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CONTENT OF SELECTED MACRO- AND MICROELEMENTS IN SURFACE FORMATIONS OF ORGANIC SOILS IN NE POLAND

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Abstract. The research was carried out in the morainic areas and in river valleys in NE Poland, where seven sites located in the macroregion of Masurian Lakeland were selected. Thirteen soil profiles representing the following organic soils were studied: earth-covered murshic soils (OMnm), murshic peat soils (OTmu), hemic murshic soils (OMhe) and sapric murshic soils (OMsa). The aim of the research was to investigate the content of selected macro- and microelements in surface formations of organic soils and to determine the influence of sedimentation processes on their spatial distribution. In terms of quantity, the analyzed macro- and microelements can be arranged as follows: Ca > Al > Fe > K > Mg > Na > P > Mn > Zn > Pb > Cr > Ni > Cu > Co. Organic soils situated in the depressions had various degrees of silting with mineral sediments from the nearby areas. Along with erosive waters, deluvial material rich in minerals was flowing along the morainic slopes. Therefore, mineral-organic formations (AO) located in the ecotone zone between mineral and organic soils had the highest content of total Mg – 4.85 g kg^{-1}, K – 5.94 g kg^{-1}, Al – 24.87 g kg^{-1}, Fe – 17.77 g kg^{-1}, Zn – 0.066 g kg^{-1}, Cr – 0.046 g kg^{-1}, Ni – 0.025 g kg^{-1}, Pb – 0.060 g kg^{-1}. The highest content of total calcium, manganese, iron, copper and cobalt was found in mineral-organic formations (AO) and strongly silted murshes (Mtsz). The contents of calcium and sodium were significantly positively and the contents of other macro- and microelements were significantly negatively correlated with the amount of organic matter, organic carbon and total nitrogen.

Keywords: macro- and microelements, organic soils, mursh, siltation

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INTRODUCTION

Young glacial area of northern Poland is distinguished by high variability of soil cover in the catenal system. This area abounds in small peatlands (having an area of up to 10 ha), most of which have been anthropogenically transformed (Gotkiewicz *et al*. 1996). Organic soils in land depressions, under the influence of human-induced or natural drainage, were transformed from the accumulation phase to the oxidation phase (Piaścik and Sowiński 2002). It is estimated that currently about 70% of hydrogenic habitats are in the oxidation phase and are under the process of mursh-formation, which leads to the transformation of organic compounds and peat decomposition (Gotkiewicz *et al*. 1996, Kalisz *et al*. 2010, Glina *et al*. 2019). As a result of the mursh-forming process, *murszik* diagnostic horizons of a thickness of ≥10 cm and permanent pedogenic structure in at least 50% vol. of the horizon were developed in topsoil of organic soils. According to the sixth edition of the Polish Soil Classification (SGP6), these soils were qualified as mursh soils (Polish Soil Classification 2019).

The content of macro- and microelements in soils depends on the mineralogical composition of parent material, the content of organic matter, soil-forming processes and anthropogenic factors such as fertilization and applied pesticides. The change in the use of soils from forestry to agricultural in the morainic young glacial landscape was the cause of the initiation of anthropogenic denudation processes (Świtoniak 2014). The soils located on the eroding slopes are distinguished by typological variability and clear variation in soil properties, which prove the spatial relationship of weathering materials, leaching, translocation and accumulation of the material in the catena (Smólczyński *et al*. 2015, Šimanský *et al.* 2019). Due to their location in mid-moraine depressions and river valleys, mursh soils are under silting processes. Consequently, the layers of mineral or mineral-organic deposits of a thickness of 10–30 cm may be accumulated on their surface. The mineral sediment deposited by surface runoff waters and river waters enrich the organic formations with macro- and micronutrients of allochthonous origin from adjacent areas. This, in turn, affects the properties, composition and rate of transformation of mursh soils (Auerswald and Geist 2018, Dudare and Klavins 2012, Kalisz *et al*. 2010, Kovacs *et al*. 2012, Li *et al*. 2011). Organic soils in young glacial landscape of northern Poland play the role of biogeochemical barriers in the biogen cycle (Sowiński *et al*. 2004a, Smólczyński and Orzechowski 2010).

The aim of this study was to investigate the content of selected macro- and microelements in surface formations of organic soils in the young-glacial landscape of northern Poland and to determine the influence of sedimentation processes on their spatial distribution.

