Total content of macroelements and trace elements in Holocene calcareous gyttja from the post-bog area of North-western Poland

Grzegorz Jarnuszewski*, Edward Meller

Department of Soil Science, Grassland and Environmental Chemistry, Faculty of Environmental Management and Agriculture, West Pomeranian University of Technology Szczecin, Szczecin, Poland *Corresponding author: grzegorz.jarnuszewski@zut.edu.pl

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Abstract: The study covered 6 sites located in the Vistula glaciation area in north-western Poland, where the Holocene calcareous (gyttja) deposits occur. Three types of such calcareous deposits were isolated: marly (groundwater calcretes) ($CaCO_3 > 80\%$, loss of ignition < 20%, non-carbonate fractions < 20%), calcareous gyttja ($CaCO_3 > 80\%$, loss of ignition < 40%, non-carbonate fractions < 40%), and clay calcareous gyttja ($CaCO_3 > 20-50\%$, loss of ignition < 30%, non-carbonate fractions < 60%). The content of major and trace elements was determined in different horizons. Several parameters of Holocene calcareous deposits were determined, namely carbonate status, total organic carbon, non-carbonate mineral fractions and several major and minor components. Close correlations between $CaCO_3$ and Ca, $CaCO_3 > CaCO_3$ and $CaCO_3 > CaCO_3$ and $CaCO_3$ and $CaCO_3 > CaCO_3$ and $CaCO_3$ and C

Keywords: calcareous (gyttja) deposits; chemical composition of major and trace elements; pedogenetic processes

The properties and composition of calcareous Holocene deposits were determined and described based on the geological setting of catchments, climate, topography, water mixing, and water composition, as well as on the biological activity (Kelts & Hsü 1978; Schnurrenberger et al. 2003; Gierlowski-Kordesch 2010; Okupny et al. 2016). Calcareous lake sediments were formed by the decalcification of carbonate-rich geological formations in the surrounding transport of Ca in water and precipitation from Ca-rich groundwater (Kelts & Hsü 1978; Hoek et al. 1999; Verrecchia 2007; Lemkowska 2015). In the lake bottom and in the vadose zone authigenic CaCO₃ (groundwater calcretes) precipitated by the

influence of physical, chemical and biogeochemical processes. The most important role in the formation of Holocene calcareous lake sediments under temperate climate is attributed to biogeochemical processes (dissolution of gastropod shells and calcified plants (*Chara* and *Naja*) (Kelts & Hsü 1978; Łachacz *et al.* 2009; Gierlowski-Kordesch 2010; Okupny *et al.* 2016). The main factor limiting the content of authigenic calcite in sediments is the concentration of Ca²⁺ and CO₂. The allogenic mineral mass was brought into the reservoir by river water, and deposited as a dust from the atmosphere. The most important source of organic matter in calcareous lake deposits is biological production within the

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reservoir, but some organic matter was brought by river water and surface runoff (Kelts & Hsü 1978; Verrecchia 2007; Gierlowski-Kordesch 2010; DEAN & DONER 2012). In Central Europe, particularly in the late nineteenth and during twentieth centuries, such wetland areas were reclaimed to agricultural land (ŁACHACZ et al. 2009; WALTER et al. 2016). The pedogenic process has led to the emergence of post-bog soils and to the modification of properties of organogenic deposits and calcareous sediments, which now constitute a natural buffer of man-made pollution around the lakes (FREYTET & VERECCHIA 2002; SCHNURRENBERGER et al. 2003). Carbonate gyttja is characterized by high Ca, significant Mg, and negligible P, K and Na contents, whereas small amounts of Cu and Zn have been recorded. The content of organic matter is very variable (BERGLUND 1996; Stüben et al. 1998; Łachacz et al. 2009; Dobrowolski et al. 2010).

The content of individual elements in sediments can be attributed to the participation of main components: organic matter, mineral mass, and calcium carbonate, but this is not always clear. The aim of the study was to determine the relationship between individual major components and the pedogenetic process of Holocene calcareous gyttja.

