THE RECORD OF GEOCHEMICAL CHANGES IN THE BIOGENIC-CALCAREOUS SEDIMENTS OF A KETTLE-HOLE IN A YOUNG GLACIAL LANDSCAPE (WESTERN KASHUBIAN LAKELAND, NORTH POLAND)

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Abstract:
The paper was focused on the reconstruction of past-environmental conditions dynamics based on the geochemical characteristics of sediments filling kettle-hole located in the western part of the Kashubian Lakeland, North Poland. Stratigraphic variability of lithogeochemical constituents and a set of 13 elements (TOC, N, P, Na, Ca, Mg, K, Al, Fe, Mn, Cu, Ni, Zn) were applied for Holocene reconstruction of certain processes and conditions in the studied kettle-hole. The detailed geochemical analysis allowed us to identify 6 phases in its development: Masz-1 stage covering sedimentation of sedge-moss peat over melting dead ice at the turn of the Preboreal and Boreal periods; Masz-2 stage of the initial phase of lake development with deep-water sedimentation; Late Boreal and Atlantic stage Masz-3 related to sedimentation of lacustrine chalk; Subboreal stage Masz-4 representing the beginning of lake terrestrialization; Subatlantic stage Masz-5 of lowland bog, and Masz-6 stage covering final phase of peatland evolution due to human activity. Principle component analysis highlighted the importance of two major factors controlling the geochemical variability of the studied sediments. These are the varied origin of supplying water reflected in the sedimentation of organic-calcareous sediments (PC1), and oxidative-reduction conditions determined by water level fluctuations (PC2).

Key words: geochemistry, Holocene, Kashubian Lakeland, biogenic-calcareous sediments, North Poland.

Manuscript received 14 February 2023, accepted 7 August 2023

INTRODUCTION

The chemical composition of sediments filling the lake basins is a function of several factors reflecting natural and anthropogenic changes in a lake catchment (Lerman, 1978; Mannion, 1978, 1981; Fortescue, 1980; Foster and Dearing, 1987; Borówka, 1992, 2007; Wojciechowski, 2000). It is affected both by the characteristics of the natural environment of the lake catchment, such as the lithology, vegetation cover, climatic conditions, advancement, and nature of soil-forming processes or the type of lake basin supply. Moreover, processes occurring in the lake basin, in particular dynamics of the intensity and character of sedimentation, the intensity of biological production, changes in oxidative-reduction conditions, and the intensity of supplying with suspended matter and ionic compounds, are also of key importance (Lerman, 1978; Gołębiewski, 1976; Fortescue, 1980; Wojciechowski, 2000; Borówka, 2007; Apolinarska et al., 2012; Karasiewicz et al., 2014). Considering knowledge of the present determinants and effects of various processes occurring in lake catchments, we can reconstruct past-environmental changes based on variability in sediment chemistry (i.a. Diggerfeld, 1972; Digerfeldt, 1977; Mannion, 1978, 1981; Gołębiewski, 1976; Engstrom and Wright, 1984; Wojciechowski, 1987, 2000; Borówka, 1992, Apolinarska et al., 2012; Hulisz et al., 2012; Karasiewicz et al., 2014, 2017; Okupny et al., 2016, 2021; Niska et al., 2017; Tu et al., 2020).

Reservoirs of biogenic accumulation frequently occur in a fresh glacial landscape of Pomerania. These include contemporary lakes, ponds, and bogs, as well as basins of the former lakes filled with sediments. Fossil lakes can be found in a variety of geological settings, including areas of glacial uplands, on sandurs, as well as in glacial troughs and
bottoms of proglacial outflow valleys, where they fill depressions preserved in the past by a dead ice. In Pomerania, the biogenic accumulation started at the beginning of the last deglaciation, and therefore the sediments accumulated in the basins can record all environmental events from the end of the Pleistocene until the modern times.

Biogenic-calcareous sediments filling the lake basins located in the fresh glacial zone of northern Poland constitute a valuable natural archive for tracking environmental changes at local and regional scales. The lakes in the Kociewie Lakeland (Błaszkiewicz, 2005), kettle lake in Osłonki (Nowaczyk, 2008), kettle-hole at Retno in the Brodnica Lakeland (Hulisz et al., 2012; Karasiewicz et al., 2014), Lake Skrzynka in Bory Tucholskie (Apolinarska et al., 2012), Wilkostowo mire in Kujawy Lakeland (Okupny et al., 2016), Żabieniec mire in the Łódź Hills (Okupny et al., 2021), organic sediments filling the ancient oxbow-lakes (Niska et al., 2017) and lake sediments at peatland bottoms of varied origin and age (Lemkowska et al., 2013) represent case studies, in which geochemical features of biogenic-calcareous sediments were analyzed in combination with sedimentological and palaeoecological data.

This study was aimed at the reconstruction of past environmental conditions based on the vertical distribution of geochemical constituents in kettle-hole sediments at Maszewo Łęborskie (NW Poland). Moreover, the identification of factors controlling the geochemical variability of sediments was also the subject of this study. The presented data constitute preliminary results of the project entitled „Palaeoecology and geochemistry of the biogenic-calcareous sediments filling paleolakes in the western part of Kashubian Lakeland (North Poland)”.

