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GEOCHEMICAL ANALYSES OF RECENT SEDIMENTS FROM LAKE MORZYCKO AGAINST SELECTED PHYSIOGRAPHIC PARAMETERS OF THE SŁUBIA RIVER CATCHMENT (WESTERN POLAND)

ANNA ADAMEK[1], PAULINA MARECZKA[2], WITOLD JUCHA[2],
STANISŁAW MUSIELAK[3], DANIEL OKUPNY[3]

Abstract. This paper presents the results of a study on the content of lithogeochemical components (organic matter, Na, K, Mg, Ca, Mn, Fe, Cu and Zn) and grain-size composition of mineral matter in the bottom sediments of Morzycko Lake (Myślibórz Lakeland, NW Poland). This lake is large (342.7 ha) and deep (69 m). The catchment has a typical forested character (mainly in the middle part of the Słubia River valley) with agricultural area (mainly in the upland areas north of the lake). The diversity of concentrations of metals was analysed based on 44 samples from 22 representative sites, including surface sediments and sediments from 5 cm below the current lake bed. The results showed that the chemical composition and granulometry of bottom sediments depends on contemporary morphogenetic processes in the catchment of the Słubia River. Geochemical and grain-size indices varied due to changes in biological productivity, intensity of weathering of postglacial material making up the catchment, and potential for migration of metals to the lake with surface or underground runoff. An important aspect in assessing the degree of enrichment of the sediments in trace elements is the location of shallow parts of the lake near the tourist districts of Moryń.

Key words: lake sediments, geochemistry, grain-size composition, land-cover photointerpretation, Myślibórz Lakeland

Introduction

Lakes exemplify complex ecosystems varying with respect to their area, depth, shoreline type, water chemistry and thermal conditions. Sediment accumulation, including terrigenous material supply via rivers, which carry large volumes of mostly mineral suspension, is responsible for a gradual decrease in lake depth and surface area. The history of the lake and how its environment has been changing through time may be learned from studying the bottom sediments. Moreover, the growing interest in lake sediments among Earth scientists and archaeologists is due to the growing support for distinguishing the Anthropocene as the most recent period in Earth's history (Wolfe *et al*. 2013). Further, there is a broad consensus that lake sediments document the history of changes in various elements of the environment, including human impact, both prehistoric and contemporary (Tobolski 2004; Florek, Majewski 2008; Kittel *et al*. 2021). Among the numerous methods applied in natural sciences, geochemistry plays an important part, as it gives a comprehensive insight into, among other things, hydroclimatic and geomorphological changes, as well as the succession of settlements and cultures contributing to the regional or local geochemical background of a given area (Gałuszka 2006; Borówka 2007; Zgłobicki 2010; Szwarczewski, Smolska 2013). One of the main aims of geochemical studies on lake bottom sediments is to determine quantitative relationships between autochthonous and allochthonous components, which in turn enables a reconstruction of environmental changes taking place not only within the lake itself, but also within its catchment (Rutkowski 2007; Więckowski 2009).

Factors controlling sedimentation rate and chemical composition of lake sediments include predominantly: climate, geology and lithology of

[1] School Complex in Moryń, Dworcowa 6a, 74-503 Moryń
[2] Pedagogical University of Cracow, Institute of Geography, Podchorążych 2, 30-084 Kraków, Poland; Witold Jucha ORCID: 0000-0002-2204-8721
[3] University of Szczecin, Institute of Marine and Environmental Science, Adama Mickiewicza 18, 70-383 Szczecin, Poland, Stanisław Musielak ORCID: 0000-0002-4770-1432; Daniel Okupny e-mail: daniel.okupny@usz.edu.pl, ORCID: 0000-0002-8836-6044

the catchment area (Ewing, Nater 2002). Furthermore, water oxygenation levels and primary production (both of which are dependent on trophic state) are responsible for shifts in redox conditions (Kajak 2001; Wesołowski *et al*. 2014). Finally, changes in land use and denudation rates within the catchment are also important (Foster, Dearing 1987; Borówka 1994; Mendyk *et al*. 2016; Okupny, Pawłowski 2021).

To compare the conditions of accumulation of individual elements, geochemical studies were often undertaken for various types of bottom sediments (Prosowicz 2008; Woszczyk *et al*. 2009; Gierszewski 2018), from various depositional zones within lake basins (Bojakowska, Sokołowska 1997; Szafran 2003; Aleksander-Kwarteczak, Prosowicz 2007; Małecka 2012), but less frequently considering the water–suspension–sediment relationship (Wicik, Więckowski 1991; Helios-Rybicka *et al*. 2005). Furthermore, the factors influencing the concentrations of selected metals in sediments were frequently determined using a selection of geochemical proxies, such as Na/K, Cu/Zn, Fe/Mn and Ca/Mg (Wojciechowski 1990; Woszczyk, Spychalski 2007; Płaza *et al*. 2013/2015; Pawłowski *et al*. 2015). The question of lake sediment enrichment in particular metals relative to the local or regional geochemical background has been addressed relatively rarely, as such an approach requires a detailed understanding of geological and hydrological conditions within the specific lake catchment (Tylmann 2005; Juśkiewicz *et al*. 2015). In aquatic ecosystems, the concentration of elements in sediments depends, among others, on weathering processes in the catchment, whose intensity is determined by geology and climatic conditions. In lake basins, regardless of their size, sediments undergo "focusing", which is why sedimentation rates are highest within deep areas, resulting in the highest sediment thicknesses. The potential for reconstructing human impact intensity in a region also depends on the sediment lithology, accuracy and temporal resolution achieved by geochemical studies (Słowiński *et al*. 2016; Kramkowski 2020; Müller *et al*. 2021).

Given the above, it is crucially important to study geochemistry of recent lake sediments, possibly considering all the relevant geographic features, including type of land use within the catchment. This may represent an important reference point for reconstructing sedimentation conditions with respect to their spatial and stratigraphic variability. Such interpretation should, however, be supported by numerous other analyses that are within the scope of broadly defined palaeolimnology (Tobolski 2007), hydroacoustics (Osadczuk 2017), and interpretation of archival maps, aerial photographs and satellite images (Siedlik, Borówka 2019).

Thus, the methods employed in the present paper, and the angle of our interpretation both follow a very important trend in geochemical studies on recent sediments deposited in surface water basins, which are also proxies essential for the assessment of natural environment pollution with heavy metals. Large lakes, often supplied with groundwater, may play a unique role in the geochemical cycle. The main aim of the present study was to determine the relationship between lithology and chemical composition of bottom sediments currently being accumulated in one of the deepest lakes of Pomerania. An additional aim was to assess the impact of topographic conditions and the level of human impact on the geochemistry of Lake Morzycko expressed by morphometric parameters (slopes, aspect, morphological units) and land cover examined in a wider perspective for the catchment area of the lake and the Słubia River. The present paper compares the concentrations of elements, and granulometric composition of surface sediments sampled in the nearshore zone and within deep areas of Lake Morzycko. The data collected in this study were used to plot geochemical maps that may represent an important reference for future studies regarding environmental monitoring of Myślibórz Lake District, which is increasingly susceptible to human pressure.