MATERIAL AND METHODS

The study included a total of 6 objects located in the vicinity of lakes in north-western Poland (Fig-

ure 1), where calcareous lake deposits (groundwater calcretes) were found under shallow organogenic formations (peat, murshic horizons) or black soils horizons. The research objects were located in the area where lake depressions have developed in subglacial gutters (objects 1, 2, 4, 5), marginal lakes (3), or small inland melting lake depressions (6). The reservoirs are surrounded by moraine deposits that form moraine hills or ground moraine composed mainly of sand and clay, sometimes loam and mud (object 1). The average annual temperature in the region ranges from 7.5°C to 8.5°C, while mean annual precipitation from 550 mm to 650 mm. A total of 55 soil test pits and drills were made, from which 216 laboratory samples were collected. The lime sediments were divided based on a percentage of CaCO₃, loss of ignition (LOI), and non-carbonate fraction content (Ncf) (Markowski 1980; Łachacz et al. 2009). Three groups of sediments were isolated: marls (lacustrine chalk) (CaCO₃ > 80%, LOI < 20%, Ncf < 20%), calcareous gyttja (CaCO₃ 50-80%, LOI < 40%, Ncf < 40%), and clay-calcareous gyttja (CaCO₃ 20-50%, LOI < 30%, Ncf < 60%). Samples were analysed for the carbonate status, applying Scheibler's method, LOI by means of combustion at 550°C, contents of major elements (P, K, Mg, Ca, Na) and some trace elements (Fe, Mn, Zn, Cu, Pb, Ni, Co, Cd) extractable in aqua regia (mixture of concentrated $\mathsf{HNO}_3 + \mathsf{HClO}_4$ acids). Phosphorus content was determined by colorimetric method, K and Na by flame photometry, and other components

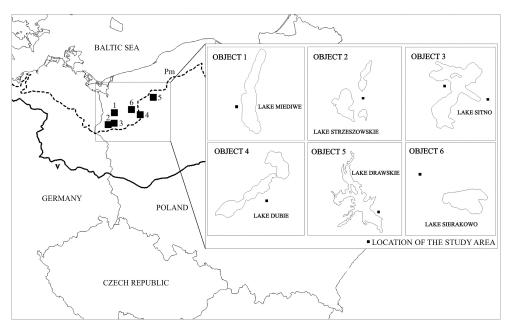


Figure 1. Location of the emerged Holocene carbonate sediments in NW Poland

by atomic absorption spectrometry. Tested sediments were arbitrarily divided into 5 zones (0–0.5, 0.5–1.0, 1.0–1.5, 1.5–2.0, and 2.0–2.5 m); mean values were illustrated graphically. Based on the obtained data, Spearman's simple correlation was calculated and PCA analysis was performed using the results subjected to standardization in Statistica software (Ver. 12.0, 2014).

RESULTS AND DISCUSSION

The ongoing pedogenesis taking up the uppermost and middle part of deposits is reflected in the morphological variability. The soils developed from sediments can be classified according to the IUSS Working Group WRB (2015) as several soil types: Sapric Histosols (Limnic), Sapric Histosols (Endolimnic), Drainic Histosols (Calcaric, Limnic), Murshic Histosols (Limnic), Umbric Gleysols (Hyperhumic), and Gleyic Phaeozems (Hyperhumic). Thickness of the studied calcareous (gyttja) deposits was not generally more than 2.5 m. In the analysed calcareous lake deposits there were residues of molluscs or clam shells. The characteristic feature of analysed sediments is marmorisation (gley phenomena) caused by the groundwater influence in the vadose zone (gleying). In the uppermost deposit horizons, there were also numerous cracks, root channels, and biopores made by the activity of soil fauna. These features are characteristic of littoral deposits that are subjected to pedogenesis (Kelts & Hsü 1978; Freytet & Verrecchia 2002; Schnurrenberger et al. 2003; Gierlowski-Kordesch 2010).