REGIONAL SETTING

The studied area is located in the western Kashubian Lakeland, approximately 10 km south of Łębork and the southern margin of the Reda-Łeba ice-marginal valley (Augustowski, 1979; Kondracki, 2009) (Fig. 1A–B). It cov-
ers a strongly varied young glacial zone, developed during a retreat of the Scandinavian ice sheet in the Pomeranian Phase (16.2 ky BP; Kozarski, 1995; Marks, 2005). A thickness of the Pleistocene sediments varies spatially (187.4 m to 5 m), due to the high altitudinal variation of the sub-Quaternary relief (Prussak, 2004, 2005; Prussak and Pikies, 2007a, 2007b). Relative heights of the western part of the Kaszuby Lakeland reach 138 m. The highest location (155 m a.s.l.) is in the Łębork Hills area, in the north-eastern part of the study area, while the lowest location (10.0 m a.s.l.) occurs in the estuarine area of the Pogorzela River, which enters the Leba ice-marginal valley (Fig. 1B). A stepped pattern of land lowering oriented slightly concentrically from SE towards NW and N is marked in the spatial pattern (Prussak, 2004, 2005; Prussak and Pikies, 2007a, 2007b).

Glacial, glaciofluvial and fluvial landforms, accompanied by biogenic accumulation landforms are the dominant in the landscape of the western Kashubian Lakeland (Sylwestrzak, 1978; Prussak, 2004, 2005; Prussak and Pikies, 2007a, 2007b) (Fig. 1C). The greatest coverage is typical for plain and undulated morainic plateaux and end moraines reaching heights of 10–30 m above the upland level (Prussak, 2004; Prussak and Pikies, 2007a). Glaciofluvial plains form height-differentiated terraces at 70–140 m a.s.l. Their formation is related to the meltwater outflow system (Sylwestrzak, 1978).

A distinctive feature of the landscape in the Kashubian Lakeland is the presence of glacial tunnel valleys, sub-latitudinal oriented, characterized by their deep incision in the surrounding upland surface, and the valleys developed during a final stage of the meltwater outflow after the marginal flow disappeared. Ice-marginal valley running south of the Łębork Hills, from the lower section of the Pogorzela River in the west to the lower section of the Okalica River near Łębork in the east, is an example (Fig. 1B–C). There are kettle holes at its bottom, developed during the Late Glacial and Early Holocene, and filled with thick biogenic-calcareous sediments. The largest kettle-holes occur in the lower reach of the Pogorzela valley, in the Unieszynka valley and near Maszewo Łębskie (Fig. 1C).

The examined lake Maszewo is located in the north-eastern part of the valley system, southwest of Maszewo Łębskie (Fig. 2). It is irregular in shape, its latitudinal axis reaches 320 m, whereas the longitudinal one is 350 m. The basin is about 9–10 ha large. It is drained by the Stream Sopot, a left-bank tributary of the Okalica River. The stream outflows from an unnamed forest lake, located east of the Krępkowo village (Hydroportal ISOK, 2023).

METHODS

Sediment sampling

The borehole was done in a shore zone of a former lake, approximately 50 m west of the buildings of the Maszewo Łębskie village (Fig. 2). Detailed location of the borehole is defined by coordinates: 54°28′09″N; 17°44′16″E, and altitude is 78.1 m a.s.l.

The sediment core, 650 cm long, was collected using Instorf corer, 7 cm in diameter and 80 cm long. A lithology of the core was described with terms of Aaby and Berglund (1986). A total of 125 sediment samples were collected at intervals of 5 cm (c. 200 cm3 each), always respecting lithological boundaries. Due to technical reasons, the 15 cm top layer of core section constituting strongly decomposed peaty material (mursh) was omitted from the analysis.

Geochemical analysis

We used the geochemical analysis protocol recommended by the International Geological Correlation Programme (IGCP), subproject No 158B, for the study of lake and mire sediments (Bengtsson, 1978; Bengtsson and Ennell, 1986) and later applied by other researchers, among others Wojciechowski (1987, 2000), Borówka (1992, 2007), Apolinarska et al. (2012), Karasiewicz et al. (2014), Okuny et al. (2016, 2021).

Sediment samples were dried at 65°C and homogenized in an agate mortar. The organic matter (OM) content was determined as the ignition loss at 550°C (4 hours), the carbonates content with the Scheibler’s volumetric method and the total silica content (SiO2tot) was calculated based on difference between contents of OM and acid-soluble matter (ASM). Moreover, the total organic carbon (TOC) content was analyzed by wet oxidation (K2Cr2O7), the total nitrogen (N) according to the Kjeldahl procedure (VELP UDK system, Italy) (Van Reeuwijk, 2002) and contents of Ca, K, Na, Al, Fe, Mn, Cu, Ni and Zn by microwave plasma atomic emission spectrometry (4100 MP-AES, Agilent, Australia) prior samples digestion in aqua regia (open system with vapor recovery). TOC/N, TOC/P, N/P, Fe/Mn and Fe/Ca ratios were calculated based on elemental concentrations to specify conditions in the lake and its catchment. The mechanical denudation index (according to Borówka, 2007) was modified to the formula \((\text{Na}+\text{K}+\text{Mg}+\text{Al})/\log \text{Ca}\), to show a stronger differentiation of its values, especially in peat layers.

