ ), organic matter ( $\text{Ca}_{\text{HCl}}$ ,  $\text{Mg}_{\text{HCl}}$  and  $\text{Na}_{\text{HCl}}$ ), clay ( $\text{Fe}_{\text{HCl}}$ ) and  $\text{CaCO}_3$  ( $\text{Ca}_{\text{HCl}}$ ).  $\text{Fe}_{\text{HCl}}$  was negatively correlated with sand. The importance of the soil properties that influence potentially labile forms of macroelements may be put in the following decreasing order:  $\text{pH}_{\text{KCl}} > \text{OM} > \text{clay} > \text{CaCO}_3$ .

Table 1

## Content of macroelements in the soils

Geochemical landscape	Profile No	Soil unit	Horizon	Depth (cm)	Ca <sub>t</sub>	Ca <sub>HCl</sub>	Mg <sub>t</sub>	Mg <sub>HCl</sub>	K <sub>t</sub>	K <sub>HCl</sub>	Na <sub>t</sub>	Na <sub>HCl</sub>	Fe <sub>t</sub>	Fe <sub>HCl</sub>	
															(g kg <sup>-1</sup> )
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
				A	0-26	0.24	0.05	0.82	0.02	3.88	0.04	0.52	0.317	0.94	
	1	Dystric Brunic Arenosol	Bv	26-120	0.49	0.08	0.89	0.03	3.67	0.05	0.48	0.02	2.53	0.65	
			C	120-150	0.71	0.16	0.75	0.03	3.35	0.04	0.47	0.04	2.45	0.56	
	19	Arenosol	Ap	0-26	0.28	0.07	1.09	0.01	3.88	0.09	0.33	0.01	3.48	1.75	
			Bv	26-80	0.58	0.37	0.46	0.01	3.16	0.17	0.28	0.06	5.91	1.08	
	2	Dystric Arenosol	C	80-150	0.75	0.18	0.81	0.04	3.23	0.05	0.39	0.07	2.31	0.58	
			A	0-28	1.21	0.14	1.12	0.02	4.51	0.13	0.61	0.03	4.94	0.99	
	13	Eluvial / trans-eluvial (1)	Dystric Arenosol	C	28-150	22.28	16.37	1.16	0.63	2.97	0.09	0.99	0.66	1.24	0.47
				A	0-22	0.55	0.38	0.41	0.01	2.97	0.04	0.99	0.05	2.15	0.91
	7	Luvic Pheozem	Luvic Pheozem	C	22-150	0.04	0.01	0.41	0.01	2.97	0.04	0.68	0.03	1.36	0.23
				Ap	0-31	1.94	1.64	2.12	0.36	13.3	0.75	0.52	0.13	5.39	4.43
	8	Luvic Umbrisol	Luvic Umbrisol	Et	31-56	1.71	0.39	5.44	0.49	17.06	0.49	0.73	0.1	12.35	4.00
Bt				56-102	5.82	1.59	5.27	1.38	13.96	1.00	0.96	0.24	16.77	13.7	
3	Haplic Umbrisol (Colluvic)	Haplic Umbrisol (Colluvic)	C	102-150	5.16	0.86	4.95	2.41	46.92	1.21	0.85	0.27	18.79	11.95	
			Ap	0-33	0.52	0.04	0.58	0.01	5.05	0.17	0.54	0.07	1.58	0.02	
9	Eutric Umbrisol (Pantocolluvic)	Eutric Umbrisol (Pantocolluvic)	Et	33-58	2.08	0.82	1.52	0.21	7.06	0.28	0.68	0.04	4.68	1.94	
			Bt	58-90	4.80	0.97	4.19	2.52	7.48	0.49	0.92	0.21	10.12	9.20	
6	Eluvial accumulative (2)	Eluvial accumulative (2)	Cg	90-150	6.58	0.92	3.27	1.03	10.01	0.56	0.68	0.26	10.79	9.77	
			A	0-68	0.90	0.56	1.65	0.15	5.63	0.04	0.66	0.05	6.14	2.41	
12	Eluvial accumulative (2)	Eluvial accumulative (2)	C	68-150	3.68	1.27	5.21	1.29	9.40	0.09	0.63	0.13	18.07	4.39	
			Ap	0-30	0.74	0.55	0.80	0.09	6.03	0.09	0.45	0.10	2.86	1.70	
9	Eluvial accumulative (2)	Eluvial accumulative (2)	A2	30-56	1.93	0.37	3.33	0.51	9.00	0.09	0.52	0.10	10.84	2.93	
			A3	56-107	0.79	0.59	2.89	0.68	8.42	0.13	0.52	0.12	9.84	5.58	
6	Eluvial accumulative (2)	Eluvial accumulative (2)	G	107-150	2.54	1.45	1.37	0.39	6.39	0.13	0.63	0.12	5.80	4.86	
			A1	0-30	1.05	0.56	0.63	0.07	3.71	0.04	1.76	0.11	2.84	1.35	
12	Eluvial accumulative (2)	Eluvial accumulative (2)	A2	30-110	5.97	0.28	3.78	0.13	6.98	0.09	1.11	0.08	8.32	0.57	
			2C	110-150	79.02	44.60	19.13	2.02	12.61	0.88	3.01	1.94	11.77	4.26	
12	Eluvial accumulative (2)	Eluvial accumulative (2)	A1	0-30	6.89	3.77	4.21	1.07	6.32	0.29	0.74	0.21	10.34	9.38	
			A2	30-110	2.60	1.62	0.51	0.12	5.88	0.25	1.18	0.11	2.18	0.79	
12	Eluvial accumulative (2)	Eluvial accumulative (2)	A3	110-150	0.62	0.42	0.46	0.06	3.71	0.09	0.66	0.04	1.90	1.25	