Study area

According to the geomorphological division of Poland (Gilewska 1968), the studied lake is located in the south-western part of Myślibórz Lake District, at its border with the Lower Odra Valley (Fig. 1). In comparison with the rest of the young-glacial relief zone, the study area is distinguished by a lower density of river network, but a higher number of small, undrained basins (Rotnicka 1987; Kostrzewski *et al*. 2008a).

The dominant terrain forms around Lake Morzycko are flat and undulating morainic plateaux (47% of the surface area) and outwash plains (16% of the area). The smallest area is occupied by river valley systems (0.2% of the area). Lake Morzycko occupies an area of 342.7 ha, and thus is classified as a large basin. Its maximum width is about 2.4 km, and maximum length is about 2.9 km. The average depth of the lake is 14.5 m, but its maximum depth is as much as 60 m (Fig. 2). Lake Morzycko is a cryptodepression: its bottom lies 8.6 m below sea level (its surface is at 51.4 m above sea level [a.s.l.]). The studied lake is kidney-shaped, with two bays (north-western bay, 5–8 m deep, and south-western bay, 13–15 m deep) that surround the town of Moryń. The lake has a regular, 12-km-long shoreline. The lake-volume-to-surface area ratio equals 0.15, which is one of the highest among lakes of northern Poland (Choiński 2007). The lake is a flow-through basin, as it is located within the valley of the Słubia River. The surface area of total catchment is 65.9 km^2, while the direct catchment surface area is less than 10% of this value (6.38 km^2).

The origin of the lake is not fully understood, but both morphometric features and catchment geology (tills forming a belt of end moraines representing the Chojna phase of the Pomeranian stage to the north, and sands and gravels forming

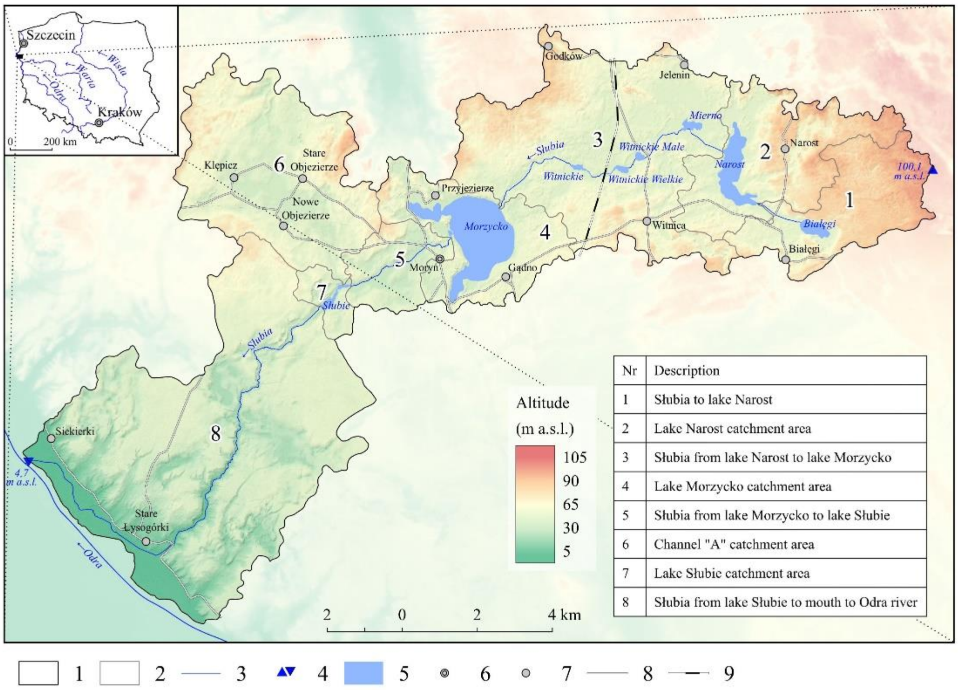

Fig. 1. Description of part of the Słubia catchment area based on Hydrographic Division of Poland

1 – border of Słubia catchment, 2 – subcatchments, 3 – rivers, 4 – extreme elevation points, 5 – lakes, 6 – cities, 7 – settlements, 8 – roads, 9 – railways

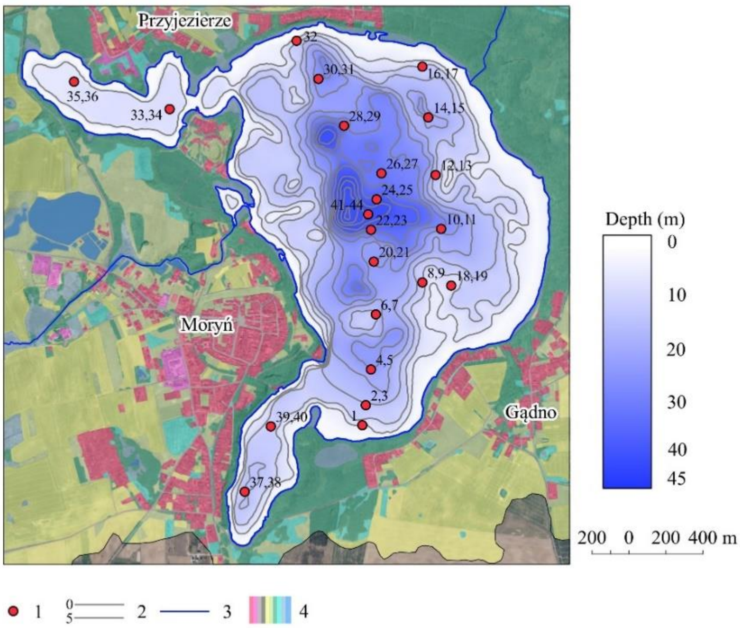

Fig. 2. Bathymetric map (after Borówka 2002) and coring sites at Lake Morzycko

1 – coring sites 2 – isobaths (every 5 m), 3 – Słubia River, 4 – land cover based on orthophotomap and consistent with caption in Fig. 4D (Polish Head Office of Geodesy and Cartography 2021)

extensive outwash plains of the Pomeranian stage to the south) may suggest evorsion as the causal mechanism for the lake basin formation (Piotrowski, Dobracki 2010). A recent study by Kotrys (2015) indicates that biogenic sedimentation was initiated during the Late Glacial (the oldest ^{14}C date is 12 640±210 conv. BP), and the first evidence of human activity in the vicinity of Lake Morzycko is represented by a distinct increase in charcoal and ruderal plant pollen frequencies dated to the late Mesolithic (^{14}C 8 270±70 conv. BP).

According to the climatic regionalisation of Western Pomerania by Koźmiński *et al*. (2007), Lake Morzycko is located within the Myślibórz subregion, which has relatively warm and long summers (mean air temperature for July is below 18°C), and mild and short winters (mean air temperature for January ranges from -0.8 to -1.5°C). The study area has the longest vegetation season in Poland (over 230 days), during which mean annual precipitation totals remain rather low (340–530 mm). With respect to the development of slope processes, it is notable that diurnal rainfall exceeding 1 mm total is rare (from 100 to 115 days).