A stratigraphically constrained cluster analysis (using the method of incremental sum of squares) was applied

![Fig. 2. Location of Maszewo 1 core in the vicinity of the village of Maszewo Łębskie. The actual and approximate (dashed line) extent of the Maszewo kettle-hole is marked.](image)
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to distinguish geochemical zones. Factors determining the geochemical variability of sediments were identified, based on principle component analysis (PCA). In total 13 elements (TOC, N, P, Ca, Mg, Na, K, Al, Fe, Mn, Cu, Ni, Zn) were used for these purposes. Lithological factors, i.a. organic matter, total silica and CaCO₃ were omitted, because these variables duplicate the information carried by TOC, Ca and lithogenic elements (Na, K, Mg, and Al), thus increasing their role in final results. PAST 3.20 software (Hammer et al., 2001) was used for a statistical analysis.

Radiocarbon dating

Radiocarbon dating of 4 peat samples using the scintillation technique was performed in the Laboratory of Absolute Dating in Kraków (Poland). Detailed results are included in Table 1. Conventional radiocarbon ages were calibrated using the OxCal ver. 4.4 software (Bronk Ramsey, 2021) and IntCal20 (Reimer et al., 2020) calibration curve. All ages are given in BP cal years in this paper.

### RESULTS

#### Lithology

The Maszewo 1 profile covers a 640 cm thick series of biogenic-calcareous sediments (Fig. 3) accumulated in a basin preserved by dead ice. In the bed of the lake there is a grey silty sand covered by a 20 cm thick (640–620 cm depth) layer of brownish-black sedge-moss peat. The sequence of lake sediments begins with a layer of brown detritus-calcareous gyttja (620–585 cm depth) overlain by a 365 cm thick layer of light grey lake chalk. The chalk is olive-grey at its bottom. The next series of sediments (220–120 cm depth) constitutes a 100 cm thick layer of brownish-black reed-sedge peat and is overlain by a sedge peat

<table>
<thead>
<tr>
<th>Depth (cm b.g.l.)</th>
<th>Laboratory Number</th>
<th>Sample description</th>
<th>Conventional radiocarbon date [BP]</th>
<th>Calibrated y BP (95.4% range)</th>
<th>Calibrated y BP (midpoint) used in a depth-age model</th>
</tr>
</thead>
<tbody>
<tr>
<td>90–95</td>
<td>MKL-5782</td>
<td>Sedge peat, dark brown</td>
<td>2630±80</td>
<td>2935–2471</td>
<td>2703</td>
</tr>
<tr>
<td>215–220</td>
<td>MKL-5783</td>
<td>Reed-sedge peat, brown</td>
<td>5300±80</td>
<td>6278–5922</td>
<td>6100</td>
</tr>
<tr>
<td>620–625</td>
<td>MKL-5852</td>
<td>Moss-sedge peat, brown</td>
<td>8770±90</td>
<td>10149–9547</td>
<td>9848</td>
</tr>
<tr>
<td>635–640</td>
<td>MKL-5853</td>
<td>Moss-sedge peat, brown</td>
<td>9050±70</td>
<td>10409–10115</td>
<td>10262</td>
</tr>
</tbody>
</table>

Fig. 3. Lithology of Maszewo 1 core. Chronostratigraphy and depth-age model based on calibrated yr ¹⁴C. The grey shading represents the 95.4% probability range. Figures next to the graph characterize the mean sedimentation rate (mm/y) between particular levels of known age. Chronostratigraphic units: 1 – after Mangerud et al. (1974), 2 – after Walker et al. (2018). Lithology: 1 – grey silty sands, 2 – black sedge-moss peat, 3 – brown detritus-calcareous gyttja, 4 – light grey lacustrine chalk, 5 – brownish-black reed-sedge peat, 6 – sedge peat, 7 – mursh.
(120–15 cm). The uppermost layer of sediments (15–0 cm depth) consists of strongly decomposed peat (mush). The concentrations of OM and TOC reach 60–80% and 330–600 mg·g⁻¹ d.m., respectively, as well as for the bottom layer of the sedge-moss peat. The highest mean sedimentation rate is 0.63 mm·y⁻¹. The lowest values were recorded for the Subatlantic period (radiocarbon date: 9050±70 yr BP) and has continued until the present day. No sedimentary gaps were identified in the lithological record and the sediment sequence reflects the natural transformation of the reservoir.

The age-depth model was developed based on linear interpolation between midpoints of individual 95.4% of the intervals calibrated years BP (Table 1, Fig. 3). In the construction of the model, the lake surface was assumed to represent the present day. Unfortunately, it was impossible to determine the age of the chosen samples of lake chalk, as no organic material that could be dated using the radiocarbon technique was found in these sediments. For this reason, the interpolated age of the sediments in the 220–585 cm depth may be a subject of some uncertainty.

The boundaries between the Holocene chronostratigraphic units are cited after Mangerud et al. (1974), and the calendar age boundaries between units were derived from Walanus and Nalepka (2010). For comparison of the range of chronostratigraphic units, a new formal division of the Holocene according to Walker et al. (2018) and Head (2019) was added (Fig. 3).