MATERIALS AND METHODS

Seven sites located in morainic areas and in river valleys in the following mesoregions of the Masurian Lakeland were selected for the study: Sępopolska Lowland (1), Olsztyn Lakeland (1), Mrągowo Lakeland (3), in the Łyna River Valley (1) and Vistula River Valley (1). As part of the field studies, 13 soil exposures were made. They represented organic soils: 1. Earth-covered murshic soils (OMnm), (SGP6) Murshic Histosols (Novic), WRB 2015 (IUSS Working Group WRB, 2015); 2. Murshic peat soils (OTmu) Murshic Histosols; 3. Hemic murshic soils (OMhe) Murshic Hemic Histosols; 4. Sapric murshic soils (OMsa) Murshic Sapric Histosols. These soils were located in mid-moraine depressions or in the areas of flat river valleys. Most of them were under permanent grasslands (meadows) or were used as ploughlands. Soil samples were taken from the depths of up to 20 cm, 20–30 cm and a peat layer (30–40 cm). These samples represented the formations with different content of organic matter and different degrees of siltation. The content of organic matter was the base for the separation of the following soil groups within the entire studied population: mineral-humus deposits of alluvial and deluvial origin (containing from 3% to 10% of organic matter – Ah), mineral-organic formations (10–20% of organic matter – AO), strongly silted mursh (20–50% of organic matter – Mtsz) and slightly silted mursh (50–80% of organic matter – Mtz) and peat formations (containing more than 80% of organic matter – Otni). The classification of the deposits was based on content of mineral matter according to Okruszko (1976).

In the collected soil samples, the following soil properties, using standard methods for soil studies, were determined: pH in H_2O and in 1 mol dm^{-3} KCl by the potentiometric method. Content of organic matter (OM) on the base of loss-on-ignition at 550°C. Organic carbon (OC) and total nitrogen (TN) using a CN Vario Max Cube elemental analyzer. The total contents of Ca, Mg, K, Na, Al, Fe, P, Mn, Zn, Co, Cr, Pb, Ni, Cu after ultrawave mineralization (Ultrawave Milestone) in 65% HNO_3 were measured by ICP (inductively coupled plasma) optical emission spectrometer iCAP 7400 ICP-OES Thermo Scientific (Van Reeuwijk 2002). Statistical calculations (mean, correlation coefficients, standard deviation) were carried out using Statistica 13.1.

RESULTS AND DISCUSSION

The thickness of mineral sediments in earth-covered murshic soils (OMnm) ranged from 20 cm to 28 cm, and the average content of organic matter in mineral deposits was 6.9%, while in mineral-organic deposits it reached 14.7% (Table 1). In the murshic peat soils, the thickness of the mursh horizons ranged from 20 cm to 25 cm, while in the hemic murshic soils and sapric murshic soils, the thickness of the mursh horizons exceeded 30 cm, and the average content of organic matter ranged from 35.0% in strongly silted mursh to 61.0% in the slightly silted mursh (Table 1). Below mursh horizons, moderately (R2) and strongly decomposed (R3) peats were accumulated. They contained 82.4% of organic matter on average, and the contents of OM between the soil formations (Ah, AO, Mtsz, Mtz and Otni) were statistically significant. The amount of total nitrogen (TN) increased with the increase of TOC, and the C/N ratio was from 8.7 in the humus horizons (Ah) to 19.5 in the peat (Otni).

Table 1. Content of TOC, TN and macroelements in the studied soil formations (g kg^{-1})