Materials and Methods

Three groups of methods are employed in the present work: geomorphological reconnaissance, field work and laboratory analyses. Detailed field work was preceded by an examination of morphometric properties and selected features of the geographic environment, including land-use structure for the direct catchment of Lake Morzycko, but also for the remaining partial catchments of the Słubia River. Spatial data developed by the Polish geodetic and cartographic survey were used to elaborate the cartographic part of the paper. An orthophotomap of the study area was used as source data, as well as an Airborne Laser Scanner (ALS) point cloud obtained using Light Detection And Ranging (LiDAR) technology. Based on the ALS ISOK, a high-resolution (1-m range) Digital Elevation Model (DEM) was generated. Additionally, to display elevation data for the wider area (Fig. 1), an open-source DEM from Shuttle Radar Topographic Mission (SRTM) was used. The study also used data and sketches prepared during previous field campaigns. For terrain cover analyses, the source of information was the 2020 Orthophotomap of Poland. For means of vectorisation (used Quantum GIS ver. 3.10 and GRASS ver. 2.8.4.), a division into four land cover classification groups: forests (forests and transitional woodland-shrub), non-forest areas (with an additional division into farmlands and meadows, pastures and green spaces), waters (water bodies and wetlands) and, lastly, built-up areas (buildings and roads). The bathymetry of the lake and the spatial variability of sediment chemical compositions were mapped using kriging interpolation with Surfer ver. 8.0 software.

Samples for laboratory analysis were collected during the ice-cover period, from selected sites along approximately meridional routes (from the southern to the north-eastern shore of the lake, and from the lake centre to the northern shore), and within the bays along a straight line in accordance with their orientation. Sediment samples were collected using a Nurek-1 corer (Mera Błonie Gdańsk). Eventually, a total of 44 samples were taken from 22 sites, including sediments located directly at the surface of the lake bed, and sediments from 5 cm below the current lake bed.

Samples were processed according to the procedure (Fig. 3) described by Borówka (1992, 2002) and Pręcikowska (2007). For geochemical analyses, the sediment samples were freeze-dried and homogenised using an agate mortar and pestle. Organic matter (OM) content was determined by loss on ignition (LOI) at 550°C. The ash produced by combustion was analysed for grain size and content of elements. Mineralisation in Teflon bombs was carried out in two microwave cycles: the first cycle, in concentrated nitric acid with 2 ml of 10% hydrochloric acid, and the second cycle in hydrogen peroxide. The solution obtained was analysed for concentrations of Na, K, Ca, Mg, Fe, Mn, Cu and Zn via atomic absorption spectrometry (AAS). All analyses were conducted at the Geochemical Laboratory at the University of Szczecin.

Mineral matter was sieved through a 250-μm sieve, and weighed in order to estimate the contribution of coarse (>250 μm) and fine (<250 μm) fractions in sediment. Eventually, a total of 39 samples (numbers: 2-5; 8-13 and 16-44) were analysed using a Mastersizer 3000 laser diffraction particle size analyser (Malvern Panalytical). Textural particle-size analysis was carried out by means of a sieve set and a Fritsch vibratory shaker only for five samples (numbers: 1, 6, 7, 14 and 15). The goal of the sieving process was to divide the mineral matter into predetermined particle-size classes. The results were interpreted using Folk and Ward (1957) indices calculated by GRADISTAT software, ver. 8.0 (Blott, Pye 2001), percentage contribution of individual modal values, SPAN parameter (a dimensionless sorting index; Foster *et al*. 2008).

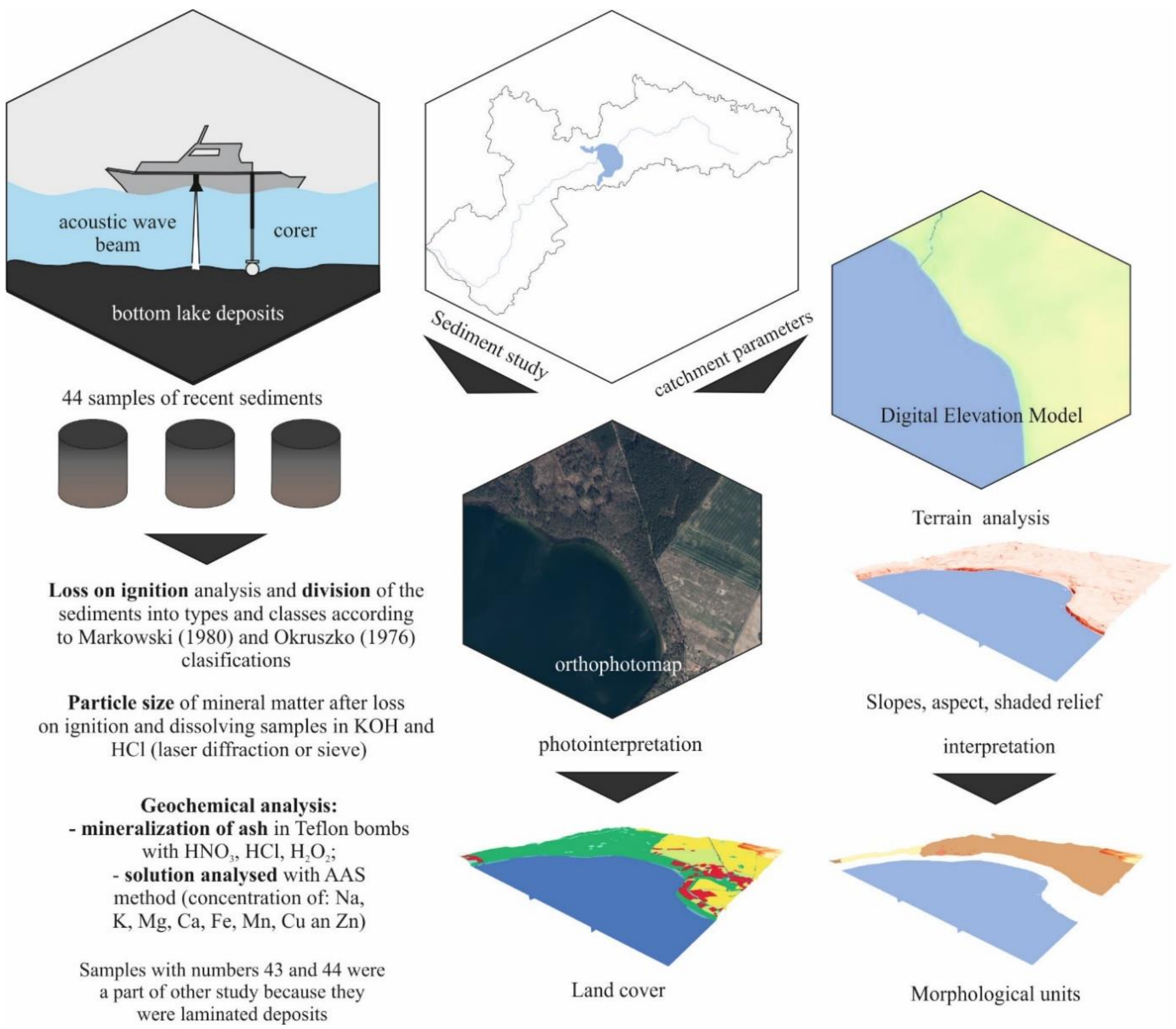

Fig. 3. Scheme of field work on Lake Morzycko (based partly on Borówka 2002 and Pręcikowska 2007), laboratory procedures (proposed by Borówka 1992) and GIS analysis for the catchment of the Słubia River (guidelines after Urbański, Kryla-Straszewska 2010; Jucha, Kroczak 2014)