cont. Table 1

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15		
Trans- super-aqual (3)	14	Dystric Fluvisol	A	0-32	7.08	2.02	3.55	0.39	9.70	0.09	0.82	0.24	19.13	12.09		
			C1	32-90	7.53	1.55	3.17	1.21	7.65	0.09	7.31	0.12	0.63	0.24	6.95	5.41
			C2	90-150	11.59	7.61	3.26	1.07	7.31	0.12	7.31	0.12	0.63	0.27	7.08	6.72
	16		A	0-18	4.57	0.69	1.56	0.48	6.39	0.09	6.39	0.09	1.06	0.18	6.55	5.32
			C1	18-60	7.13	1.91	1.48	1.29	5.17	0.13	5.17	0.13	0.52	0.26	2.39	1.58
	17		C2	60-150	9.29	4.31	0.85	0.77	3.71	0.09	3.71	0.09	1.15	0.30	1.99	1.35
			A	0-16	3.08	2.28	1.86	0.29	4.51	0.06	4.51	0.06	0.52	0.13	7.32	6.72
			C1	16-50	1.19	0.62	1.04	0.27	5.29	0.05	5.29	0.05	0.31	0.08	4.49	2.38
			C2	50-150	5.95	2.00	1.54	0.78	5.63	0.04	5.63	0.04	1.08	0.15	3.50	2.62
	10		A1	0-23	6.09	3.47	4.41	1.00	6.22	0.09	6.22	0.09	0.71	0.19	11.84	11.28
A2		23-90	8.77	3.30	3.30	5.23	1.30	9.70	0.25	1.90	0.38	0.40	15.74	14.8		
AC		90-150	8.67	1.46	3.78	3.19	5.63	0.13	5.63	0.13	1.36	0.40	18.10	10.64		
A1		0-26	8.52	3.36	5.45	0.84	8.53	0.25	8.53	0.25	1.01	0.44	19.52	17.61		
11	A2	26-73	7.72	2.04	5.38	0.99	10.9	0.52	10.9	0.52	1.60	0.27	26.64	22.52		
	A3	73-100	3.42	1.92	4.82	0.6	6.73	0.17	6.73	0.17	1.06	0.23	25.91	22.97		
	AC	100-150	1.67	0.87	1.55	0.36	4.65	0.09	4.65	0.09	0.54	0.11	5.71	5.34		
	A	0-32	5.89	3.17	3.81	1.14	6.13	0.11	6.13	0.11	0.64	0.18	11.24	10.28		
15	C1	32-90	11.51	9.88	4.70	1.15	6.90	0.09	6.90	0.09	1.95	0.33	8.29	4.47		
	C2	90-150	8.73	3.12	1.20	0.63	4.36	0.04	4.36	0.04	0.52	0.26	3.24	1.76		
	Lc	0-50	3.83	1.70	0.92	0.20	8.21	0.04	8.21	0.04	0.63	0.14	3.23	1.25		
	Oa	50-120	8.20	5.04	3.44	0.83	8.21	0.09	8.21	0.09	0.54	0.21	7.10	2.16		
4	G	120-150	8.43	3.02	1.27	0.68	4.36	0.11	4.36	0.11	0.55	0.24	3.14	1.61		
	Lc	0-90	6.80	3.58	4.16	0.41	8.32	0.09	8.32	0.09	1.08	0.26	23.1	11.07		
	Oa	90-117	25.75	11.65	2.72	0.69	5.05	0.04	5.05	0.04	1.06	0.63	22.33	9.22		
	Lcm	117-150	18.28	12.11	4.74	1.11	7.92	0.17	7.92	0.17	1.58	0.27	22.95	14.84		
18	Lc	0-60	7.89	4.18	3.26	0.88	8.02	0.25	8.02	0.25	0.54	0.30	7.99	3.15		
	G	60-150	6.22	2.67	0.61	0.40	3.88	0.09	3.88	0.09	0.73	0.23	0.91	0.75		
5	18	Mollic Gleysol (Limnic)	Lc	0-90	6.80	3.58	4.16	0.41	8.32	0.09	1.08	0.26	23.1	11.07		
			Oa	90-117	25.75	11.65	2.72	0.69	5.05	0.04	1.06	0.63	22.33	9.22		
			Lcm	117-150	18.28	12.11	4.74	1.11	7.92	0.17	7.92	0.17	1.58	0.27	22.95	14.84
			Lc	0-60	7.89	4.18	3.26	0.88	8.02	0.25	8.02	0.25	0.54	0.30	7.99	3.15
5	18	Mollic Gleysol (Limnic)	G	60-150	6.22	2.67	0.61	0.40	3.88	0.09	0.73	0.23	0.91	0.75		