As indicated by the age-depth model, the mean sedimentation rate in the analyzed Maszewo 1 profile is 0.63 mm·y⁻¹. The lowest values were recorded for the Subatlantic and Subboreal peats, 0.34 mm·y⁻¹ and 0.37 mm·y⁻¹ respectively, as well as for the bottom layer of the sedge-moss peat (0.43 mm·y⁻¹). The highest mean sedimentation rate is characterized by the lake chalk (1.09 mm·y⁻¹) (Fig. 3).

Relationship between chemical composition and lithology

The concentration of the majority of constituents in the Maszewo 1 profile is affected by lithology, showing clear differences dependent on the sediment type (Fig. 4). It is due to different sedimentation processes and various sources of matter supplied to the reservoir.

In biogenic sediments (sedge peat, reed-sedge peat) the highest contents of Ca between 300 and 400 mg·g⁻¹ d.m. The contribution of other constituents is low, except for Mg, reaching a maximum of 3.4 mg·g⁻¹ d.m. at 380–400 cm depth (Fig. 4). Similarly, the contribution of SiO₂tot and lithogenic elements in a lake chalk is low and reaches values below detection limits for Na, 0.1–0.2 mg·g⁻¹ d.m. for K, and 0.3–0.5 mg·g⁻¹ d.m. for Al. This record excludes their terrigenous origin (Fig. 4).

Vertical variability in Mn content showed another trend as compared to other components. In the sedge and reed peat (0–220 cm depth) Mn content is generally low (0.21–0.61 mg·g⁻¹ d.m.), whereas the lake chalk reaches from 0.52 to 3.70 mg·g⁻¹ d.m. The highest Mn content (24.1 mg·g⁻¹ d.m.) was recorded in the detritus-calcareous gyttja at 585–620 cm depth. This may indicate the periodic occurrence of anaerobic conditions in the deep-water lake (Apolinarska et al., 2012; Zander et al., 2021).
Fig. 4. Differentiation of geochemical properties of sediment in the Maszewo 1 core in relation to lithology and chemical zones; for lithology see Fig. 3.
The content of trace elements (Cu, Ni, and Zn) was generally low across the profile. It was within the geochemical background and is comparable to those reported for other lakes of the Kaszubian Lakeland (Bojakowska and Sokolowska, 1996). The highest concentration of these elements was noted at the bottom part of the profile, in the basal peat (altogether 63–70.1 µg·g⁻¹ d.m.), in the bottom of a reed peat at 215–220 cm depth (altogether 70 µg·g⁻¹ d.m.), and in the top of peat (altogether 71.4 µg·g⁻¹ d.m.) (Fig. 3). Based on similar studies (e.g. Niska et al., 2017), the highest concentration of trace elements should be expected in the top. Considering a low environmental contamination, predicted values of the summarized content of Cu, Ni, and Zn are between 100 and 150 µg·g⁻¹ d.m.

**DISCUSSION**

**Factors controlling geochemical variation of sediments at the kettle-hole in Maszewo**

A principle component analysis (PCA) was used to identify factors influencing the variability of geochemical constituents in the kettle-hole sediments at Maszewo. PCA allowed to reduce a large number of variables into a few uncorrelated components and to identify substantively new factors to understand the nature of the obtained data (i.a. Wojciechowski 2000; Kaiserli et al., 2002; Panahi et al., 2004; Okupny et al., 2016, 2021).

Using the Kaiser’s criterion (Braeken and van Assen, 2017), only the components for which the eigenvalue is greater than 1 were included in the PCA of the Maszewo 1 profile. Two components are significant (PC1 and PC2) for the analyzed dataset, which together explains 84.59% of the total variance (Table 2, Fig. 6). The spatial distribution of the analyzed samples in the PC1 and PC2 coordinate system differentiates samples with different affiliations concerning the projected axes of the variables (Fig. 7). The first principal component (PC1) is strongly positively correlated with TOC, N, Na, K, Al and Cu (r >0.89) and with Ni (r = 0.81), and strongly negatively correlated with contents of Ca (r = -0.95) and Mg (r = -0.73) (Table 2). Such distribution of correlation coefficients between the variables and PC1 reflects lithochemical features of sediments, separating components of organic sediments (peat) from calcareous sediments (lake chalk) (Fig. 7). From this reason the first principal component may be defined as a lithochemical component, which depends on supply sources of the reservoir.

For biogenic-calcareous sediments, dominated by a high proportion of organic matter and its constituents on
one hand and calcium carbonate on the other, antagonism is very often recorded, expressing strongly positive and strongly negative correlations within the distinguished principal component, resulting from different sedimentary processes and sources of matter supply to the reservoir. A similar antagonism between organic matter and calcium carbonate was found among others, in the biogenic-calcareous sediments of the Kórnicko-Zaniemyskie lakes (Wojciechowski, 2000) and the Wilkostowo mire (Okupny et al., 2016).

