

# **CONTENT OF Ca, Mg, Na, K, P, Fe, Mn, Zn, Cu IN SOILS DEVELOPED FROM THE HOLOCENE DEPOSITS IN NORTH-EASTERN POLAND\***

**Mirosław Orzechowski, Sławomir Smólczyński**

**Chair of Soil Science and Soil Protection  
University of Warmia and Mazury in Olsztyn**

## Abstract

Mineral alluvial and deluvial soils, mineral-organic mucky soils and organic peat-muck soils were developed from the Holocene deposits in northern Poland. The total content of Ca, Mg, K, P, Na, Fe, Mn, Zn and Cu was analysed in the following soils: alluvial soils which were formed from riverine deposits in delta and riverine landscapes, deluvial soils which were developed from slope deposits in a landscape of moraine hills and plains and in a riverine landscape as well as in mucky soils and peat-muck soils located in a landscape of moraine hills and plains and delta landscape. The aim of the paper was to determine total amount of the elements in a soil profile and catena sequence in the mentioned landscapes.

Total content of analysed elements in the soils developed from the Holocene deposits varied considerably among the soil types, in a soil profile, among catena sequences and landscapes. The highest content of Fe, Mn, Mg, K, Zn and Cu was reported in alluvial soils whereas Ca reached the highest level in peat-muck soils. In the riverine landscape, the highest accumulation of total Ca, Mg, K, P, Na, Fe, Mn, Zn and Cu was stated for alluvial soils, having the lowest location in the catena. In the landscape of moraine hills and plains, total content of K, Zn and Cu was the highest in deluvial soils and mucky soils located in the lower part of the slope. The total content of Ca and P was the highest in peat-muck soils having the lowest location in the catena. Statistically significant differences in the content of Ca, Mg, K, and Cu were stated between alluvial soils in the riverine and delta landscapes. The differences in the content of analysed elements, excluding Cu, were also statistically significant between alluvial and deluvial soils.

**Key words:** macro- and microelements, alluvial soils, deluvial soils, mucky soils, peat-muck soils.

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dr inż. Mirosław Orzechowski, Chair of Soil Science and Soil Protection, University of Warmia and Mazury in Olsztyn, pl. Łódzki 3, 10-727 Olsztyn, Poland, e-mail: miroslaw.orzechowski@uwm.edu.pl

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## ZAWARTOŚĆ Ca, Mg, Na, K, P, Fe, Mn, Zn, Cu W GLEBACH WYTWORZONYCH Z OSADÓW HOLOCENSKICH W POLSCE PÓŁNOCNO-WSCHODNIEJ

### Abstrakt

Z holocenских осадков на территории северной Польши выщитаются минеральные почвы аллювиальные и делювиальные, минерально-органические почвы намуршзые и органические почвы торфово-муршзые. Исследования содержания Ca, Mg, K, P, Na, Fe, Mn, Zn, Cu проводились в почвах аллювиальных выщитанных из осадков речных в ландшафте дельтовом и долин речных. Почвы делювиальные возникают из осадков стоковых в ландшафте равнин и возвышенностей моренных и ландшафте долин речных. Анализируемые почвы намуршзые и торфово-муршзые встречаются в ландшафте равнин и возвышенностей моренных и ландшафте дельтовом. Целью проведенных исследований было определение содержания Ca в почвах – в отношении профилей и катенальных – в выщитанных ландшафтах.

В почвах выщитанных из осадков holocenских подтверждено большое различие содержания Ca в почвах исследуемых элементов между выщитанными типами почв, в отношении профилей и в отношении выщитанных катен и ландшафтов. Наибольшее содержание Ca, Mg, K, Zn и Cu подтверждено в почвах аллювиальных, тогда как Ca – в почвах торфово-муршзых. В ландшафте долин речных наибольшее содержание Ca, Mg, K, P, Na, Fe, Mn, Zn и Cu подтверждено в почвах аллювиальных выщитанных в катен. В ландшафте равнин и возвышенностей моренных содержание Ca, Mg, K, Zn и Cu было наибольшее в почвах делювиальных и намуршзых выщитанных в нижней части стока, тогда как Ca и P – в почвах торфово-муршзых выщитанных в катен. Подтверждено статистически значимые различия в содержании Ca, Mg, K и Cu между почвами аллювиальными в ландшафте дельтовом и долин речных и в содержании всех исследуемых элементов, кроме Cu, между почвами аллювиальными и делювиальными.