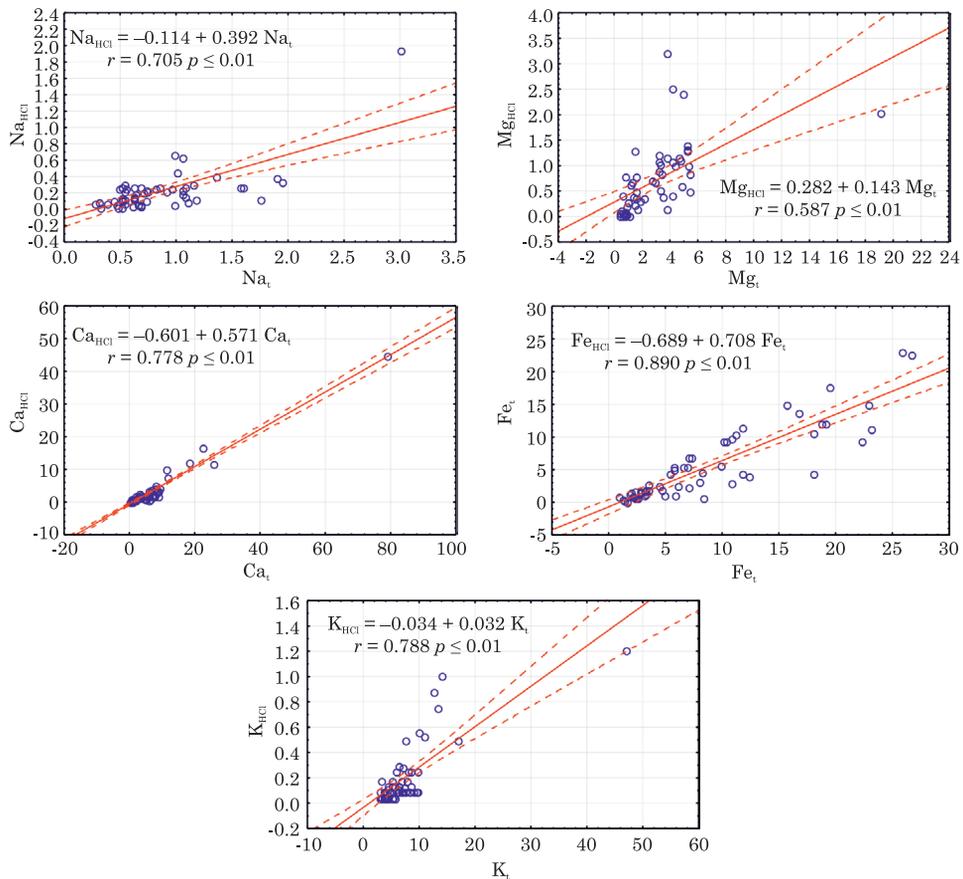


Fig. 2. Relationships between pseudo-total and potentially labile forms of macroelements in the soils

Table 2

Content of macroelements in the parent material in the Lyna River valley as reference local background levels

Parent material	Number of samples	Ca <sub>t</sub>	Mg <sub>t</sub>	K <sub>t</sub>	Na <sub>t</sub>	Fe <sub>t</sub>
		(g kg <sup>-1</sup> )				
Pleistocene loams and clays	4	23.61	8.14	19.74	1.29	14.86
Fluvioglacial sediments including:	13	7.57	1.88	4.89	0.95	5.99
sands	9	6.75	1.24	4.24	0.81	4.55
sandy loam	4	9.43	3.32	6.37	1.26	9.24
Average for all studied samples of parent materials	17	11.35	3.35	8.38	1.03	8.08

Table 3

Spearman's correlation coefficients ( $r$ ) between soil physical and chemical properties and content of macroelements in the soils