Results

Geographic catchment features of the Słubia River

The catchment of the Słubia River is characterised by a diverse bedrock geology and morphological features (Fig. 4; Table 1). They are responsible for the shape of the contemporary slopes of the terrain. Slope angle displays a high spatial diversity, providing favourable conditions for rapid surface runoff of rainfall and meltwaters in selected parts of the partial catchment of the Słubia valley (Fig. 4A). In turn, conditions are more favourable for infiltration and evaporation in partial catchments to the north-west and north-east of Lake Morzycko. Overall, despite steep slopes, the river network density is low. River network density is highest in the east of the catchment, and equals 0.8 km/km^2, while in the north-west of the catchment the river network density remains below 0.4 km/km^2. Slopes exposed toward the north and toward the south prevail in the catchment of Lake Morzycko (Fig. 4B), which significantly alters and diversifies water relations in this area. The orientation of the slopes in the highest parts of the catchment in relation to westerly winds bringing humid air masses can clearly increase the sums of precipitation, especially between the Siekierki and Narost regions. In turn, the dominance of southern exposure over south-eastern exposure in the partial catchment between Lake Narost and Lake Morzycko may be responsible for the increased intensity of evapotranspiration.

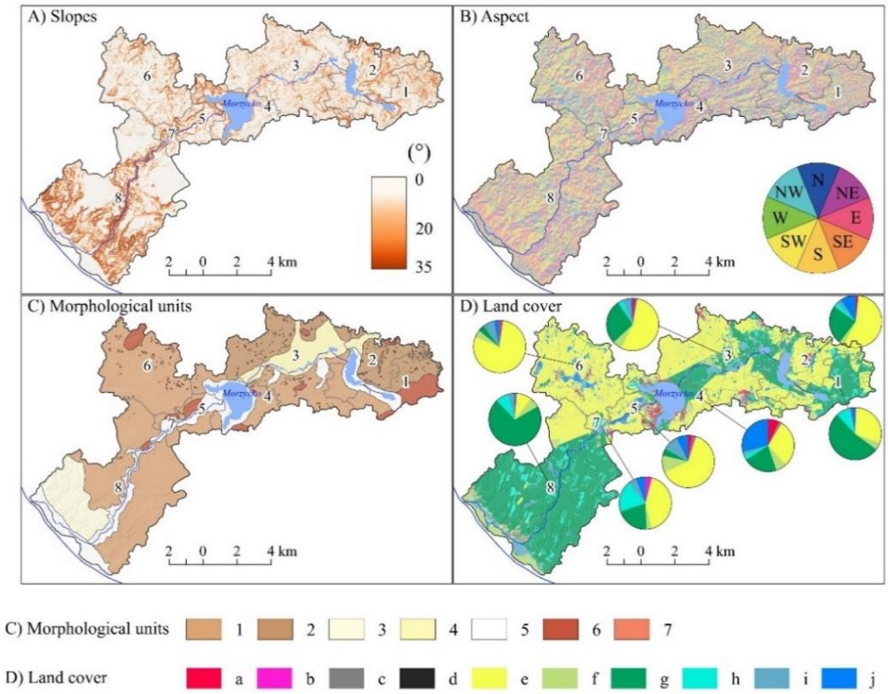

Fig. 4. Thematic maps of the Słubia catchment
(based on LiDAR model, orthophotomap and Karczewski 1968)

A. Slopes
B. Slope exposure
C. Morphological units
1 – flat and undulating morainic plateau, 2 – morainic plateau with numerous kettle-holes, 3 – outwash plain of maximal subphase, 4 – outwash plain of Chojna subphase, 5 – bottom of valleys and lake channels, 6 – end moraines and other marginal forms, 7 – kettle-holes
D. Spatial variability of land cover and a percentage statement for individual subcatchments
a – built-up areas, b – industrial and commercial facilities, c – roads, d – railways, e – arable lands, f – meadows and pastures, g – forests, h – transitional woodland-shrub, i – wetlands, j – water bodies

The studied catchment is dominated by forests, which make up 54% of the total area. The share of agricultural areas is 38%. Urbanised and industrial areas represent only 0.2% of the total catchment area, but in the immediate vicinity of the lake they increase to above 1.4% (Fig. 4D). In general, the results obtained here are consistent with the morphometric classification of Southern Baltic Lake Districts (Dmowska 2008), and with spatial diversity in intensity of contemporary morphogenetic processes in the young glacial zone, considering the levels and distribution of annual rainfall sums, soil types and land cover, as compiled by Kostrzewski *et al*. (2008b).

Chemical composition and grain-size distributions of Lake Morzycko sediments according to sedimentation zones

The content of organic matter in research biogenic sediments was low, but varied significantly (between 2 and 38%). The average value for the central part of the lake was 18.2%, while for the shore parts of the lake it was only 9% (Fig. 5). According to the classification of lake sediments by Markowski (1980), the bottom sediments from Lake Morzycko conform mostly to clay-detritus gyttja (75% of samples examined). Notably, Markowski's classification is based on extensive research material consisting of several hundred samples collected from various lakes of Western Pomerania. Lake Morzycko was among the 43 basins studied by Markowski (1980), who examined ten samples taken only from the deepest parts of the lake. According to the Okruszko (1976) classification, silt contents in the sediments of Lake Morzycko are very high (91% of samples) and high (9% of samples), because the average mineral matter content is above 63%, but is usually up to 84%.

Table 1

Selected parameters of the slope and the area of slopes with different exposure in the distinguished parts of the Słubia River catchment

Description of part of the Słubia catchment area	Area (km^2)	Slopes (°)					Aspect (% of the catchment area)							
		Min.	Max.	Average	Median	Standard deviation	N	NE	E	SE	S	SW	W	NW
Słubia to Lake Narost	10.25	0.01	18.37	3.15	2.65	2.36	12.87	11.95	10.81	11.40	13.18	13.49	13.31	12.95
Lake Narost catchment area	12.66	0	25.54	3.02	2.59	2.46	0.68	11.87	12.50	13.63	14.49	15.08	15.77	15.95
Słubia from Lake Narost to Lake Morzycko	28.5	0	23.52	2.55	2.16	2.03	11.73	11.86	13.10	14.29	13.47	11.66	11.77	12.08
Lake Morzycko catchment area	11.07	0	31.1	2.38	1.53	3.01	11.25	12.47	12.28	12.06	12.61	13.07	13.13	13.08
Słubia from Lake Morzycko to Lake Słubie	4.74	0	24.5	3.17	2.43	2.82	12.21	10.88	12.35	14.96	13.26	11.30	11.96	13.05
Channel „A” catchment area	19.94	0	31.86	2.60	2.15	2.07	11.47	12.00	13.28	13.63	11.90	11.87	13.19	12.65
Lake Słubie catchment area	1.84	0.01	24.15	3.45	2.31	3.58	11.47	12.02	13.70	15.33	13.04	10.87	11.50	12.04
Słubia from Lake Słubie to Siekierki	47.37	0.01	36.65	3.74	2.20	4.07	10.65	10.19	11.55	13.91	13.86	13.44	13.52	12.85
All area of Słubia River subcatchments	136.4	0	36.65	3.08	2.21	3.11	11.36	11.19	12.15	13.51	13.24	12.70	13.01	12.80