Слова ключевые: макро- и микроэлементы, почвы аллювиальные, почвы делювиальные, почвы намуршзые, почвы торфово-муршзые.

## INTRODUCTION

The landscape of north-eastern Poland was shaped during the Vistula glaciation and is distinguished from other landscapes by the morphogenesis, lithogenesis and soil cover (KONDRACKI 1988). The land relief, various texture of soil parent materials as well as geological processes and soil-forming processes contributed to spatial diversity of the soil cover. In young glacial landscape, soil properties, soil chemical composition and soil cover are modified by natural and anthropogenic denudation processes (WOCŁAWEK 1973, BIENIEK 1997, ORZECZOWSKI 1999, ORZECZOWSKI et al. 2004b). In the soils which are not changed by human activities, natural content of elements depends mainly on parent material, weathering and soil-forming processes (KABATA-PENDIAS 1981, CZARNOWSKA 1996, ZGŁOBICKI 2008). Changes in the environment induced by diverse human activity increased the amounts of macro- and microelements not only in soil surface layers but also in the slope and riverine deposits (CZARNOWSKA 1996, ZGŁOBICKI 2008). The soils which were formed from the Holocene alluvial and deluvial deposits as well as from organic formations play an important role in nutrient cycles. Moreover, changes in the total content of elements are imprinted in these deposits.

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The aim of the paper was to determine the total content of some elements in the soils which were formed from the Holocene deposits. The study was carried out in various landscapes of north-eastern Poland, which differed in distribution of the elements in a soil profile and in a catena sequence.

## MATERIALS AND METHODS

Total content of Ca, Mg, K, P Na, Fe, Mn, Zn and Cu was analysed in alluvial soils, deluvial soils, mucky soils and peat-muck soils. The chemical elements were analysed in genetic horizons of 26 soil profiles. Alluvial soils and mucky soils in a delta landscape were located in Nowa Kocicelnica and Jeg<sup>3</sup>ownik in the region of <sup>3</sup>u<sup>3</sup>awy Wi<sup>3</sup>lane and in Baranowo in Staropruska Lowland (KONDRACKI 1988). The soils were formed from fine alluvial delta deposits in the Vistula and Pas<sup>3</sup>eka River basins. The soils in the delta landscape were situated on a plain, at the sea level. These soils had high moisture content and were drained with open ditches. Peat-muck soils in Jeg<sup>3</sup>ownik were developed from drained, silted alder and reed peats.

In the riverine landscape, the following sites were chosen: Smolajny on the <sup>3</sup>yna River, R<sup>3</sup>wnina G<sup>3</sup>rna on the Guber River and Krzeczewo on the Liwna River. The river valleys were surrounded by the following soil types: arenosols, lessive soils and black earths. On the slopes of the valley, proper and humic deluvial soils occur. In land depressions, alluvial and organic soils were situated. In the mentioned landscape, the soils were formed as a result of slope and alluvial processes under the impact of groundwater as well as of the water flowing down and across.

In the landscape of moraine hills and plains, Reszel in Sepopol Plain was chosen. In this area, the risk of erosion is low, the slope gradient is up to 3°, and slopes are gentle. The study comprised black earths developed from loam, located in the upper parts of slopes, humic deluvial soils situated in the middle of and in the lower part of slopes as well as mucky soils and peat-muck soils situated at the bottom of slopes and in a depression.

The research was carried using soil catena method, with which it is possible to determine the toposequence and spatial diversity of soils.

Total content of Ca, Mg, K, P, Na, Fe, Mn, Zn and Cu was measured in 96 soil samples after digestion in a mixture of HClO<sub>4</sub> and HNO<sub>3</sub>. Calcium, potassium and sodium were measured photometrically using a Jenway flame photometer; phosphorous was analysed colorimetrically using a Specol EK 1 spectrophotometer and magnesium was measured using an AAS 1 Zeiss Jena analyzer. The total content of Fe, Mn, Zn and Cu was estimated applying the AAS techniques on a 30 Zeiss Jena analyser.

Statistical analyses were conducted using Statistica 8.0. The significance tests and correlation analyses were applied (Statistica pl for Windows 1997).