The lake marl and calcareous gyttja were mainly composed of fine microcrystalline carbonate-micritic calcium (Kelts & Hsü 1978; Żurek-Pysz 1992; GIERLOWSKI-KORDESCH 2010). In the case of clay-calcareous gyttja, its main components are allogenic clay minerals, dust and sand (Kelts & Hsü 1978; Schnurrenberger et al. 2003; Gierlowsкі-Кордеясн 2010). Clay-calcareous gyttja most frequently occurred in the bottom lake deposits indicating that their genesis can reach the young age of lakes (in the cold-climate conditions during Pleistocene-Holocene transition) when there were the best conditions for deposition of fine siliciclastic material as caused by thin vegetation and an unstable relief of the catchment (HAMMARLUND et al. 2003; Kaiser et al. 2012).

In the lake marl and calcareous gyttja, the main component was calcium carbonate (on average 90.7%

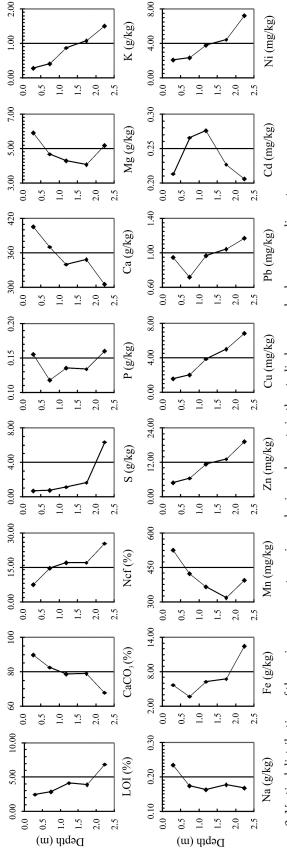
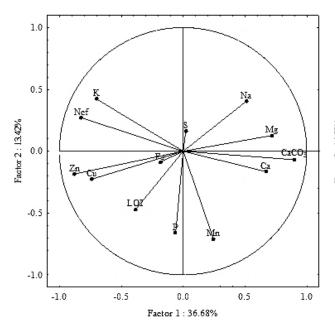
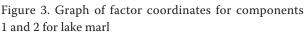


Figure 2. Vertical distribution of the main components, major and minor elements in the studied emerged calcareous sediments LOI – loss of ignition; Ncf – non-carbonate fraction content

and 68.1%). For clay-calcareous gyttja sediments, the main components were Ncf - mean 59.7%, while the content of CaCO₃ was 36.2%. The characteristic feature of the sediments was vertical variability of the main components (Figure 2). The CaCO₃ share decreased with depth and that of Ncf and LOI increased, reaching the maximum in the deposit floor. Similar results for carbonate sediments of middle latitudes were also obtained by Hoek et al. (1999), Wennrich et al. (2005), Rutkowski et al. (2007), Andrič et al. (2008), Dean and Doner (2012), Okupny et al. (2016). The PCA analysis (Figure 3–4), according to the Kaiser criterion (eigenvalue > 1), showed that among tested components, four new factors determine variance values in 66.08% for lake marl, and in 83.52% for clay-calcareous gyttja. In calcareous gyttja, these were 5 factors that accounted for 75.09% of variance values. The lake marl contained the highest levels of Ca, Mg and Na, while the lowest S, P and K (Table 1). The clay-calcareous gyttja contained the highest amounts of S, P and K, whereas the smallest Ca, Mg and Na. Calcium showed a significant correlation with $CaCO_3$ in lake marl (r = 0.55), in calcareous gyttja (r = 0.50), and in clay-calcareous gyttja (r = 0.72). There was also a significant relationship between $CaCO_3$ and Mg (r = 0.52) and Na content (r = 0.36). The relationship can be explained by the similarity of Ca, Mg and Na, which belong to good water migrants (Perelman 1971). Dobrowolski et al. (2010) and OKUPNY et al. (2016) indicated the relationship between Mg and Na contents in sediments with allogenic mineral material. This theory is confirmed by the investigated calcareous gyttja, for which the statistical analysis showed a correlation (r = 0.60) of Mg content with Ncf percentage. JONES and BOWSER (1978) attributed the elevated Mg content in sediments to periodic blooms of algae. The K content was related to the Ncf share in lake marl (r = 0.64) and lime gyttja (r = 0.54), which confirms the supply of this element to the reservoirs along with clastic materials, especially clay minerals (Jones & Bowser 1978; Andrič et al. 2008; Do-BROWOLSKI et al. 2008; OKUPNY et al. 2016). Also P and S are found in the reservoirs along with the mineral materials, which are present in waters in the form of water-soluble phosphates and sulphates (Jones & Bowser 1978; Holmer & Storckholm 2001; DEAN & DONER 2012), however, deposition of these elements in sediments is mainly related to the accumulation of organic matter. In a reservoir, this process mainly occurs through the deposition of decayed phytoplankton, higher plants, and aquatic fauna. In all studied sediments, concentrations of P and S are related to organic matter content with a significant correlation being recorded only in lake marl (for sulphur r = 0.29 and for phosphorus r = 0.25). Vertical distribution of major elements in emerged carbonate sediments indicates the enrichment of the