The highest values of PC1 in the Maszewo 1 profile were observed within the sledge and reed-sedge peat at 15–220 cm depth and within the sedge-moss peat (580–640 cm depth) (Fig. 8). The maximum values of PC1 duplicate the contents of Na, K, Al, Fe, Cu, and Ni, indicating their strong correlation with organic matter and affinity with the inorganic matter in a peat. This is particularly evident in the case of the sedge peat (zone Masz-5), samples of which are dominated by TOC and N. On the other hand, location on the biplot sedge peat (zone Masz-6) and reed-sedge peat shows a strong correlation with lithophilic elements: Na, K, Al and heavy metals of Ni and Cu (Fig. 7). The minimum values of PC1 are recorded in the lake chalk (220–580 cm depth). And the detrital-calcareous gyttja dominated by the maximum values of Ca and Mg.

The second principal component (PC2) is strongly positively correlated with contents of Mn (r = 0.81), Zn (r = 0.65), and less with Fe (r = 0.48). Therefore, it is defined as a component of oxidation-reduction conditions, resulting from the variable saturation of the lake water with oxygen (Wojciechowski, 2000; Apolinarska et al., 2012).

Hydroclimatic condition in the Maszewo kettle-hole during the Holocene

Geochemochemical variability of the sediments of the Maszewo 1 profile allowed to identify 6 geochemical zones that reflect sedimentation changes due to environmental evolution (Fig. 9). Distinguished geochemical zones were assigned to chronostratigraphic units of the Holocene.

Pre-Late Preboreal (650–640 cm depth; before 10,262 cal BP)

The origin of the Maszewo and many other reservoirs located in the fresh glacial zone, is associated with melting of dead ice buried in the sediments (Nowaczyk and Tobolski, 1980; Marks, 1996; Błaszkiewicz, 2005, 2007, 2011; Karasiewicz 2019). According to Błaszkiewicz (2007), three generations of the kettle-holes can be distin-
guished in the area of the last glaciation. These are the oldest, developed before the Alleröd, the Late Glacial developed between the Alleröd and the Younger Dryas, and ones in the Early Holocene. Buried dead ice survived in bottoms of these kettle-holes throughout the Late Glacial until the beginning of the Holocene. They melted in the second half of the Preboreal Period and consequently, lakes of the younger, Early Holocene generation were initialized (i.a. Florek, 1991; Nowaczyk, 1994; Böse, 1995; Błaszkiewicz 2005, 2007, 2011).
Late Preboreal–Early Boreal (zone Masz-1; 640–620 cm depth; 10,262–9,848 cal BP)

The sedimentological record of the beginning of the development of the Maszewo lake is recorded by a thin (20 cm) layer of sedge-moss peat on a grey silty sand. According to radiocarbon dating, its sedentation took place between 10,262 to 9,848 cal BP, i.e. from the end of the Preboreal to the beginning of the Boreal Period, still on a dead ice covered by a thick mineral series. This zone is characterized by a dominance of organic matter, reaching a maximum of 75% of sediment dry weight, TOC (>400 mg·g\(^{-1}\) d.m.) and nitrogen (1–3 mg·g\(^{-1}\) d.m.). Within this zone, the highest contents reached Na (0.23 mg·g\(^{-1}\) d.m.), K (2.88 mg·g\(^{-1}\) d.m.), Mg (3.75 mg·g\(^{-1}\) d.m.), Al (10.76 mg·g\(^{-1}\) d.m.), Fe (33.09 mg·g\(^{-1}\) d.m.) and trace elements (Cu, Ni, Zn) (Fig. 4). The observed tendency is due to a superficial supply to the lake and intensive mechanical denudation of the catchment, as a source of those elements (Fig. 9). Low coverage with vegetation was the factor that accelerated erosion (Latalowa, 1988; Ralska-Jasiewiczowa et al., 1998).

Early Boreal (zone Masz-2; 620-585 cm depth; 9848–c. 9480, yr. BP)

The Masz-2 zone entirely comprises a layer of a brown detritus-calcareous gyttja that starts a sequence of carbonate lake sediments. Similarly to other kettle lakes, e.g.: Truman Lake (Digerfeldt, 1972), Körniki-Zaniemyśl lakes (Wojciechowski, 2000) and Skrzynka Lake (Apolinarska et al., 2012), sedimentation took place in a deep water. This indicates a very rapid process of melting of buried dead ice, leading to a full isolation of lake basins in the younger period of the Boreal Period. In this way, a lake was created, a further development of which depended on climate and hydrogeological processes in the Late Glacial (Petelski and Sadurski, 1987). A groundwater replacement in the regional circulation system began after degradation of permafrost and dead ice, followed by exposition along the slopes of bicarbonate-rich water sources. This process occurred in the area of the Last Glaciation, mainly at the turn of the Preboreal and Boreal periods. Water that began to participate in the underground circulation at this time was richer in bicarbonates, as a result of CaCO\(_3\) freezing-out processes in the Late Glacial (Petelski and Sadurski, 1987). Crystallization of carbonates in the Maszewo Lake was driven by volatilization of CO\(_2\), the solubility of which reaches several dozen mg dm\(^{-3}\) in a groundwater. A reduction of CO\(_2\) in surface water could also be supported by photosynthetic organisms (Apolinarska et al., 2012).