Specification	Value	Soil formation					Statistically significant differences
		Ah*	AO	Mtsz	Mtz	Otni	
		1	2	3	4	5	
pH H_2O		5.9–6.7	6.2–7.3	6.5–7.5	6.6–7.7	5.8–7.4	
pH KCl		5.6–6.2	5.9–6.5	6.1–6.8	6.0–6.7	5.5–6.8	
MO (%)	X	6.9	14.7	35.0	61.0	82.4	1<2<3<4<5
	S	1.72	2.63	9.04	7.28	3.21	
	CV	24.88	17.93	25.84	11.93	4.39	
TOC (g kg^{-1})	X	28.91	59.55	182.58	307.59	387.39	1<2<3<4<5
	S	7.61	13.32	80.06	44.69	41.84	
	CV	26.34	22.36	43.85	14.53	10.80	
TN (g kg^{-1})	X	3.44	6.51	15.04	22.71	21.08	1<2<3<4; 1<5; 2<5; 3<5
	S	0.95	1.18	4.44	3.12	5.16	
	CV	27.56	18.18	29.51	13.73	24.49	
	X	8.7	9.2	11.8	13.6	19.5	1<3<4<5; 2<3<4<5
C/N ratio	S	2.18	1.14	1.86	1.89	5.38	
	CV	25.13	12.42	15.74	13.87	27.53	
Ca	X	8.39	9.43	45.70	42.35	32.31	1<3; 1<4, 1<5; 2<3; 2<4; 2<5
	S	5.25	5.65	48.99	37.88	18.14	
	CV	62.57	59.89	107.22	89.46	56.12	
P	X	0.49	0.91	1.76	1.12	0.55	1<2<3<4; 2<3; 2>5; 3>4; 3>5; 4>5
	S	0.13	0.40	0.86	0.44	0.28	
	CV	26.60	44.20	48.76	39.41	50.17	
	X	3.28	4.85	3.29	1.70	1.28	1>4>5; 2>4>5; 3>4>5
Mg	S	0.65	1.49	1.52	0.47	0.48	
	CV	19.62	30.75	46.29	27.85	37.11	
K	X	3.71	5.94	4.28	1.06	0.48	1>4; 1>5; 2>4>5; 3>4>5
	S	1.14	2.89	2.43	0.51	0.46	
	CV	30.83	48.71	56.77	47.61	95.70	
Mn	X	0.41	0.54	0.56	0.38	0.20	1>5; 2>5; 3>5; 4>5
	S	0.04	0.19	0.25	0.37	0.11	
	CV	10.34	35.48	45.62	96.48	55.84	
Al	X	16.15	24.87	17.07	5.73	2.21	1<2; 1>5; 2>3>4>5; 3>4>5
	S	1.63	5.34	10.86	2.66	2.53	
	CV	10.07	21.46	63.61	46.41	114.12	

Specification	Value	Soil formation					Statistically significant differences
		Ah*	AO	Mtsz	Mtz	Otni	
Fe	X	11.41	17.77	15.70	8.30	5.02	1<2; 1>5; 2>4>5; 3>4>5
	S	1.77	4.96	10.21	5.21	2.50	
	CV	15.51	27.89	65.04	62.77	49.75	
Na	X	0.86	1.18	1.14	1.03	1.20	
	S	0.24	0.36	0.42	0.36	0.45	
	CV	27.31	30.37	36.76	35.15	37.35	

* Ah – humus horizon; AO – humus horizon of mursh soils; Mtsz – strongly silted mursh; Mtz – slightly silted mursh; Otni – peat; X – mean; S – standard deviation; CV – coefficient of variation (%)

The average total amounts of macroelements in the studied soils were as follows: Ca – 27.63 g kg^{-1}, Al – 13.20 g kg^{-1}, Fe – 11.64 g kg^{-1}, K – 3.10 g kg^{-1}, Mg – 2.88 g kg^{-1}, Na – 1.02 g kg^{-1}, P – 0.97 g kg^{-1}, Mn – 0.42 g kg^{-1}. The highest mean contents of total calcium were found in strongly silted mursh (45.70 g kg^{-1}) and slightly silted mursh (42.35 g kg^{-1}), and lower contents – in peat formations (32.31 g kg^{-1}) (Table 1). Average amounts of calcium were 3–5 times higher in murshes and peats than in humus and mineral-organic formations. Significantly greater accumulation of Ca in silted mursh and peat was due to the fact that calcium is an unstable component and is translocated from higher-lying mineral soils to organic soils, which are located in the depressions (Smólczyński *et al.* 2020, Smólczyński and Orzechowski 2010, Sowiński *et al*. 2004a, 2004b). The greater accumulation of calcium in organic soils should also be associated with the high content of organic matter and its beneficial effect on the sorption capacity. The content of total calcium was significantly positively correlated with the amount of organic matter (0.458), TOC (0.405) and TN (0.390) (Table 3). The strongly silted murshes were also distinguished by the highest content of total phosphorus, significantly higher than in other soil formations (Table 1).