Soil parameter	Ca <sub>t</sub>	Ca <sub>HCl</sub>	Mg <sub>t</sub>	Mg <sub>HCl</sub>	K <sub>t</sub>	K <sub>HCl</sub>	Na <sub>t</sub>	Na <sub>HCl</sub>	Fe <sub>t</sub>	Fe <sub>HCl</sub>
Organic matter	0.561	0.641*	0.531	0.696*	0.334	0.130	0.457	0.674*	0.351	0.561
CaCO <sub>3</sub>	0.643*	0.745*	0.437	0.617	0.116	0.004	-0.024	0.287	0.255	0.417
pH <sub>KCl</sub>	0.664*	0.708*	0.534	0.647*	0.365	0.324	0.552	0.809*	0.391	0.609
Sand: ø 2.0-0.05 mm	-0.539	-0.359	-0.387	-0.331	-0.600	0.255	0.067	-0.584	-0.612	-0.650*
Silt: ø 0.05-0.002 mm	0.413	0.319	0.251	0.345	0.343	-0.246	-0.050	0.475	0.344	0.493
Clay: ø < 0.002 mm	0.492	0.227	0.462	0.091	0.819*	-0.117	-0.064	0.472	0.851*	0.606

\* Significant values

In the literature, stronger correlation between the content of macroelements and soil properties, especially organic matter content, soil pH and particle-size fractions content (mainly silt and clay), was reported (ORZECOWSKI, SMÓLCZYŃSKI 2010, ROGÓZ, TAKAM 2015, SMÓLCZYŃSKI, ORZECOWSKI 2010a,b, SMÓLCZYŃSKI et al. 2015.)

In a horizontal approach, the highest amounts of pseudo-total macroelements were determined at catena I and catena II. Parent material of Eutric Umbrisol (Pantocolluvic) at catena I contained 79.02 g kg<sup>-1</sup> of Ca<sub>t</sub>, 19.13 g kg<sup>-1</sup> of Mg<sub>t</sub> and 3.01 g kg<sup>-1</sup> of Na<sub>t</sub>. Luvic Pheozem (in C horizon) at catena II contained 46.92 g kg<sup>-1</sup> of K<sub>t</sub>. Whereas the humus horizon (A2) in Fluvisol Pheozem at catena II contained 26.64 g kg<sup>-1</sup> of Fe<sub>t</sub>. Generally, higher amounts of pseudo-total macroelements (except for Fe<sub>t</sub>) were found in parent materials and they were increasing with the depth into a soil profile. In the soil parent material, these amounts were even over 70-fold higher. Vertical distribution of Fe<sub>t</sub> varied. The highest amounts of Fe were detected in upper parts of sub-surface horizons or in the parent material. This was related to water properties and redox conditions. Iron is frequently accumulated in a reduced form as a result of capillary rise and is later oxidized (ORZECOWSKI et al. 2004).

The lowest amounts of Ca<sub>t</sub> (0.04 g kg<sup>-1</sup>) were determined in C horizon of Dystric Arenosol (profile 13) formed from sand. The lowest amounts of Mg<sub>t</sub> (0.41 g kg<sup>-1</sup>) and K<sub>t</sub> (2.97 g kg<sup>-1</sup>) were noted also in Dystric Arenosol (profiles 6) in horizons A and C. The lowest amounts of Na<sub>t</sub> (0.28 g kg<sup>-1</sup>) were detected in Bv horizon of Brunic Dystric Arenosol (profile 19) formed from sand. C horizon of Mollic Gleysol (Limnic; profile 18) had the lowest amounts of Fe<sub>t</sub> (0.91 g kg<sup>-1</sup>).

The lowest amounts of potentially labile forms of Ca<sub>HCl</sub>, Mg<sub>HCl</sub>, K<sub>HCl</sub> and Fe<sub>HCl</sub> were found in Dystric Arenosols (profile 13) formed from sands, whereas the lowest amounts of Na<sub>HCl</sub> occurred in Brunic Dystric Arenosol formed

also from sand. The share of potentially labile forms in pseudo-total forms of macroelements amounted to 5-86% for Ca (42.7% on average), 1-91% for Mg (25.1% on average), 1-7% for K (2.4% on average), 3-67% for Na (24.5% on average) and 1-95% for Fe (56.5% on average), and were proportionally distributed in relation to the pseudo-total form of macroelements.

One of the features related to the location of soil in the landscape is the soil's ability to accumulate or translocate nutrients. That explains significant differences in the macroelement content in soils representing four types of geochemical landscapes, distinguished within the Łyna River valley.