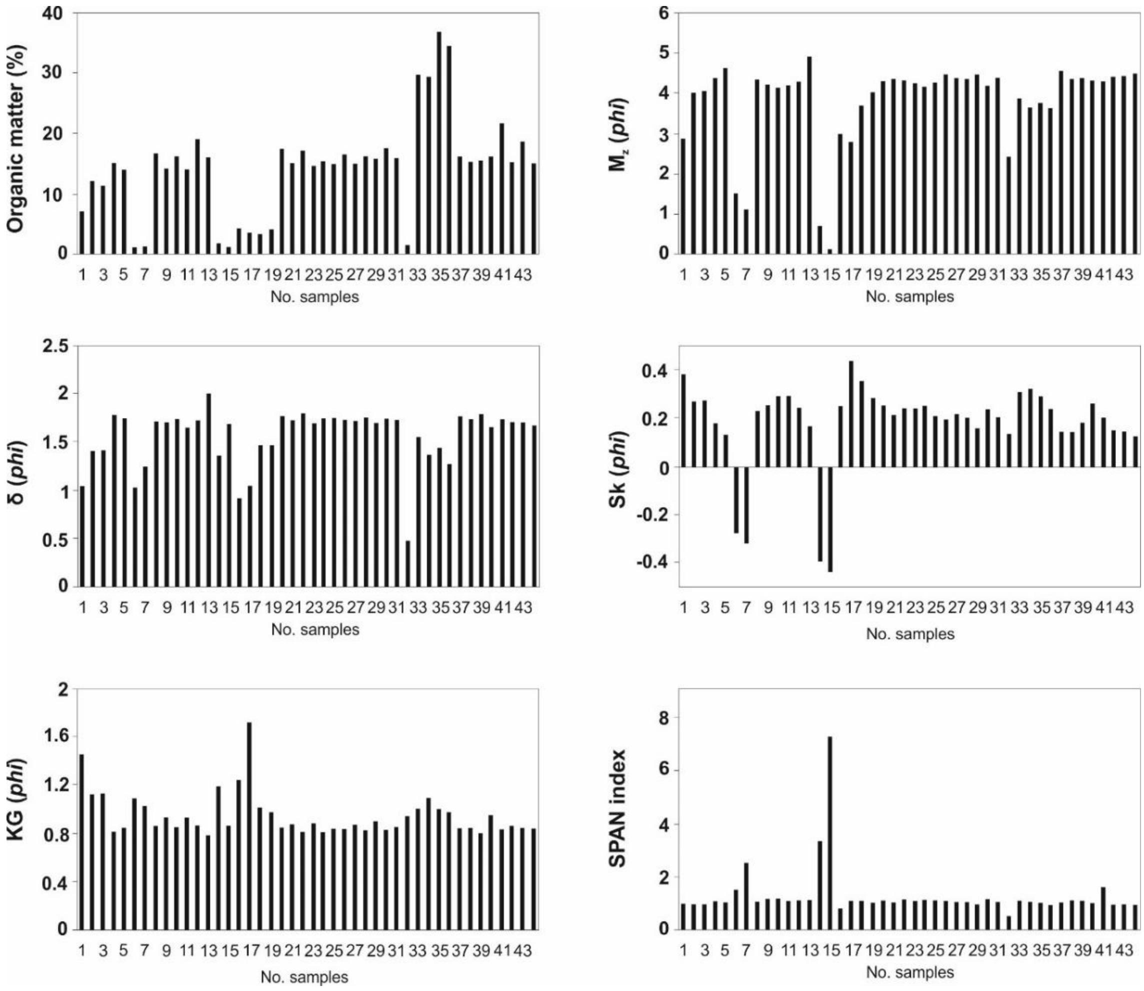

Fig. 5. Organic matter content of sediments, Folk and Ward coefficients and SPAN index for mineral fraction from recent sediments from Lake Morzycko

Despite the differences in grain-size distribution in individual types of sediments, most samples include two basic fractions, i.e., sand and silt (Fig. 6). Among those sediments that include two basic fractions are only sands, where modal values in the ranges 2.0–2.25 and 1.5–1.74 phi characterise 40 and 60% of samples, respectively. In sandy silts, which represent slightly more than half of the samples examined here (52%, to be exact), only one modal value is relatively strongly expressed in the sand fraction, ranging from 2.75 to 3.00 phi. In silty sands, however, a modal value of sand fraction in the range 2.5–2.75 phi characterises 22% of samples in this population.

The relations between the distribution of individual fractions described above are reflected in the values of Folk and Ward (1957) grain-size parameters. For most samples, the values of mean grain size (M_z) range from 3 to 5 phi (Fig. 5). The lowest M_z values were documented in four samples taken from the southern and north-eastern

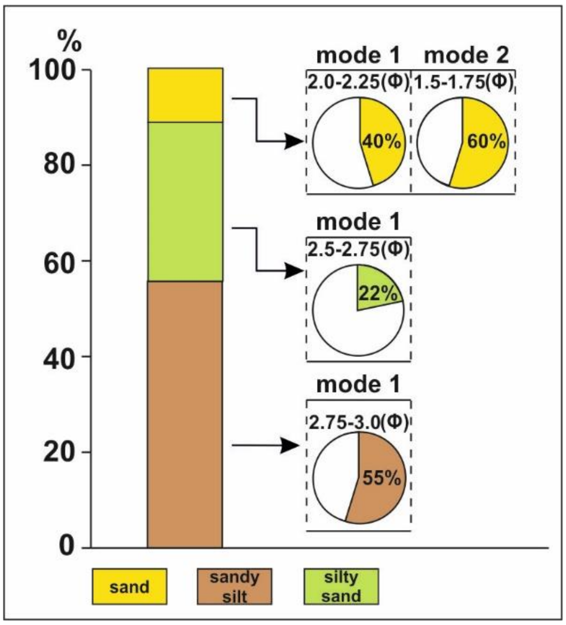

Fig. 6. Frequency (%) of occurrence of modal fraction values (in phi) in various types of lake sediments from Lake Morzycko

parts of the lake, in which the bottom was at a depth of about 14 m. Standard deviation (δ) values for most samples oscillate around 1.5 phi, indicating poorer sorting of mineral material. The lowest scatter of individual grain-size classes relative to the mean value, i.e., the best sorting, was found in single samples taken in the nearshore zone of the lake, at depths below 13 m. Negative skewness values (S_K) are displayed by only 4 samples: the same samples that yielded the lowest values of the M_z parameter. The remaining samples are characterised by moderate positive skewness values (ranging from 0.1 to 0.3 phi), except for samples collected from the vicinity of the southern and north-eastern shores of the lake. The least diverse are the kurtosis values (K_G), where values of ≥1.2 phi were assessed for only 3 samples (Fig. 5). In the case of silty sands and sandy silts, the SPAN parameter values are very similar (variation coefficient is below 10%), and in sand group, the coefficient values vary from 0.52 to 7.26 (variation coefficient is above 85%).