Deluvial material rich in minerals was flowing along the moraine slopes with erosive waters. Therefore, mineral-organic formations (AO) located in the ecotone zone between mineral and organic soils act as biogeochemical barriers, accumulating macro- and microelements flowing down the slope (Sowiński *et al.* 2004b). These deposits were the site of the greatest accumulation of total magnesium, potassium, aluminum, iron, zinc, chromium, lead and nickel (Table 1, 2).

Table 2. Content of microelements in the studied soil formations (g kg^{-1})

Specification	Value	Soil formation					Statistically significant differences
		Ah	AO	Mtsz	Mtz	Otni	
		1	2	3	4	5	
Zn	X	0.047	0.066	0.046	0.027	0.015	1<2; 1>4>5; 2>3>4>5
	S	0.01	0.02	0.03	0.02	0.01	
	CV	11.81	24.55	63.04	57.43	65.12	

Specification	Value	Soil formation					Statistically significant differences
		Ah	AO	Mtsz	Mtz	Otni	
Cr	X	0.029	0.046	0.035	0.015	0.006	1<2; 2>4>5; 3>4>5
	S	0.01	0.01	0.02	0.01	0.01	
	CV	7.44	25.66	68.05	68.11	80.65	
Cu	X	0.009	0.016	0.015	0.008	0.005	1<2; 1>5; 2>4>5; 3>4>5
	S	0.01	0.01	0.01	0.01	0.01	
	CV	10.03	33.65	63.10	37.72	49.29	
Ni	X	0.014	0.025	0.020	0.010	0.005	1<2; 1<5; 2>5; 3>4>5
	S	0.01	0.01	0.02	0.01	0.01	
	CV	12.93	30.60	70.35	59.31	53.29	
Pb	X	0.036	0.060	0.047	0.032	0.019	1>5; 2>4>5; 3>4>5
	S	0.01	0.03	0.03	0.02	0.01	
	CV	58.31	54.07	49.90	57.69	64.01	
Co	X	0.009	0.013	0.011	0.005	0.002	1>4>5; 2>4>5; 3>4>5
	S	0.01	0.02	0.01	0.01	0.01	
	CV	30.01	42.93	88.94	73.94	55.13	

In the case of aluminum and zinc, the amounts were statistically significant. In the mineral-organic formations, the average content of magnesium amounted to 4.85 g kg^{-1}, and potassium to 5.94 g kg^{-1}. In humus horizons and strongly silted murshes, the amounts of these macronutrients were lower, approximately by 1.50 g kg^{-1}, while in slightly silted murshes and peat formations these amounts were distinctively lower, even 3–12 times. Smólczyński *et al*. (2010) obtained similar amounts of total Ca, Mg, K, Na, Fe, Mn, Zn for mineral-organic formations as well as strongly and slightly silted murshes, whereas Orzechowski *et al*. (2020) found more Fe, Cu and Mn. The contents of magnesium and potassium were significantly negatively correlated with the amount of organic matter (-0.733 for magnesium, -0.635 for potassium) and total nitrogen (-0.673 for magnesium, -0.539 for potassium) (Table 3). For surface humus horizons (Ah), mineral-organic (AO) and strongly silted (Mtsz) murshes, strong enrichment of magnesium and very strong enrichment of potassium was stated in relation to peats located deeper in the soil pedons (Table 4), which was confirmed by the research of Orzechowski and Smólczyński (2010). Therefore, it should be assumed that the high contents of magnesium and potassium in these formations were the result of leaching of Mg and K from agricultural soils and runoff of deluvium to the land depressions.

Table 3. Correlation coefficients between the contents of macro-, microelements and OM, TOC, TN

Specification	Ca	P	Mg	K	Mn	Al	Fe	Na
	g kg^{-1}							
OM	0.458*	-0.321*	-0.733*	-0.635*	-0.341*	-0.766*	-0.538*	0.361*
TOC	0.405*	-0.353*	-0.765*	-0.650*	-0.358*	-0.787*	-0.568*	0.443*
TN	0.390*	-0.246	-0.673*	-0.539*	-0.329*	-0.645*	-0.422*	0.303
	Zn	Cr	Cu	Ni	Pb	Co		
	g kg^{-1}							
OM	-0.703*	-0.659*	-0.505*	-0.590*	-0.586*	-0.720*		
TOC	-0.740*	-0.684*	-0.549*	-0.612*	-0.633*	-0.740*		
TN	-0.561*	-0.530*	-0.314*	-0.426*	-0.413*	-0.577*		