In the eluvial/trans-eluvial geochemical landscape (1), the lowest amounts of macroelements (excluding  $Fe_e$ ) were determined in Dystric Arenosol and Brunic Dystric Arenosol formed from sand (Table 1, Figure 3). In turn, Luvic Pheozem contained the highest amounts of  $K_t$  (46.92 g kg<sup>-1</sup>) and  $K_{HCl}$  (1.21 g kg<sup>-1</sup>).

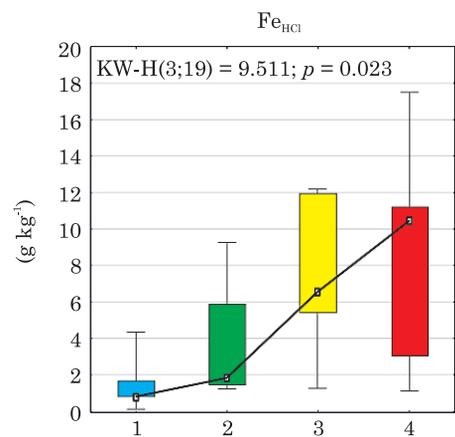
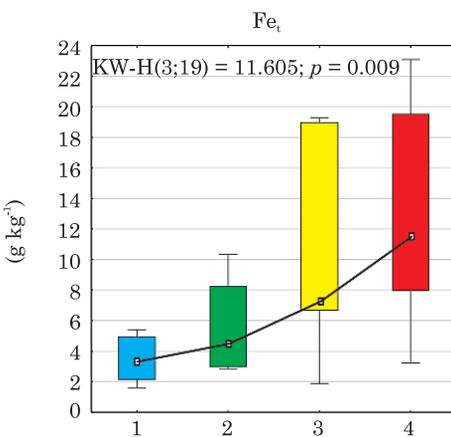
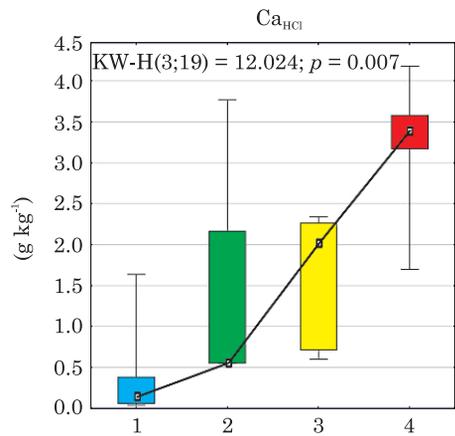
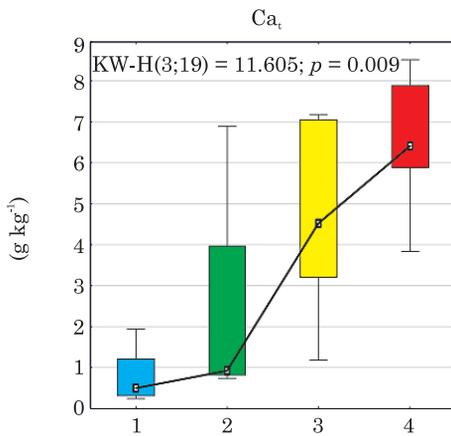
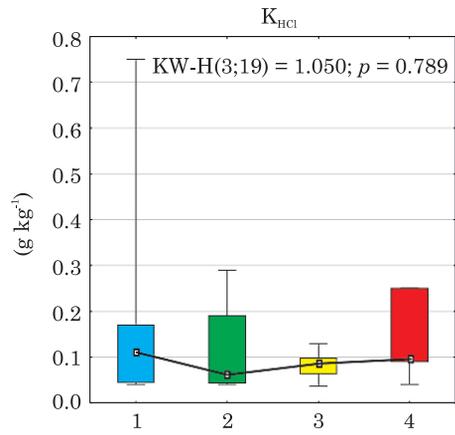
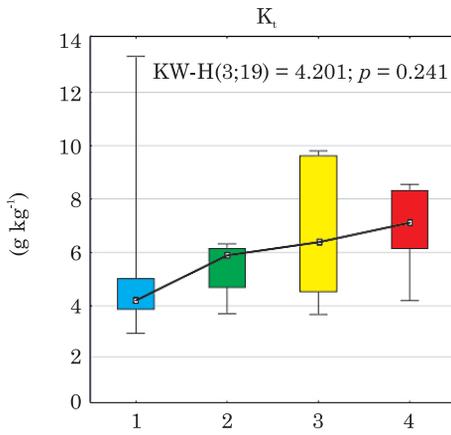
In the eluvial accumulative geochemical landscape (2), the highest amounts of  $Ca_t$ ,  $Ca_{HCl}$ ,  $Mg_t$ ,  $Na_t$ ,  $Na_{HCl}$  were detected in Eutric Umbrisol (Pantocolluvic) in horizon C formed from silty clay loam (Table 2, Figure 3). The humus horizon (A) in Eutric Umbrisol (Pantocolluvic) and Haplic Umbrisol (Colluvic) had the lowest amounts of  $K_{HCl}$  (0.04 g kg<sup>-1</sup>).