The sediments of Lake Morzycko are characterised by a high spatial diversity in concentrations of the examined geochemical components (Figs. 7, 8). Geochemical analysis indicated the narrowest range of concentrations for Na (0.02–0.36 mg/g) and Mn (0.2–1.2 mg/g). The broadest range of concentrations was documented for Fe (2.3–16.2 mg/g). Several times higher concentrations of Fe (11–17 mg/g), Mn (0.6–0.8 mg/g), Ca (240–260 mg/g), and, to a lesser extent, Mg (3.5–4.3 mg/g) were documented at the deepest sampling sites. This pattern concerns both the surface sediments, and those sampled from 5 cm below the lake bed. For lithophilic elements, mean concentration values formed the following series: Na<K<Mg, and their mutual proportions were as follows: 0.15<0.97<2.46.

Discussion

The morphometric analysis of Słubia River catchment confirms features typical of young glacial relief, i.e., high elevation diversity and a complex network of valleys with numerous wetlands and lakes. In the context of the immediate surrounding of Lake Morzycko, the spatial diversity of relief in individual segments of the Słubia valley is responsible also for the diversity in soil cover and plant assemblages, type of land use and intensity of human activity. These elements of the geographic environment exert control over the cycling of matter, including water, which is significant for distinguishing elementary geochemical landscapes (Wicik 1992; Rycharski, Piórkowski 2001).

Given the above determinants of morphology responsible for the chemical composition of Lake Morzycko bottom sediments, chemical and mechanical denudation processes have played an important part. The high density of undrained depressions acting as depositional collectors restricts the supply of lithophilic elements from the northern part of the Słubia River catchment. The density of undrained depressions in this part of Myślibórz Lake District exceeds 2 per km^2 of surface area (Fig. 4D). Peats overlain by humic clays dominate in the stratigraphy of the deposits infilling typical basins in this region (Pieńkowski 2008). Models representing the type and intensity of denudation processes based on chemical composition of sediments infilling typical western Pomeranian accumulation basins (Borówka 1992) suggest that the average quantity of material supplied to small lake basins within the Słubia catchment may have exceeded 240 kg/ha/thousand years. The intensity of mechanical denudation processes increases downstream along the Słubia River. Alluvial fans have been deposited where the Słubia flows into Lake Morzycko and in the nearshore part of the lake, where glaciofluvial sediments are being eroded (Fig. 4C). This is corroborated by granulometric composition results, and especially so by the broad range of the SPAN index values for samples with the lowest M_z values. The sand supplied to Lake Morzycko was accumulated mainly in the open water zone between the littoral and bottom zones, where the depth of the basin is below 15 metres.

Several times higher Ca concentrations (of the order 240–267 mg/g) in bottom sediments of the southern and south-eastern parts of Lake Morzycko suggest that a more important part was played by chemical denudation in shaping the chemical composition of sediments. In the case of Lake Morzycko, the intensity of individual geochemical processes is made more spatially diverse by the catchment's diverse lithology (e.g., highly soluble rocks, mainly sands and gravels, being overlain by insoluble rocks, such as the mud and silty clay that built the proglacial lake), which manifests also in low values of average specific discharge. The compilation by Jokiel (2004) indicates that average specific discharge values in the west of Myślibórz Lake District are close to 2–3 dm^3/s/km^2, i.e., even five times lower than in the rest of the Polish Lowland. Previous studies on sedimentary conditions of lake sediment accumulation indicate that the variation in type and intensity of denudation processes, regardless of location within a given morphogenetic zone of Poland, was the key factor responsible for the chemical composition of biogenic sediments in the