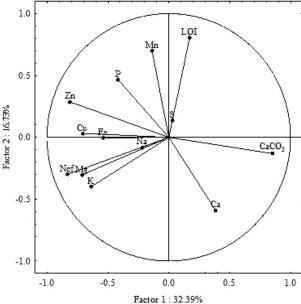


Figure 4. Graph of factor coordinates for components 1 and 2 for calcareous gyttja

Table 1. Chemical properties of the studied emerged calcareous sediments in NW Poland

Kind of gyttia		LOI	CaCO ₃	Ncf	S	P	Ca	Mg	K	Na	Fe	Mn	Zn	Cu	Pb	Cd	Ni
		%			(g/kg DM)							(mg/kg DM)					
Lake marl n = 162	x	2.77	90.71	6.53	0.96	0.114	399.7	5.08	0.37	0.195	3.85	438	5.60	2.09	0.54	0.224	2.11
	SD	2.09	5.45	4.98	1.14	0.051	59.7	1.64	0.38	0.084	2.34	212	3.91	2.00	1.36	0.279	2.37
Calcareous- calcaric gyttja <i>n</i> = 38			68.09														
	SD	5.73	9.77	11.16	3.73	0.092	93.6	1.95	1.14	0.080	5.77	213	7.56	3.06	1.85	0.315	4.01
Clay-calcaric	\boldsymbol{x}	4.03	36.23	59.74	3.50	0.182	190.4	3.40	1.42	0.140	10.09	254	14.9	3.75	1.41	0.129	4.63
gyttja $n = 16$	SD	7.68	9.00	13.25	8.62	0.094	66.5	1.51	1.36	0.043	9.98	106	12.9	3.74	1.32	0.149	5.17

LOI – loss of ignition; Ncf – non-carbonate fraction content; x – mean, SD – standard deviation

uppermost layers (0–50 cm) with P, Ca, Mg, and Na, induced by the extraction of these elements from organogenic levels subjected to intensive mineralization processes. However, the highest concentrations of Ca in the uppermost layers can also be caused by calcite formation in the capillary fringe zone - processes of calcite precipitation through evaporation or CO₂ degassing of vadose waters (FLÜGEL 1982). In the deepest layers, the highest K content was recorded, the source of which is directly related to the catchment erosion and accumulation of mineral material in the lake bottom. The high levels of Mg, P and S in the bottom layers of calcareous deposits can be attributed to the deposition of clastic materials and organic matter during the formation and during an early stage of the reservoir functioning. Approximately similar distribution of major elements in carbonate sediments was also obtained by Wennrich et al. (2005), Andrič et al. (2008), Dobrowolski et al. (2010), and Okupny et al. (2016). Hammarlund et al. (2003), Wennrich et al. (2005), Rutkowski et al. (2007) and OKUPNY et al. (2016) reported that an increased content of organic matter and major elements in sediments was recorded during the reservoir formation (subsidence and sedimentation of organic matter) during a subsequent warmer period (enhanced biological production in water and on land, mainly in Alleröd).