In the trans-super-aqual geochemical landscape (3), the lowest content of  $K_{HCl}$  in the parent material (C) in Dystric Fluvisol was determined. It should be noted that the content of  $K_{HCl}$  in the other horizons of this soil was also very low (0.04-0.06 g kg<sup>-1</sup>) – Table 2.

Super-aqual geochemical landscapes (4) are typical for floodplain depressions, in the form of overgrowing floodplain lakes. Within these depressions,  $Mg_{HCl}$  (3.19 g kg<sup>-1</sup>),  $Fe_t$  (26.64 g kg<sup>-1</sup>) and  $Fe_{HCl}$  (22.97 g kg<sup>-1</sup>) showed the highest values among all of the profiles across the floodplain in Fluvisol. The lowest content of  $Fe_t$  (0.91 g kg<sup>-1</sup>) and  $K_{HCl}$  (0.04 g kg<sup>-1</sup>) occurred in Mollic Gleysol (Limnic).

Earlier studies on the catenal distribution of macroelements in soils of riverine and moraine young glacial landscape suggest the accumulation of nutrients in soils which are situated in the foot-slopes (SMÓLCZYŃSKI, ORZECZOWSKI 2010b, SOWIŃSKI et al. 2004b) or in soils occurring in land depressions, for example in river valleys, midmoraine depressions (ORZECZOWSKI, SMÓLCZYŃSKI 2010, SMÓLCZYŃSKI, ORZECZOWSKI 2010a, SOWIŃSKI, LEMKOWSKA 2010, SOWIŃSKI et al. 2004a) or at the edge of river valleys, where colluvial and alluvial processes overlap (SMÓLCZYŃSKI et al. 2015). Migration of macroelements (especially Ca, Mg and K) is associated with the translocation of soil material. The elements can be translocated in the soluble form (suspension) or with soil particles (CHODAK et al. 2005).

To assess relationships between the content of the studied elements and environmental variables such as:  $CaCO_3$ , pH, OM and the share of soil fractions, a multivariate method of PCA was applied (Figure 4). The cumulative percentage variance by PCA1 and PCA2 explained as much as 89.8% of spe-