## RESULTS AND DISCUSSION

Mineral alluvial and deluvial soils, mineral-organic mucky soils and organic peat-muck soils were developed from the Holocene deposits in northern Poland. Alluvial soils in the delta and riverine landscapes had similar amounts of clay ( $\varnothing < 0.002$  mm) and silt ( $\varnothing 0.05-0.002$  mm). The content of these mineral fractions was higher than in deluvial soils. The differences in the content of clay and silt were statistically significant between alluvial and deluvial soils (Table 1).

The highest amounts of Mn and Fe were recorded in alluvial soils developed from silt, loam and clay formations in the delta and riverine landscapes (Table 1). The amounts of the mentioned elements were 1.5-2-fold higher than in deluvial soils and organic soils. Considerable concentrations of iron ( $35.1 \text{ g}\cdot\text{kg}^{-1}$ ) and manganese ( $681.3 \text{ mg}\cdot\text{kg}^{-1}$ ) in alluvial soils were accompanied by a high groundwater level and changeable redox processes (ORZECZOWSKI et al. 2004a). Iron and manganese undergo processes of oxidation and reduction, which affect their solubility and mobility (GLIŃSKI, STĘPNIEWSKI 1984). The highest amounts of Fe and Mn were reported in surface horizons in the aerobic zone. The content of iron in alluvial soils was significantly positively correlated with the clay content ( $r = 0.485^*$ ). For silt content, however, the correlation was negative ( $r = -0.360^*$ ) – Table 2. High soil moisture may increase solubility and simultaneously activate the mobility of some trace elements, for instance manganese (DIATTA 2008).

Among the analysed soils, alluvial soils in the riverine landscape had the highest total content of Mg, K, Zn and Cu. An average total content of magnesium and potassium in these soils was  $8.9 \text{ g}\cdot\text{kg}^{-1}$ , being significantly positively correlated with the clay content (Table 2). Peat-muck soils contained on average three-fold less magnesium ( $2.9 \text{ g}\cdot\text{kg}^{-1}$ ) and four-fold less potassium ( $2.1 \text{ g}\cdot\text{kg}^{-1}$ ).

The deposits which were accumulated at the bottom of river valleys reveal the changes in the catchment area. Some trace elements which were accumulated in alluvial deposits reflect the influence of climate, human settlement as well as agricultural and industrial human activity (CZARNOWSKA 1996, ZGĘBICKI 2008). The highest average content of Zn ( $124.8 \text{ mg}\cdot\text{kg}^{-1}$ ) and Cu ( $25.9 \text{ mg}\cdot\text{kg}^{-1}$ ) was reported in alluvial soils in the riverine landscape (Table 1). In the profiles of alluvial soils, the highest concentration of these elements was recorded in surface horizons which were developed from the late Holocene deposits. Such high concentrations might have been induced by anthropogenic transformation of the environment (ZGĘBICKI 2008).

Table 1

Content of Ca, Mg, Na, K, P, Fe, Mn, Zn, Cu in alluvial soils, deluvial soils and peat-muck soils in different landscapes of north-eastern Poland