The Early Boreal zone Masz-2 is characterized by the highest concentration of Mn (reaching 24 mg·g\(^{-1}\) d.m.) and high content of Fe (15–18 mg·g\(^{-1}\) d.m.) that occurs as oxides (Pawlikowski et al., 1982; Borówka, 1992). High Fe amount in the Early Holocene sediments may reflect intensive leaching of this component from young, poorly developed soils in the postglacial landscape. Shortly after deglaciation, soils previously affected by frost weathering and other processes typical for a periglacial zone, were rich in sesquioxides (Kowalkowski, 2004). Mobility of these substances could be accelerated by presence of humic substances as factors that inhibited a crystallization (Cornell and Schwertmann, 1979). In addition, the values of the Fe/Mn ratio indicate reductive conditions during the initial phase of the lake development, probably due to a rising water level and meromixis in the water column (Engstrom and Wright 1984; Apolinarska et al., 2012; Zander et al., 2021).

The Late Glacial and Early Holocene peak of Mn, typical for the initial phase in lake development, has been recorded in sediments of many European water bodies, i.a. Swedish Truman and Flarken Lakes (Digerfeldt, 1972; Digerfeldt, 1977), the lake in Woryty (Pawlikowski et al., 1982), Gościąż Lake (Starkel et al., 1998), Peresplin Lake (Goslar et al., 1999), Körniki-Zaniemyśl Lakes (Wojciechowski, 2000), Skrzynka Lake (Apolinarska et al., 2012), kettle-hole sediments in Retno (Hulisz et al., 2012, Karasiewicz et al., 2014), and drainless depressions of intramorainic plateau of North-West Poland (Borówka, 1992). The presence of Mn peaks may indicate the convergence of climatic-environmental conditions and sedimentary processes on a regional scale.

Late Boreal-Atlantic Period (zone Masz-3; 585–220 cm depth; c. 9,480–6,100 cal BP)

This zone covers the entire (365 cm) layer of the lake chalk characterized by the high content of carbonates (>90%) and Ca (300–410 mg·g\(^{-1}\) d.m.), at the relatively low contribution of organic matter (8–10%) and TOC (50–70 mg·g\(^{-1}\) d.m.), as well as biogenic and lithogenic constituents (Fig. 4, Table 3). The predominance of calcareous sediments recorded in this zone, in comparison with the underlying peat, may indicate an increasing role of groundwater in the supply of the studied lake. A thickness of such sediments depends on abundance of dissolved calcium carbonate-rich waters drained through the lake. According to Petelski and Sadurski (1987), a groundwater replacement in the regional circulation system began after degradation of permafrost and dead ice, followed by exposition along the slopes of bicarbonate-rich water sources. This process occurred in the area of the Last Glaciation, mainly at the turn of the Preboreal and Boreal periods. Water that began to participate in the underground circulation at this time was richer in bicarbonates, as a result of CaCO\(_3\) freezing-out processes in the Late Glacial (Petelski and Sadurski, 1987). Crystallization of carbonates in the Maszewo Lake was driven by volatilization of CO\(_2\), the solubility of which reaches several dozen mg dm\(^{-3}\) in a groundwater. A reduction of CO\(_2\) in surface water could also be supported by photosynthetic organisms (Apolinarska et al., 2012).

Accumulation of a lake chalk in the studied lake indicates quite a rapid change of denudation in the lake catchment – from mechanical to chemical, which is highlighted by a considerable drop in contents of lithogenic constituents (Fig. 4). Additionally, a development of the dense mixed deciduous forest communities during the Atlantic Period (Latalowa, 1988; Ralska-Jasiewiczowa et al., 1998) has prevented or successfully reduced, a leaching of soils and a delivery of terrigenous matter to the lake. For this reason, sediments of this zone contain low amount of SiO\(_2\) (average 3%) and lithogenic elements: Na (0–0.1 mg·g\(^{-1}\) d.m.),
Table 3. Mean value and min–max range (in parentheses) of chemical parameters of the geochemical zones in Maszewo 1 log.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>geochemical zones</th>
<th>Geochemical zones</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Masz 1 (640–620 cm)</td>
<td>Masz 2 (620–585 cm)</td>
</tr>
<tr>
<td></td>
<td>N = 4</td>
<td>N = 7</td>
</tr>
<tr>
<td>OM (mg·g⁻¹)</td>
<td>52.9 (36.3–75.0)</td>
<td>18.5 (12.2–23.2)</td>
</tr>
<tr>
<td>SiO₂ (mg·g⁻¹)</td>
<td>27.9 (13.9–47.1)</td>
<td>8.4 (0.6–13.8)</td>
</tr>
<tr>
<td>CaCO₃ (%)</td>
<td>14.1 (4.9–38.4)</td>
<td>68.7 (60.4–80.7)</td>
</tr>
<tr>
<td>TOC (mg·g⁻¹)</td>
<td>309.5 (235.5–438.3)</td>
<td>117.6 (84.2–148.6)</td>
</tr>
<tr>
<td>Fe (µg·g⁻¹)</td>
<td>2.7 (1.5–3.7)</td>
<td>2.5 (2.1–2.6)</td>
</tr>
<tr>
<td>Mg (mg·g⁻¹)</td>
<td>23.7 (17.3–33.1)</td>
<td>16.2 (13.6–19.9)</td>
</tr>
<tr>
<td>Mn (mg·g⁻¹)</td>
<td>7.3 (1.5–24.0)</td>
<td>17.3 (4.6–24.4)</td>
</tr>
<tr>
<td>Al (mg·g⁻¹)</td>
<td>7.5 (3.8–10.8)</td>
<td>3.3 (1.4–4.1)</td>
</tr>
<tr>
<td>Cu (µg·g⁻¹)</td>
<td>7.0 (6.7–7.6)</td>
<td>3.2 (1.5–5.3)</td>
</tr>
<tr>
<td>Ni (µg·g⁻¹)</td>
<td>12.7 (8.0–16.4)</td>
<td>8.3 (4.9–9.5)</td>
</tr>
<tr>
<td>Zn (µg·g⁻¹)</td>
<td>4.3 (444.5–551.1)</td>
<td>24.2 (13.2–35.7)</td>
</tr>
<tr>
<td>TOC/N</td>
<td>22.2 (19.1–28.9)</td>
<td>25.0 (20.7–30.4)</td>
</tr>
<tr>
<td>TOC/P</td>
<td>555.9 (420.5–762.9)</td>
<td>257.9 (216.8–293.2)</td>
</tr>
<tr>
<td>N/P</td>
<td>25.9 (15.3–35.2)</td>
<td>10.5 (218.6–293.2)</td>
</tr>
<tr>
<td>Fe/Mn</td>
<td>9.4 (1.4–13.4)</td>
<td>1.3 (0.6–3.1)</td>
</tr>
<tr>
<td>Fe/Ca</td>
<td>0.7 (0.2–0.9)</td>
<td>0.1 (0–0.1)</td>
</tr>
</tbody>
</table>