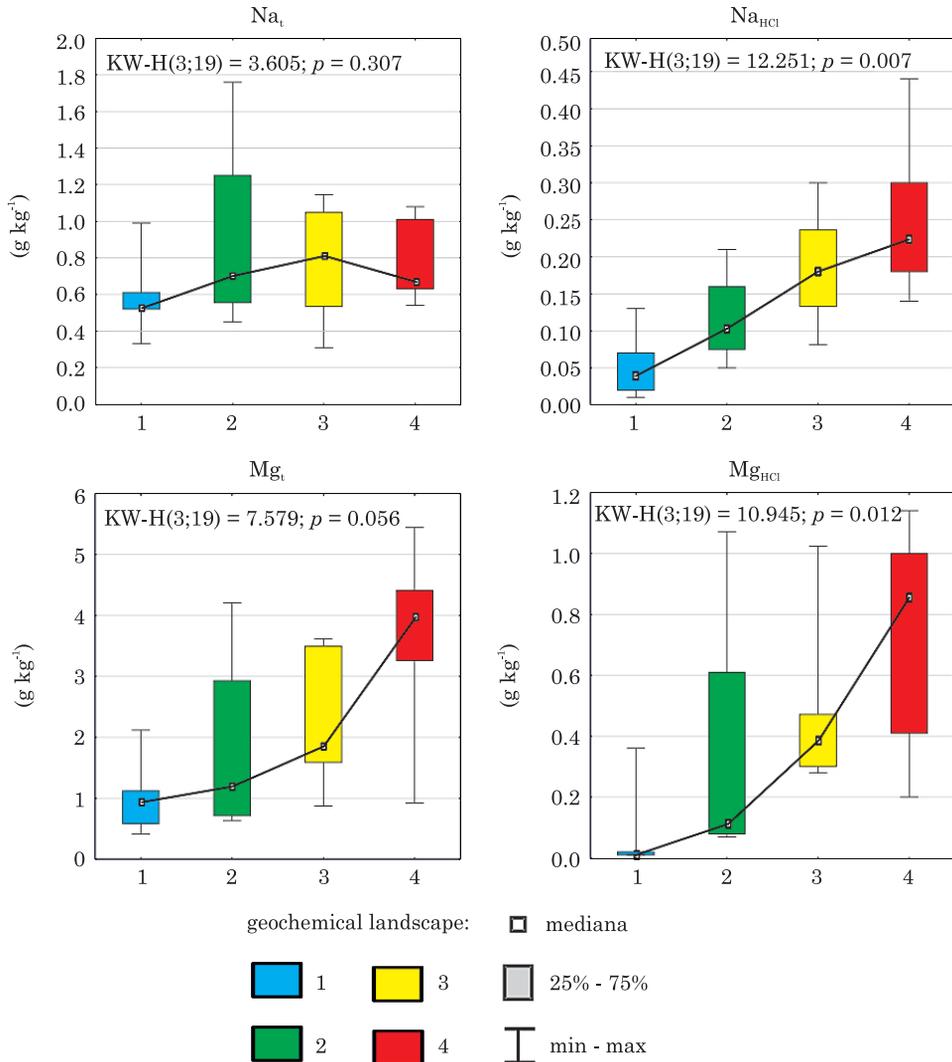
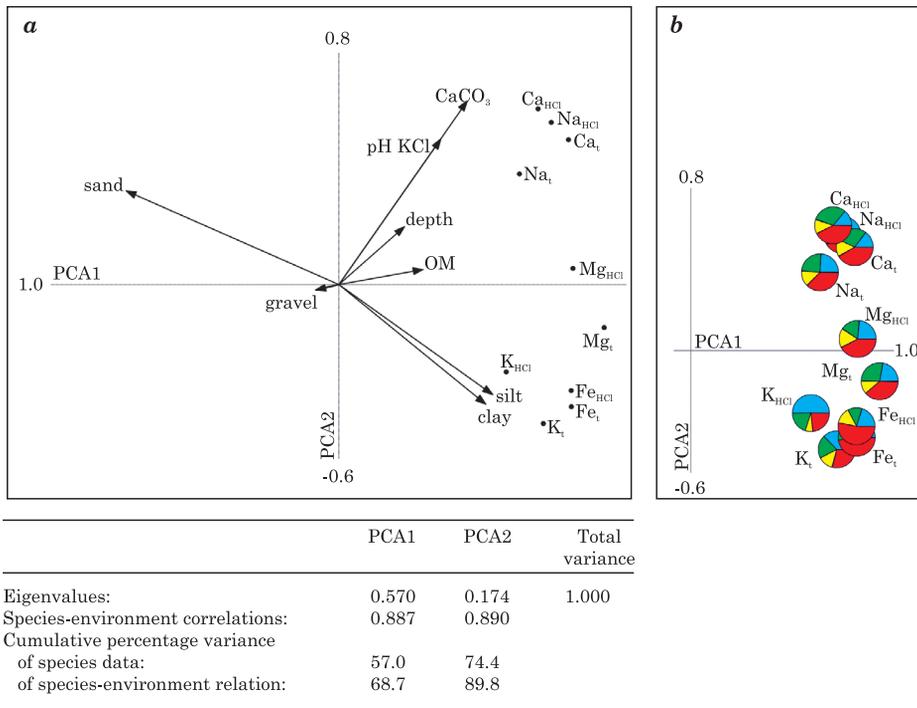


Fig. 3. Distribution of total and plant available forms of Ca, Mg, K, Na and Fe across the middle Lyna River valley: 1 – eluvial/trans-eluvial, 2 – eluvial accumulative, 3 – trans-super-aqual, 4 – super-aqual

cies-environment relationship. The first axis (PCA1) explained 68.7% of the total variance of the original data set. Most of the variance contained in PCA1 was negatively associated with the sand fractions, while being positively correlated with fine fractions of the substratum (silt and clay) and subsequently the content of Mg<sub>t</sub>, K<sub>t</sub>, K<sub>HCl</sub>, Fe<sub>t</sub>, Fe<sub>HCl</sub>. PCA2 explained 17.4% of the variance. The source of variability in the content of Ca<sub>t</sub>, Ca<sub>HCl</sub>, Na<sub>t</sub>, Na<sub>HCl</sub> and Mg<sub>HCl</sub> was the content of CaCO<sub>3</sub> and the value of pH. In turn, the OM content and sampling depth had a weaker impact.



geochemical landscape:

- 1 – eluvial/trans-eluvial    ■ 2 – eluvial accumulative  
■ 3 – trans-super-aqual    ■ 4 – super-aqual

Fig. 4. Ordination diagram of PCA computed for the macroelements and soil properties studied. Pie charts denote the shares of the elements in the geochemical landscapes defined for the Łyna River valley (explanations: see Table 1)

The super-aqual geochemical landscape was favourable to the immobilization of almost all macroelements (excluding  $\text{Na}_t$ ) – Table 1, Figure 3.