* correlations significant at $p \leq 0.05$, n = 42

Table 4. Enrichment factors of elements for surface layers in relation to peat horizons

Macro- and microelements	Soil formation			
	Ah	AO	Mtsz	Mtz
Ca	0.48* 0.33–0.66	0.38 0.31–0.52	0.64 0.47–0.79	1.08 1.07–1.08
Mg	1.06^{++} 1.57–3.04	2.72^{++} 0.94–5.06	3.57^{++} 1.87–5.78	1.96^{+} 1.24–2.08
P	0.52 0.44–0.60	1.66^{+} 0.50–3.45	2.41^{++} 0.95–5.21	2.29^{++} 1.92–2.65
K	7.21^{+++} 6.25–8.18	8.07^{+++} 2.80–12.07	9.54^{+++} 3.77–23.22	3.95^{++} 3.84–4.06
Al	3.13^{++} 1.82–5.47	8.85^{+++} 3.35–12.76	7.10^{+++} 2.88–11.72	2.82^{++} 2.34–3.71
Fe	1.56^{+} 1.28–1.85	3.71^{++} 1.92–5.82	4.12^{++} 1.64–7.88	1.74^{+} 1.43–3.15
Na	1.00 0.80–1.20	0.87 0.68–1.01	0.91 0.5–1.36	0.64 0.56–0.72
Mn	1.87^{+} 1.51–2.91	3.25^{++} 1.54–4.78	3.37^{++} 1.52–5.55	1.68^{+} 1.25–2.53
Zn	1.77^{+} 1.56–1.99	4.81^{++} 1.76–11.31	3.84^{++} 2.75–4.71	1.82^{+} 1.10–2.43
Cu	0.95 0.89–1.00	4.97^{++} 1.03–6.97	3.22^{++} 1.17–8.10	3.54^{++} 1.18–5.90
Ni	1.20^{+} 0.63–1.84	8.28^{+++} 2.33–11.24	5.79^{+++} 1.42–9.75	1.86^{+} 1.13–2.78
Cr	1.90^{+} 1.66–2.28	6.97^{+++} 4.41–9.96	6.22^{+++} 3.18–10.52	1.84^{+} 1.19–4.10
Pb	1.56^{+} 1.36–1.78	4.60^{++} 1.35–9.54	4.04^{++} 1.51–8.17	1.77^{+} 1.09–4.14
Co	2.15^{++} 1.75–2.58	5.41^{+++} 2.59–8.08	5.50^{+++} 2.17–9.68	3.42^{++} 1.60–5.23

* – mean value and range; 1.20–2.00 – evident enrichment ($^{+}$); 2.01–5.00 – strong enrichment ($^{++}$); > 5.01 – very strong enrichment ($^{+++}$)

Variable oxidation-reduction conditions in the transition zone between mineral and organic soils favored the accumulation of iron and manganese. The average iron content in the mineral-organic formations amounted to 17.77 g kg^{-1}, whereas in strongly silted marshes to 15.70 g kg^{-1} and it was 1.5–3 times higher than in other soil formations (Table 1). In the case of manganese, its average content was slightly higher than in mineral humus horizons, non-silted murshes and peats (higher by 0.13–0.36 g kg^{-1}). For surface mineral-organic formations (AO) and strongly silted murshes (Mtsz) strong enrichment of iron and manganese was noted in relation to peat formations (Table 4). The content of iron and manganese was significantly negatively correlated with the amount of organic matter, organic carbon and total nitrogen (Table 3).

In mineral-organic formations, the average concentration of aluminum amounted to 24.87 g kg^{-1} and was significantly higher than in other surface formations and peat. The average sodium content was similar in the studied surface formations and showed no enrichment in relation to peat.

The average total amounts of microelements in the studied soil formations were as follow: Zn – 0.040 g kg^{-1}, Pb – 0.039 g kg^{-1}, Cr – 0.026 g kg^{-1}, Ni – 0.015 g kg^{-1}, Cu – 0.010 g kg^{-1}, Co – 0.008 g kg^{-1}.