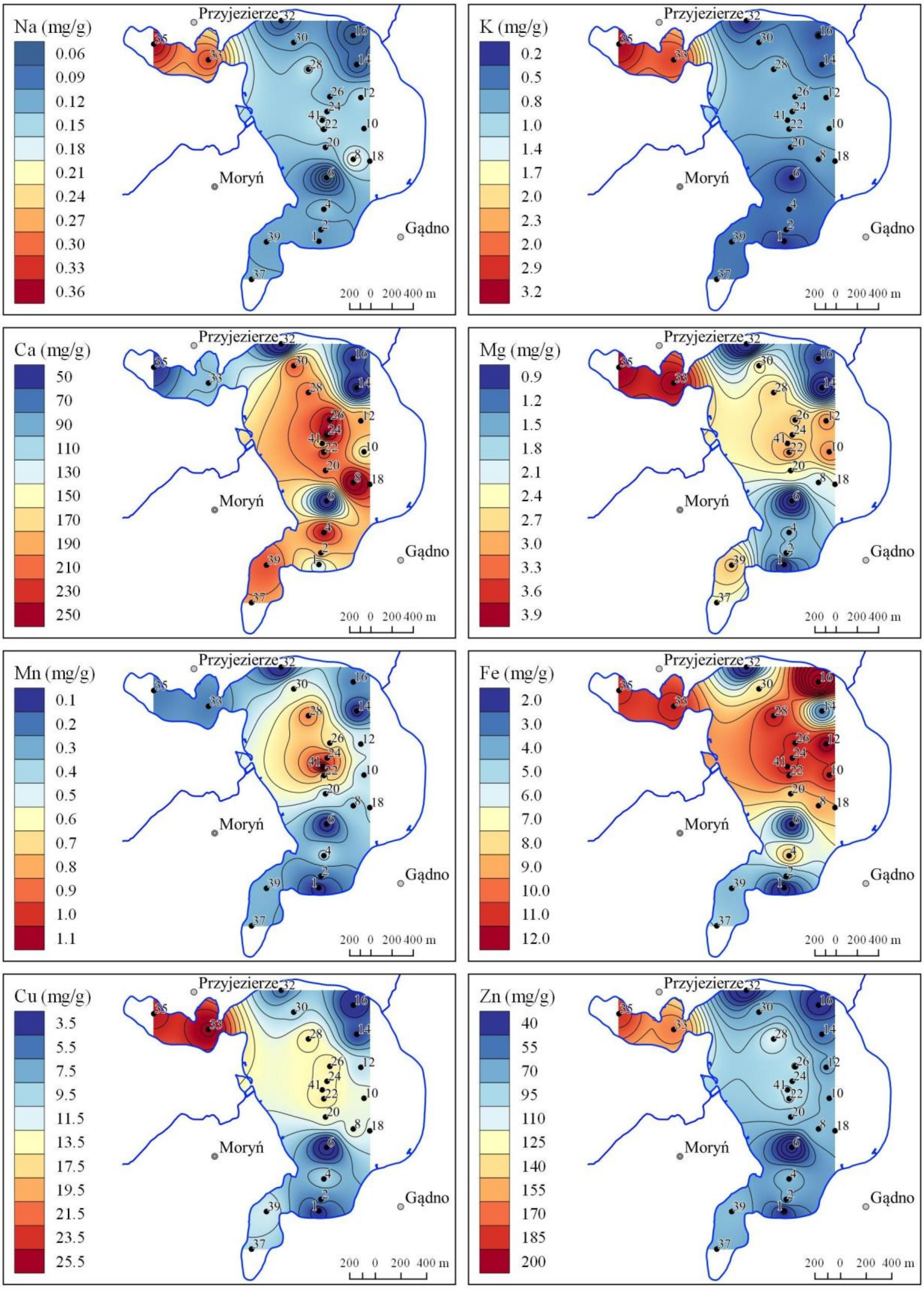

Fig. 7. Spatial distribution of researched elements
in recent Lake Morzycko sediments taken from bottom surface

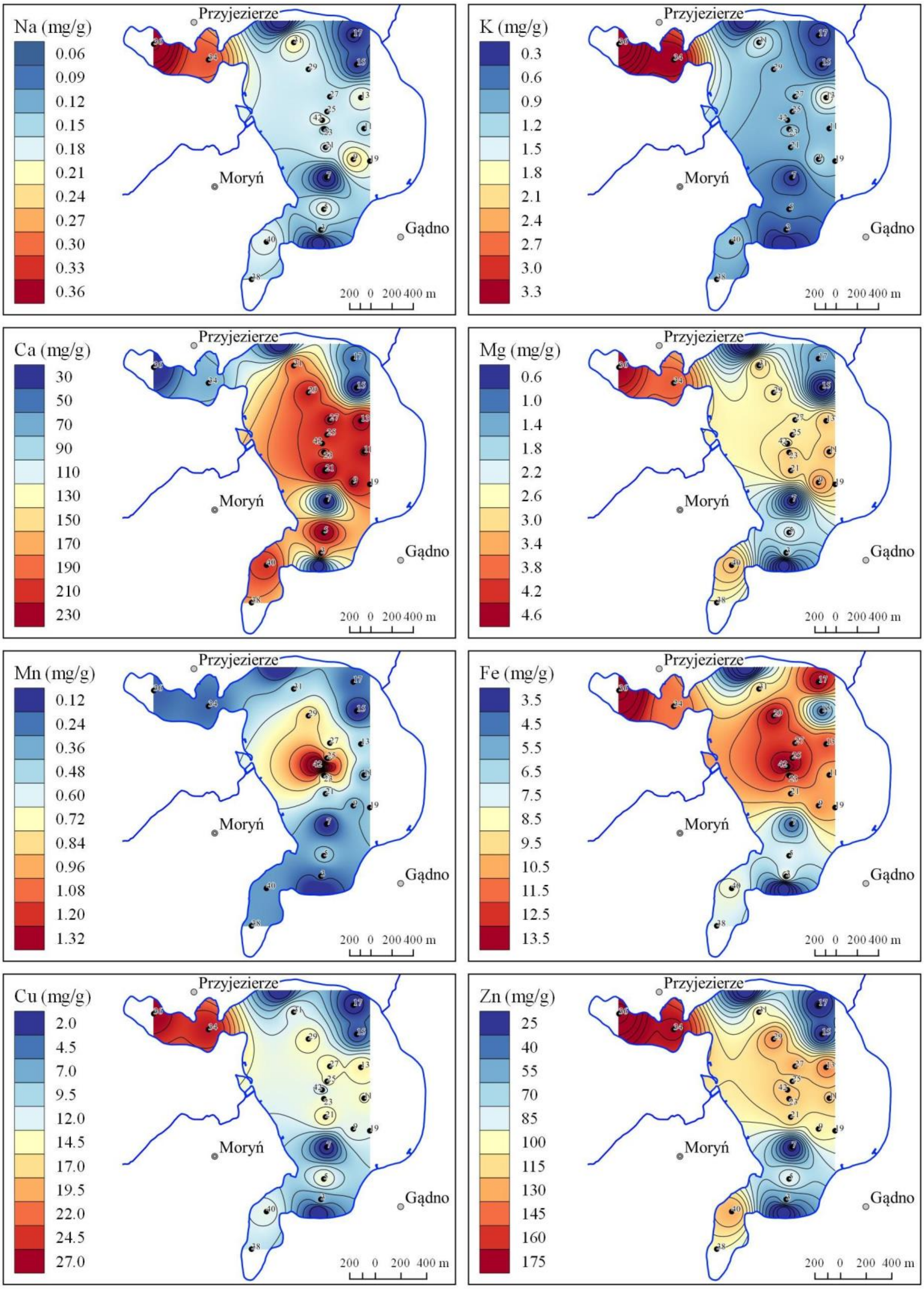

Fig. 8. Spatial distribution of researched elements in recent Lake Morzycko sediments taken from 5 cm below bottom surface

Holocene (Wojciechowski 1990; Bałaga 2007; Apolinarska *et al*. 2012; Plak *et al*. 2015; Siedlik, Borówka 2019; Okupny *et al*. 2020).

Furthermore, bedrock geology and the resultant soil cover with dominant clay component and coarser skeletal fractions favour the development of intracover discharge, which is an important factor responsible for the concentrations of ion input in groundwaters in small catchments within the Pomeranian Lake District (Kostrzewski, Stach 1992; Szpikowska 2005). In the case of Lake Morzycko, an intensification of intracover discharge may have been associated with synchronous thaw and rainfall – a phenomenon that occurs considerably more frequently in Myślibórz Lake District than in other climatic subregions of Western Pomerania (Koźmiński *et al*. 2007). Considering the mutual relationship between Na and K concentrations in the bottom sediments of Lake Morzycko, there was a distinct prevalence of passive supply of allochthonous mineral matter (Na/K index values below 0.2 in middle and north of the lake bed). Importantly, the role of chemical denudation in the case of sediments resting directly on the lake bed in the north-eastern part of the lake (Na/K index values between 0.5 and 0.8) is more important compared to the sediments sampled from greater depths. This situation indicates selective Na concentrations resulting from leaching and has been recorded in other lakes in the north-western part of the Polish Lowlands (Borówka 1992). This may be due to an increase in surplus water entering the underground phase of the cycle, and its drainage via the lake. For catchments in the young glacial zone, an important part in supplying aquifers is ascribed to endorheic areas, and numerous undrained depressions, often those at watershed positions (Gocłowski 1975/76; Kostrzewski *et al*. 2008b; Pietruszyński *et al*. 2015). Further, the higher Na concentrations may result from a diminished supply of potassium ions to the lake waters. Previous research by Mazurek (1999) based on the Kłuda catchment in Western Pomerania indicates that potassium concentrations in aquatic environments are highly variable dependent on soil humidity, the potential for mobilising metals from soil colloids, and conditions of biological cycling functioning (e.g., displacement of potassium ions from leaves and decaying plant matter in autumn and winter). In addition to the factors discussed above, factors shaping water erosion also include locally varying weather conditions. A monitoring of the catchment of Potok Jeleni, located just 6 km to the northeast of Lake Morzycko and adjacent to the Słubia catchment, indicated that the moderate to medium degree of water erosion intensity is associated predominantly with waters from the early spring thaw (Koćmit *et al*. 2006).