Specification	Value	Alluvial soils*			Deluvial soils	Peat-muck soils
		delta landscape and riverine landscape $n = 39$	delta landscape $n = 16$	riverine landscape $n = 23$	riverine landscape of moraine hills and plains $n = 29$	delta landscape of moraine hills and plains $n = 28$
<0.002 (mm) Percentage of fraction in diameter 0.05-0.002	$x$	25.7 <sup>+</sup>	24.8	26.4	19.0 <sup>+</sup>	–
	$S$ $CV (%)$	14.61 56.8	14.51 58.5	14.97 56.7	10.21 53.7	–
Organic matter ( $g \cdot kg^{-1}$ )	$x$	42.0	35.3	46.6	50.2	637.5
	$S$ $CV (%)$	24.70 58.8	16.30 46.1	28.60 61.3	42.3 84.2	212.60 33.3
Ca	$x$	13.9 <sup>++</sup>	9.5 <sup>**</sup>	17.0 <sup>**</sup>	8.4 <sup>++</sup>	34.3
	$S$	5.19	3.20	3.92	4.96	20.90
	$CV (%)$	37.3	33.6	23.0	59.0	60.9
Mg	$x$	7.4 <sup>++</sup>	5.2 <sup>**</sup>	8.9 <sup>**</sup>	4.7 <sup>++</sup>	2.9
	$S$	3.65	1.30	4.01	1.97	1.60
	$CV (%)$	49.3	25.0	45.0	41.9	55.1
K ( $g \cdot kg^{-1}$ )	$x$	8.0 <sup>+</sup>	6.8 <sup>*</sup>	8.9 <sup>*</sup>	6.2 <sup>+</sup>	2.1
	$S$	3.06	1.30	3.62	2.75	1.40
	$CV (%)$	38.2	19.1	40.6	44.3	66.7
P	$x$	1.3 <sup>+</sup>	1.0	1.5	0.9 <sup>+</sup>	1.4
	$S$	0.79	0.20	0.97	0.61	1.00
	$CV (%)$	60.7	20.0	64.6	67.7	71.4
Na	$x$	0.4 <sup>++</sup>	0.4	0.5	0.2 <sup>++</sup>	0.3
	$S$	0.12	0.10	0.14	0.04	0.10
	$CV (%)$	30.0	25.0	28.0	20.0	33.3
Fe	$x$	35.1 <sup>++</sup>	35.5	34.8	20.1 <sup>++</sup>	20.8
	$S$	9.56	11.00	8.67	8.38	10.92
	$CV (%)$	27.2	30.9	24.9	41.6	52.5
Mn	$x$	681.3 <sup>++</sup>	732.7	645.5	368.4 <sup>++</sup>	411.9
	$S$	259.27	206.22	289.57	137.92	238.61
	$CV (%)$	38.0	28.1	44.8	37.4	57.9
Zn ( $mg \cdot kg^{-1}$ )	$x$	107.6 <sup>++</sup>	82.9	124.8	50.9 <sup>++</sup>	28.2
	$S$	69.38	25.50	83.97	18.33	11.63
	$CV (%)$	64.4	30.7	67.2	36.0	41.2
Cu	$x$	20.0	11.6 <sup>**</sup>	25.9 <sup>**</sup>	18.3	17.8
	$S$	16.72	8.96	18.42	6.53	9.04
	$CV (%)$	83.6	77.2	71.1	35.6	50.8

\* Taxonomy of Polish soils (1989),  $x$  – mean,  $S$  – standard deviation,  $CV$  – coefficient of variation

<sup>\*</sup>  $\alpha = 0.05$ ; <sup>\*\*</sup>  $\alpha = 0.01$  significant between alluvial soils in delta and riverine landscape;

<sup>+</sup>  $\alpha = 0.05$ ; <sup>++</sup>  $\alpha = 0.01$  significant between alluvial soils and deluvial soils;  $n$  – number of soil samples

The total content of zinc and copper in alluvial soils was positively correlated with the content of < 0.002 mm fraction, although this relationship was statistically insignificant (Table 2).

In the alluvial soils, the total content of K and Mn was similar to that in alluvial soils of Poland investigated by ANDRUSZCZAK and CZUBA (1984), and the content of Mg, Zn, Cu was slightly higher than the amounts reported by those authors. The content of Fe, Mn, Zn and Cu was considerably higher than in alluvial soils or in parent materials of Polish soils, which are considered as geochemical background levels (CZARNOWSKA 1996).

Peat-muck soils, which have the lowest location in the catena in the landscape of moraine hills and plains and in the delta landscape, contained the highest amounts of calcium (on average  $34.3 \text{ g} \cdot \text{kg}^{-1}$ ). Calcium compounds which are dissolved during erosion are translocated with river waters as well as with waters flowing down to peat-muck soils situated lower in the catena. With regard to a high cation exchange capacity, these soils accumulate calcium in the ionic form  $\text{Ca}^{2+}$  (ORZECZOWSKI et al. 2004a). When compared to the surrounding alluvial and deluvial soils, peat-muck soils contained 2-4-fold more calcium (Table 1) and considerably less total Mg, K, Zn. The content of Mg, K, Fe, Zn and Mn in peat-muck soils was significantly negatively correlated with organic matter content (Table 2). In these soils, total content of Ca and Na was higher than the amounts in organic soils in the delta of the Vistula River reported by PIAŁĘCIK et al. (2001). However the amounts of Mg, K, P, Fe, Cu were similar and Zn, Mn lower than those reported by PIAŁĘCIK et al. (1998, 2001).