The highest average content of zinc (0.066 mg kg^{-1}), chromium (0.046 mg kg^{-1}), nickel (0.025 mg kg) and lead (0.060 mg kg^{-1}) was found in mineral-organic (AO) formations (Table 2). The contents of these microelements were approximately 1.5 times higher than in humus horizons (Ah) and 2–3 times higher than in slightly silted murshes (Mtz). Mineral-organic formations and strongly silted murshes were distinguished by higher contents of copper (AO – 0.016 g kg^{-1}, Mtsz – 0.015 g kg^{-1}) and cobalt (AO – 0.013 g kg^{-1}, Mtsz – 0.011 g kg^{-1}) than other soil formations (Table 2). The lowest concentrations of these microelements were found in peat formations, which contained 3 times less copper and 6 times less cobalt than the AO and Mtsz formations. Zadrożny *et al*. (2015) stated much higher contents of chromium, copper and lead for the surface layers of organic soils in the Błędowskie wetlands. For surface mineral-organic formations (AO) and strongly silted murshes (Mtsz), strong and very strong enrichment of Zn, Cu, Cr, Ni, Pb and Co was noted, while for humus horizons (Ah) and slightly silted murshes (Mtz), evident enrichment and strong enrichment in relation to peats (Otni) was observed (Table 4). Becher (2011) obtained similar contents of Fe, Mn, Ni, Cr and Zn, and slightly lower of Pb for organic soils in the Liwiec river valley in the Siedlce Plateau. Similarly, the author found greater concentration of these elements in the topsoil formed from murshes than in the peats lying beneath.

The contents of the analyzed microelements were significantly negatively correlated with the amount of organic matter, organic carbon and total nitrogen (Table 3). Becher (2011) noted positive correlation between the contents of heavy metals and the amount of organic carbon. On the other hand, Zadrożny *et* *al*. (2015) noted negative correlation for nickel and lead. Differences related to the influence of organic matter on the content of macro- and microelements may be related to the changing environmental conditions, as well as the direction of the pedogenic process. In studied soils, there has been a transition from the accumulation phase to the oxidation phase, and the soils have been intensively silted with mineral deposits from surface runoff (Kõlli *et al*. 2010). Along with the increase of mineral sediments in organic soils, the content of microelements also increased, which was confirmed by the research of Piaścik *et al*. (1998).

The contents of the analyzed micronutrients were much lower than the concentrations specified in the Regulation of the Minister of the Environment (2016) for the land group II: soils of agricultural land.

Statistical analyzes showed that the values of the coefficients of variation for sodium, phosphorus, magnesium and lead in all soil formations were similar (Table 1, 2). In strongly silted murshes, the concentration of calcium and cobalt, and in peats, the concentration of potassium, aluminum and chromium showed wide dispersion from mean values.

CONCLUSIONS

In terms of quantity, the analyzed macro- and microelements can be arranged as follows: Ca > Al > Fe > K > Mg > Na > P > Mn > Zn > Pb > Cr > Ni > Cu > Co. Organic soils situated in the depressions showed various degree of silting with mineral sediments from the nearby areas. Deluvial material rich in minerals was flowing along the slope with erosive waters. Therefore, mineral-organic formations (AO) located in the ecotone zone between mineral and organic soils were characterized by the highest contents of total Mg – 4.85 g kg^{-1}, K – 5.94 g kg^{-1}, Al – 24.87 g kg^{-1}, Fe – 17.77 g kg^{-1}, Zn – 0.066 g kg^{-1}, Cr – 0.046 g kg^{-1}, Ni – 0.025 g kg^{-1}, Pb – 0.060 g kg^{-1}. On the other hand, the highest content of total calcium, manganese, iron, copper and cobalt was found in mineral-organic formations (AO) and strongly silted murshes (Mtsz). The surface mineral-organic formations and strongly silted murshes were characterized by strong enrichment of Mg, Fe, Mn, Zn, Cu, Pb and very strong enrichment of K, Al, Ni, Cr and Co in relation to peat formations located deeper in the soil pedons. The contents of the analyzed micronutrients were much lower than the values in the Regulation of the Minister of the Environment of 2016 for the land group II: agricultural land. Only the content of calcium and sodium was significantly positively correlated with the amount of organic matter, organic carbon and total nitrogen, while the contents of other macro- and microelements were significantly negatively correlated.

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