K (0–0.7 mg·g⁻¹ d.m.), Mg (1.6–3.4 mg·g⁻¹ d.m.) and Al (0.1–2.8 mg·g⁻¹ d.m.) (Table 3, Fig. 4); an indicator of mechanical denudation defined as a sum of Na+K+Mg+Al/ log Ca reaches 1.2, being the lowest in the whole profile (Table 3, Fig. 9). Since the end of the Boreal Period (c. 8,800 cal BP), the Maszewo lake has become a well-oxygenated low trophy hard-water body as evidenced by a very high concentration of carbonates. Highly oxidizing conditions were confirmed by a very low Fe/Mn ratio (average 2.4) and zero Fe/Ca ratio in almost the entire sediment sequence of this zone (Fig. 9, Table 3). The presence of sediments with a high carbonate content may also be an indicator of intensive biological activity in the lake. It was highlighted by decreasing the TOC/N ratio from 25.4 at the bottom of this zone to 7.5 at its top. Low TOC/N values, typical for algal phytoplankton (Müller and Mathesius, 1999; Borówka, 2007; Apolinarska et al., 2012) (Table 3, Fig. 9), reflect progressive eutrophication. Similarly, the N/P ratio enables the identification of limiting factors in biomass production in the water bodies. A low N/P ratio in the upper section of the Masz-3 zone accelerates the production of cyanobacteria and reinforces their predominance over other phytoplankton.
organisms, while the high N/P ratio in the lower section favors growth of other groups of organisms (Berman, 2001; Wilk et al., 2017; Zhang et al., 2018).

**Late Atlantic–Subboreal** (zone Masz-4; 220–120 cm depth; 6,100–c. 3,380 cal BP)


As a consequence of the lower water level around 6,200 cal BP, associated with a dry phase recorded in Western and Central Europe at 6,300–6,100 cal BP (Wojciechowski, 1999, 2000) and filling with sediments of the former Lake Maszewo, there was a transformation of the water body into a terrestrial environment. At the same time filling of the lake with telmatic sediments began, which is represented by a brownish-black sedge-reed peat.

The zone Marsz-4 comprises the most geochemically dynamic section of the profile with very large fluctuations of almost all elements (Fig. 4) and geochemical parameters, including TOC/N, TOC/P, N/P, Fe/Mn and Fe/Ca (Fig. 5). It may indicate water level changes in a heavily overgrown water body. In the geochemical record, the beginning of this zonation records a significant decrease in carbonate and Ca contents, to 6.6% and 39.2 mg·g⁻¹ d.m., respectively. From 220 cm depth, contents of organic matter (76.4%), TOC (389.1 mg·g⁻¹ d.m.) and N (2.8 mg·g⁻¹ d.m.) increase rapidly. Also sharply increases and culminates the content of Na (0.2 mg·g⁻¹ d.m.), K (1.9 mg·g⁻¹ d.m.), Al (10.5 mg·g⁻¹ d.m.), Fe (18.8 mg·g⁻¹ d.m.) and trace elements, including Cu (13.3 µg·g⁻¹ d.m.), Ni (20.3 µg·g⁻¹ d.m.) and Zn (17.7–29.6 mg·g⁻¹ d.m.) (Fig. 4, Table 3), which may indicate strong leaching of the soils in the lake catchment and supply of these elements by a surface flow (Borówka, 1992, 2007). Wind erosion should be also considered as a probable source of mineral matter in the present surface layer of sediments (An et al., 2012; Nielsen et al., 2016).