Further factors that may significantly shape the chemical composition of inflowing waters and sediments deposited at the bottom of Lake Morzycko are locally diverse retention conditions and the duration of water contact with the substrate. In the upper course of the Słubia valley, slightly lower terrain slopes gradients at the morainic plateau, in conjunction with poor substrate permeability, mean that surface water retention and evapotranspiration play a major part. This is especially important given that Lake Morzycko represents the second-last unit in a system of lake basins connected by the Słubia River. All the lakes in the Słubia catchment form a cascade of flow-through lakes, in which Lake Białęgi (61 m a.s.l.) is the first and highest step, from which the Słubia originates. Water flows through a narrow bed of about 800 m long to the next step of the cascade, Lake Narost (58.1 m a.s.l.), and continues through a peat-infilled depression to four subsequent lakes (Mierno, Witnickie Małe, Witnickie Wielkie, Witnickie). The surface area of each of these lakes ranges from 6 to 8 ha. These lakes receive allochthonous material and create a buffer system which is crucial for the entire valley, as the sum of their partial catchments represents as much as 42% of the entire Słubia catchment. Furthermore, the map of dispersed downwash threat by Józefaciuk and Józefaciuk (1992) indicates that soil cover characterised by the highest degree of potential erosion occurs only within partial catchments of the upper course of the Słubia valley. Over the remaining 1.2-km-long course, the Słubia flows to Lake Morzycko through a broad and highly marshy valley whose slope does not exceed 1.2‰. Over its outlet stretch, about 14.6 km long, the Słubia flows to the Odra River through a slightly deeper, narrow depression representing a gap with a slope of about 3.9‰. The autumn discharge is merely 0.39 dm^3/s, but note that the Słubia has no tributaries along its entire length. The results of the present study may indicate that waters with highly contrasting chemical features mix within the basin of Lake Morzycko, which leads to the accumulation of mineral-organic sediments with varying concentrations of mineral components on the lake bed.

Lake Morzycko sediments are characterised by a notably higher contribution of both lithophilic elements (Na, K and Mg), and Ca and Zn concentrations in sediments, as compared to sediments from other water basins of northern Poland (cf. Bojakowska, Sokołowska 1996; Borówka 2001;

Trojanowski, Antonowicz 2005; Woszczyk *et al*. 2009; Podlasińska, Szydłowski 2017; Korzeniowski *et al*. 2020). This is caused by intense leaching of mineral components and their transport by groundwaters over relatively flat surfaces characterised by favourable infiltration conditions. Such conditions occur mainly to the north-west and south of Lake Morzycko, where despite almost 30% lower potential hydrologically active zone relative to the upper course of Słubia catchment (Mądry, Połaniecka 2000), fluvioglacial sands and gravels prevail, with local occurrences of tills superjacent to sands and gravels with moderate and high permeability. The conditions of migration**,** transport and bonding of research metals depends on regional geochemical background, depth of Lake Morzycko, variable erosion on the individual subcatchments and the redox conditions. This is supported by the maximum values of Fe/Mn index, whose spatial distribution indicates a relationship with the location of wetlands in the north-western part of Lake Morzycko.

According to the classification of contamination by trace elements proposed by Bojakowska (2001), the studied sediments of Lake Morzycko are classified as 1^{st}- and 2^{nd}-class sediments. The first group includes sediments considered unpolluted, while the second group are weakly polluted sediments with sporadic impact on biota. With respect to Cu concentrations, only four samples were included in the second purity class, i.e., sediments sampled in the north-western bay of Lake Morzycko, which are directly prone to anthropogenic pollution by the village of Przyjezierze. These same samples yielded elevated concentrations of Zn, close to or slightly exceeding the geochemical background. A similar observation has been made for other aquatic sediments in north-western Poland, especially for samples collected from Odra River valley between Kostrzyn and Szczecin (Bojakowska, Sokołowska 1998), Lake Wonieść in Poznań Lake District (Hildebrandt-Radke *et al*. 2011), and Lake Gostyń in Myślibórz Lake District (Korzeniowski *et al*. 2020). Higher concentrations have been found only for Ca and Mg in bottom sediments of Lake Racze in Pyrzyce Lowland, where a larger proportion of land is being farmed (Bloom 2015). A study by Burczyk *et al*. (2015) indicates that in agricultural catchments of Western Pomerania, farming activity does not display a direct impact on seasonal changes in Ca-to-Mg ratio in ground waters supplied to water basins. A more important role in Ca and Mg cycling should therefore be ascribed to the values of the local geochemical background of the bedrock. The amount of these elements in the recent sediments of Lake Morzycko is mainly of natural origin. They come from dissolution of the bedrock by acid rainwater and alkaline groundwater. Therefore, these are the denudation components of all the displaced dissolved material, which in northern Poland depend on, among other things, season or water hardness (Kostrzewski, Zwoliński 1992).

Conclusion

The present study, conducted on Lake Morzycko and accompanied by a detailed reconnaissance of factors influencing contemporary potential morphogenetic processes in the catchment of the Słubia River confirmed the key role of differences in functioning of a morainic plateau and outwash plain denudational system on the chemical composition and granulometry of bottom sediments. Most of the studied samples (75%) conform to the clay-detritus gyttja group in the classification of lake sediments compiled for Western Pomerania.

A comparison of the results of geochemical studies on lake sediments indicated that the concentrations of most of the elements examined is higher in the samples taken from deep areas than in sediments sampled in the nearshore zone. The relationship between the examined metals and organic matter or fine mineral fraction confirms that, in stratigraphic interpretations, it is imperative to include variability in chemical composition of biogenic sediments such processes as bioaccumulation and intensity of weathering processes, as well as passive supply of lithogeochemical components to the basin.

The spatial relationship between lithophilic elements concentrations, regardless of the sampling depth, is not always strong in individual parts of Lake Morzycko. This is due to thew various sources of supply and transport of these components to the lake, including leaching of catchment bedrock by ground waters, but also penetration of the shallow substratum by rainfall or meltwaters associated with the Słubia River.

In studies on lake bottom sediments characterised by heterogeneous chemical composition statistical indices may provide necessary information for reconstructing sedimentary conditions. In the case of Lake Morzycko sediments, such a part was played by Na/K and SPAN indices. Changes in research elements were due to varying biological productivity, intensity of weathering of postglacial material making up the catchment, and potential for migration of metals to the lake with surface or underground runoff.

Assessment of the contamination state of Lake Morzycko sediments using the local geochemical background showed significant differences in pollution of the shallow parts of the lake near the tourist districts of Moryń. At the same time, the central and southern parts of the lake, despite higher surface water supply and widespread farming, show a lower degree of contamination.

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