Alluvial soils and peat-muck soils contained similar average amounts of phosphorus and sodium whereas deluvial soils contained less P and Na (Table 1). In the analysed catena sequences, these elements were accumulated in the lowest land relief parts, which were occupied by peat-muck soils, mucky soils and alluvial soils (Table 3).

The analysed soils, which were formed from the Holocene deposits, contained more Ca, Mg, P and alluvial soils additionally had more Fe, Zn and Cu as compared to an average content of these elements in surface layers of Polish soils studied by DUDKA (1992).

In the riverine landscape, humus horizons of alluvial soils, located in the lowest parts of catena, contained three-fold more calcium, magnesium and potassium and 1.5-2-fold more iron, manganese, zinc and copper than deluvial soils and the soils surrounding the valleys (Table 3). However, in Reszel, in the catena of the landscape of moraine hills and plains, the highest concentration of K, Zn and Cu was reported in slope deposits which formed deluvial soils and mucky soils. Permanent and repeating losses of microelements from eroded soils in Masurian Lakeland were noticed by WOCŁAWEK (1973). The author qualified Cu, Mn and Zn as elements sensitive to transformation and translocation with flowing water. In peat-muck soils, calcium and phosphorus were predominant. SOWIŃSKI et al. (2004) and SMÓLCZYŃSKI

Table 2

Pearson's correlation coefficients between silt, clay, organic matter and total content of analysed elements

Properties	Ca	Mg	K	P	Na	Fe	Mn	Zn	Cu
	g·kg <sup>-1</sup>								mg·kg <sup>-1</sup>
Alluvial soils, n = 39									
Clay (fraction Ø < 0.002 mm)	0.184	0.402*	0.342*	-0.166	0.290	0.485*	-0.070	0.137	0.197
Silt (0.05-0.002 mm)	-0.161	-0.546*	-0.326*	-0.299	-0.399*	-0.360*	0.077	-0.520*	-0.538*
Organic matter (g·kg <sup>-1</sup> )	0.329*	0.454*	-0.147	0.626*	0.408*	0.023	-0.305	0.616*	0.582*
Deluvial soils, n = 29									
Clay (fraction Ø < 0.002 mm)	0.567*	0.895*	0.800*	0.206	0.295	0.780*	0.613*	0.235	0.230
Silt (0.05-0.002 mm)	0.469*	0.872*	0.666*	0.248	0.338	0.632*	0.839*	0.108	0.031
Organic matter (g·kg <sup>-1</sup> )	0.669*	0.260	0.230	0.588*	-0.206	0.286	-0.185	0.109	0.659*
Peat-muck soils, n = 28									
Organic matter (g·kg <sup>-1</sup> )	0.065	-0.448*	-0.494*	-0.209	-0.232	-0.450*	-0.432*	-0.594*	-0.348

\*correlations significant at  $p \leq 0.05$

Table 3  
 Average amounts of elements in surface horizons (A, AO, Mt) of soils in catena sequences in the landscape of moraine hills and plains and in the riverine landscape

Horizon and soils	Ca	Mg	K	P	Na	Fe	Mn	Zn	Cu
	g·kg <sup>-1</sup>								
Landscape of moraine hills and plains – catena Troksy									
Ap (black earths)	10.4	6.2	1.0	0.6	0.2	26.8	506.9	46.4	15.6
A (deluvial soils)	11.0	5.9	8.1	1.1	0.2	27.3	417.9	56.4	22.1
AO (mucky soils)	13.8	6.6	6.0	1.6	0.4	26.8	578.8	68.7	26.0
Mt (peat-muck soils)	69.7	4.5	2.8	2.5	0.4	13.7	542.8	33.2	17.4
Riverine landscape – catena Smolajny, Krzczewo and Równina Górna									
Ap (arensols, black earths, lessives soils)	3.9	3.5	3.0	1.2	0.2	14.0	387.0	72.4	18.3
A (deluvial soils)	6.3	3.7	4.7	0.7	0.2	14.2	328.2	46.5	15.2
A (alluvial soils)	16.9	9.2	9.1	1.6	0.5	35.5	628.3	128.3	26.8