**Middle Ages–modern times** (zone Masz-6; 40–15 cm depth; since 850 AD)

The last phase of lake development covers the top layer of the sedge peat and the overlying murs. A formation of these sediments is related to the drainage of the bog that took place during the Medieval Warm Period (950–1350 AD). The temperature during this period was 0.5–1.5°C higher when compared to the previous period (Goose et al., 2006; Luterbacher et al., 2016). Moreover, intensive evaporation and lower precipitation were other characteristic features. As a result of the water level drop, the peaty layers have been exposed to accelerated mineralization. Therefore, the sediments of this zone have low OM (average 28.8 mg·g⁻¹ d.m.), TOC (average 133.1 mg·g⁻¹ d.m.), and N (average 10.7 mg·g⁻¹ d.m.) contents compared to the underlying sediments (Table 3). In the top layer of the peat, the TOC/N ratio decreased again to an average value of 12.1 (Table 3, Fig. 9), which was probably a result of the biological decomposition of the peat due to drainage and the formation of murs. Terrigenous silica plays a predominant role in this zone (above 50% and a maximum of 71% at a depth of 20–15 cm), as well as lithogenic elements, including Na (0.1 mg·g⁻¹ d.m.), K (1.2 mg·g⁻¹ d.m.), Mg (1.2 mg·g⁻¹ d.m.) and Al (7.3 mg·g⁻¹ d.m.) (Fig. 4, Table 3), which may indicate strong leaching of the soils in the lake catchment and supply of these elements by a surface flow (Borówka, 1992, 2007). Wind erosion should be also considered as a probable source of mineral matter in the present surface layer of sediments (An et al., 2012; Nielsen et al., 2016). High intensity of mechanical denudation during this period is also indicated by the (Na+K+Mg+Al)/log Ca ratio, reaching a maximum throughout the profile of 14.7 (Table 3, Fig. 9). The sediments of this zone are characterized by elevated concentrations of trace elements Cu, Ni and Zn (Table 3), which may be due to bioaccumulation by vegetation through their uptake from deeper layers and return to the soil surface via litterfall (Jonczak et al., 2014).

As it results from the interpolation of the age-depth model curve, the accumulation of a superficial, non-analysed murs (0–15 cm depth) started around 1440 AD and is associated with intensive human agricultural activity, which is consistent with historical data. The first record of the Maszewo village is dated back to 1360 AD (Budkowski and Mikusiński, 2012), when the land of Lębork, together with Maszewo (ger. Grof Massow), came under the ownership of the Teutonic Order, and from 1466 was administrated by the Royal Prussia administration.
CONCLUSIONS

The geochemical analysis of the studied biogenic-carbonate sediment profile enabled determination of trophic, climatic and hydrological changes in the Maszewo lake, located in the temperate climatic zone of Central Europe. Due to its small size, the lake has responded rapidly to environmental changes over the last 10,200 years, and the sediment sequence of the Maszewo 1 profile indicates the gradual, natural phases of lake transformation from the termination of the Preboreal Period to the modern times. The results obtained allowed the following conclusions:

1. A high stratigraphic variability in the chemical composition of the Maszewo kettle-hole sediments is a result of the regional hydroclimatic changes modified by local sedimentary processes within the lake basin and erosional processes within its catchment area.

2. The vertical variability of TOC, N and P contents, as well as TOC/N and N/P ratios in the sediments of the Maszewo 1 profile reflect the temporal variability of trophic conditions in the water body, strongly dependent on sources of the supplying water. In its early development, the Maszewo lake was an oligotrophic, well-oxygenated, and highly mineralized water body. From the mid-Atlantic period, there was a gradual and significant increase in the trophic status, reaching the highest levels in the upper part of the lake chalk layer and the peat.

3. The intensity of mechanical denudation in the catchment of the Maszewo lake was affected by climatic conditions and the type of lake supply. During the Holocene thermal optimum in the Atlantic Period, when a forest cover stabilized and the intensity of soil leaching decreased, mechanical denudation was the lowest. The highest rates of denudation occurred during the Late Preboreal, the older Boreal, and the Subboreal Periods, and were driven by natural factors. The high rate of mechanical denudation observed during the last millennium is probably a result of increasing anthropogenic activity.

4. The relative water level fluctuations in the Maszewo lake reflect the general trends observed in the lakes of the Polish Lowlands and western Europe. The maximum water level was recorded in the early Boreal Period, while the lowest was recorded at the end of the Atlantic Period. During the Subboreal Period, several fluctuations resulting from climatic changes were also observed.

5. Principal component analysis allowed to identify two main factors controlling the geochemical variability of sediments filling the kettle-hole at Maszewo. These are different sources of water supply to the lake, leading to changes in sedimentation type from biogenic- through carbonaceous and again, to biogenic dominated mode (PC1) and oxidation-reduction conditions determined by water level fluctuations (PC2).

6. The recorded changes in the lithology and geochemistry of the sediments and their time borders reflect a general trend of environmental changes observed in the young glacial landscape of the Polish Lowlands and neighboring areas.

Acknowledgments

This study was supported by the statutory funds of the Pomeranian University in Słupsk (research task no. 22.4.17 “Paleoecology and geochemistry of the biogenic-calcareous sediments filling paleolakes in the western part of Kashubian Lakelands, North Poland”). The authors thank to Prof. Marek Krapiec (Laboratory of Absolute Dating in Kraków) for performing the radiocarbon dating. We would like to thank two anonymous reviewers for careful reading of our manuscript. Their constructive comments and suggestions helped to improve the quality of this article.

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