Based on soil properties (soil texture, pH, content of OM and  $\text{CaCO}_3$ ) and concentration of macroelements (Ca, Mg, K, Na and Fe), the Ward's method of clustering was used to present similarities in the elemental content between all 19 soil profiles, belonging to four geochemical landscapes (Figure 5). The most distinct differences were observed between profile 18 (Mollic Gleysol (Limnic)) in geochemical landscape (4) and profile 1 (Brunic Dystric Arenosol) in geochemical landscape (1). Cluster 1 groups soils occurring in geochemical landscapes (1) and (2) excluding Mollic Gleysol (Limnic) (profile 4). Cluster 2 aggregated soils of landscapes (3) and (4) excluding Luvic Pheozem (profile 7). Soil properties in geochemical landscapes enabled us to form two clusters regardless of the content of macroelements. This fact proved the similarity of soils in the eluvial / trans-eluvial and eluvial accumulative geochemical landscapes (cluster 1) and in the trans-super-aqual and super-aqual geochemical landscapes (cluster 2).

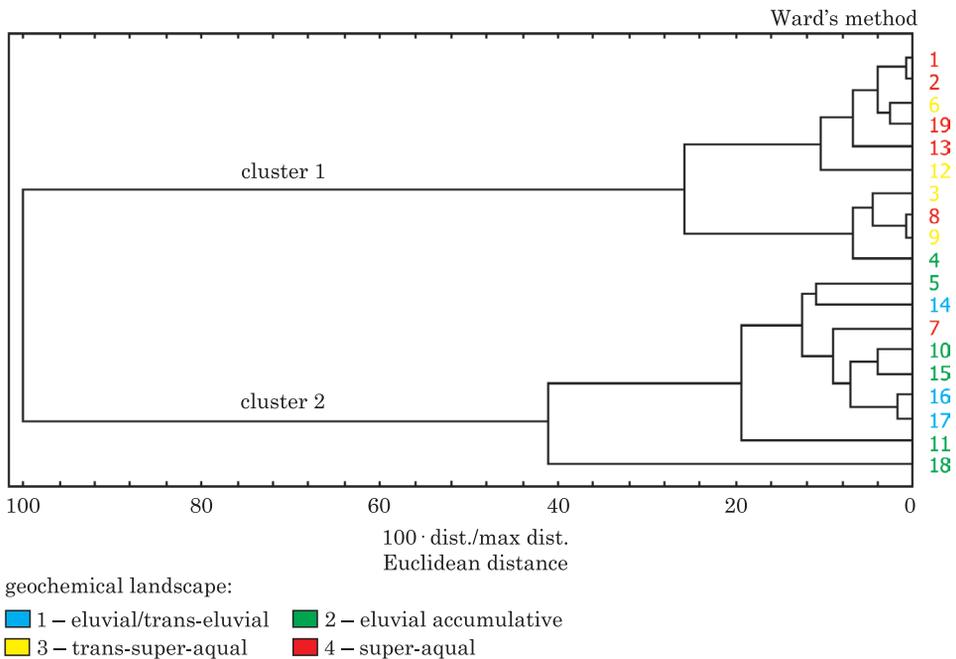


Fig. 5. Clustering of soil types based on concentrations of Ca, Mg, K, Na and Fe in soils as well as soil texture, pH and content of organic mater and  $\text{CaCO}_3$ ; 1-19 – numbers of soil profiles

## CONCLUSIONS

1. The variations in the content of the analysed macroelements were related to the type of the parent material, translocation of soil material (alluvial and colluvial processes), accumulation of organic matter and location of soil in a geochemical landscape.

2. The analysed macroelements were significantly positively correlated with some soil properties. The strongest correlation was stated between soil fine fractions (silt and clay) and  $\text{Mg}_t$ ,  $\text{K}_t$ ,  $\text{K}_{\text{HCl}}$ ,  $\text{Fe}_t$ ,  $\text{Fe}_{\text{HCl}}$ . Correlations with  $\text{CaCO}_3$  content and pH value were of minor importance for  $\text{Ca}_t$ ,  $\text{Ca}_{\text{HCl}}$ ,  $\text{Na}_t$ ,  $\text{Na}_{\text{HCl}}$ ,  $\text{Mg}_{\text{HCl}}$ . The correlation with the OM content was weaker and the gravel content had no influence on the content of macroelements.

3. The most typical sites of macroelement accumulation were the following geochemical landscapes: super-aqual > trans-super-aqual > eluvial accumulative > eluvial / trans-eluvial.

4. The clustering method enabled us to assign the soils studied to two different clusters. Cluster 1 contains soils occurring in eluvial / trans-eluvial and eluvial accumulative geochemical landscapes while cluster 2 contains soils occurring in trans-super-aqual and super-aqual geochemical landscapes.

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