Table 4

Correlation coefficients between the content of macro- and microelements in the mineral Holocene deposits (1) and organic Holocene deposits (2)

Elements	Mg	K	P	Na	Fe	Mn	Zn	Cu
Ca (1)	0.627*	0.249*	0.338*	0.501*	0.514*	0.311*	0.426*	0.407*
(2)	0.026	-0.266	0.286	0.088	-0.443*	0.081	-0.166	-0.111
Mg (1)		0.427*	0.419*	0.537*	0.627*	0.185	0.654*	0.576*
(2)		0.765*	0.660*	-0.235	-0.116	0.076	0.450*	0.087
K (1)			0.080	0.191	0.327*	0.250*	0.213	0.155
(2)			0.297	0.001	0.114	0.206	0.476*	0.214
P (1)				0.466*	0.268*	-0.101	0.747*	0.732*
(2)				-0.494	-0.299	0.351	0.112	0.448*
Na (1)					0.606*	0.320*	0.738*	0.449*
(2)					0.309	0.351	0.359	0.449*
Fe (1)						0.530*	0.431*	0.246*
(2)						0.527*	0.545*	0.693*
Mn (1)							0.037	-0.186
(2)							0.598*	0.591*
Zn (1)								0.806*
(2)								0.703*

\*correlations significant at  $p \leq 0.05$

et al. (2004) stated that in moraine landscapes, in a catena sequence, the highest content of macroelements and microelements was found in the soils of midmoraine depressions (mucky soils and peat-muck soils).

The examined soils were not contaminated with zinc and copper. It was only in the Livna riverine landscape, in the surface horizon (Aa) of alluvial soils, that increased levels of Zn ( $71.1 \text{ mg} \cdot \text{kg}^{-1}$ ) and Cu ( $303.0 \text{ mg} \cdot \text{kg}^{-1}$ ) were recorded – I° of contamination (KABATA-PENDIAS et al. 1993). High concentration of Zn and Cu appeared to be related to the humus content ( $98.1 \text{ g} \cdot \text{kg}^{-1}$ ). The content of these chemical elements in alluvial soils was significantly correlated with organic matter content (Table 2). ORZECOWSKI (1999) reported that in the delta landscape of u³awy Wi³dane, there are small areas with humic alluvial soils developed from clay containing increased amounts of Zn, Cu and Ni.

Differences in the total content of Ca, Mg and Cu between alluvial soils in delta and riverine landscapes proved to be statistically significant (at significance level  $\alpha=0.01$ ). The differences for potassium were statistically significant at significance level  $\alpha=0.05$ . Also the differences in the content of analysed elements, excluding Cu, were statistically significant between alluvial and deluvial soils (Table 1).

The correlation analyses proved that in both alluvial soil and deluvial soil, total content of Mg, K, and Fe was significantly positively correlated with the content of clay and the amounts of Ca, P and Cu were significantly positively correlated with organic matter content (Table 2). Total content of iron and calcium in the mineral Holocene deposits was significantly positively correlated with other elements. However, in organic deposits the content of iron was significantly positively correlated with manganese, zinc and copper. The content of calcium was not correlated with the other analysed elements (Table 4).

## CONCLUSIONS

1. Alluvial soils, deluvial soils, mucky soils and organic soils were formed from the Holocene deposits in northern Poland. Alluvial soils which were developed from riverine deposits contained more silt and clay than deluvial soils which were formed from slope deposits.

2. In the soils which were developed from the Holocene deposits, considerable differences in total amounts of Ca, Mg, K, P, Na, Fe, Mn, Zn and Cu were recorded. Qualitative differences in the content of the analysed elements were also reported for the distribution in the soil profile and among catenae and landscapes.

3. The highest amounts of Fe, Mn, Mg, K, Zn and Cu were noted in alluvial soils whereas Ca was the most abundant in peat-muck soils.

4. In the riverine landscape, the highest content of Ca, Mg, K, P, Na, Fe, Mn, Zn and Cu was reported in alluvial soils, which are situated in the lowest part of the catena. In the landscape of moraine hills and plains, the highest level of K, Zn and Cu was reported in deluvial soils and mucky soils, which are found in lower parts of slopes and at the bottom of the slope. Calcium and phosphorus were largely accumulated in peat-muck soils located in the lowest part of catena.

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