The content of trace elements in lake sediments is mainly due to the geological development of the catchment and deposition area of the sediment in the reservoir, as well as due to anthropogenic impacts, especially in the uppermost sediment layers (Jones & Bowser 1978; Wennrich et al. 2005; Andrič et al. 2008; Okupny et al. 2016). Among the trace elements the highest Fe content (10.09 g per kg) in the analysed sediments was detected in clay-calcareous gyttja, whereas Mn (436 mg/kg) in

lake marl. A similar dependence in the case of Mn was also observed by Wällstadt and Borg (2003). The Fe content in carbonate sediments varies within very wide limits (Dobrowolski et al. 2010; Окир-NY et al. 2016). Both the Fe and Mn content in the uppermost layers of sediments showed increased concentrations caused by marmorisation processes related to successive reduced and oxidised states of these elements and their migration, while the high concentration of Fe and Mn in bottom sediment layers was related to mineral materials (JONES & Bowser 1978; Verrecchia 2007). Vertical distribution of Fe content indicates a clear enrichment of the carbonate sediment floor with this element. The Fe content increasing with depth indicates that groundwater is the main source of this element, although the influence of illuviation is also visible in the sediment floor. The highest contents of Zn, Cu, Pb, Cd and Ni were observed in carbonate gyttja sediments, while the lowest contents of Zn, Cu, Pb, and Ni were recorded in lake marl sediments (Table 1). Zinc and copper show significant correlations with Ncf in lake marl (r = 0.62 and r = 0.50, respectively) and carbonate gyttja (r = 0.44 and r = 0.48, respectively). It is therefore possible to attribute the deposition of these elements in sediments mainly to the erosion of geological formations in catchments and transport of material into the lake basin, especially clay minerals (Dobrowolski et al. 2010; OKUPNY et al. 2016). This theory is also confirmed by the vertical distribution of Zn and Cu contents in sediments. There is also a relationship between the content of these elements in studied sediments and the organic matter; the significant correlation of Cu and Zn contents with LOI in lake marl (r = 0.34 and r = 0.32, respectively) and loamy-lime gyttja (r = 0.67and r = 0.57, respectively). In the redox condition of gyttja soils free sulphide ions exist, the concentra-

tion of which determines the accumulation of Cu, Zn and Fe by metal sulphide precipitation, organic complexing or both. Metal sulphides (Cu, Zn and Fe) and metal-organic complexes are insoluble. The redox potential, pH, and sulphide ion availability determine the form of metals in sediments (Timperley & Allan 1974). Significant correlations between Pb content and Ncf were observed for lake marl and carbonate gyttja (r = 0.20 and r = 0.33), which should be connected with the transport of eroded mineral matter of the catchment to the lake basin along with water, but also with atmospheric deposition (Aleksander-Kwaterczak & Kostka 2011). Significant relationships were also reported for Cd and Ni contents vs. LOI (r = 0.30 and r = 0.20) and Ncf (r = 0.26 and r = 0.41) in lake marl.

CONCLUSION

Among trace elements, maximum concentrations were recorded in the lowest layers of studied sediments in the case of Fe, Zn, Cu, Pb, and Ni. For Pb, increased amounts of the element in the uppermost layer were observed, which should be linked to anthropogenic factors (Wennrich et al. 2005; Rutkowski et al. 2007; Aleksander-Kwaterczak & Kostka 2011). Organic matter has the potential to adsorb metals and affects the content of trace elements in calcareous sediments. A similar distribution of trace metals in calcareous sediments (maximum in the lower and upper zones or associated with them increased OM content) was also obtained by Wennrich et al. (2005), Andrič et al. (2008), Rutkowski et al. (2007), Aleksander-Kwaterczak and Kostka (2011), as well as Okupny et al. (2016).

The characteristic features of the studied sediments are high Ca Mg, Fe, and Mn contents, and low P, Na, S, K, Zn, and Cu abundance. Two characteristic major and trace element concentrations in emerged sediments were observed during the study. The high contents of tested elements in the lower layers of sediment deposits are related to the early formation of reservoirs and prevailing climate in central Europe. During this period, the deposition of organic matter occurred as a result of its production within the reservoir, especially in the later phase of climate warming or peat accumulation during the ice melting phase. Further peak concentrations for Ca, Mg, Na, P, Fe, Mn, and Pb were recorded in the uppermost layers of sediments, where the pedogenesis associated with mineralization of organic matter and transport of components (Fe) to groundwater plays a crucial role.

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