

GEOCHEMISTRY OF SURFACE SEDIMENTS OF A COASTAL LAKE SARBSKO (NORTHERN POLAND)

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Abstract

The main goal of the presented research was to investigate spatial distribution of surface sediments and to recognize relationships between chemical composition of water and sediments in a coastal Lake Sarbsko (northern Poland). The Lake Sarbsko is a freshwater basin. The water column is well oxygenated and waters exhibit only minor spatial variability of chemical composition indicating rapid and good mixing. Surface sediments of Lake Sarbsko are strongly diversified with respect to chemical composition.

The sediments of Lake Sarbsko are characterized by elevated content of terrigenous silica indicating enhanced input of clastic material from the watershed and/or increased dynamics of the lake waters. Moreover, $\text{SiO}_{2\text{ter}}$ is strongly negatively correlated with $\text{SiO}_{2\text{biog}}$, organic matter and element contents, which argues for diluting effect of the former towards authigenic components of sediments. Basically, terrigenous silica (quartz) content is highest in the lake shores and declines towards the lake center. Biogenic silica, organic matter and most of elements display reversed tendency. CaCO_3 was encountered in three isolated areas, where it co-occurs with FeS. It is anticipated that precipitation of calcite in Lake Sarbsko resulted from postdepositional processes. Spatial distribution of Fe, Mn, Ca, Mg, Na and K in Lake Sarbsko is also governed by their geochemical affinities to organic matter (Fe), Fe/Mn oxides (Fe, Mn), sulphides (Fe), clay minerals (Na, K, Mg, Mn) and carbonates (Ca, Mn).

Key words: coastal lake, lake sediment geochemistry, Gardno-Łeba Coastal Plain, southern Baltic, Poland

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INTRODUCTION

Coastal basins are located at the contact of marine and terrestrial environments, within the zone of mixing of saline and fresh waters. These water bodies are subdivided into two categories: estuaries, which are inundated river valleys, and lagoons, being water reservoirs separated by sandy barriers and having restricted connection with the sea (Nichols, Allen 1981). On non-tidal coastlines lagoons are usually completely isolated by continuous barriers and receive considerable freshwater input (Nichols, Allen 1981). These lagoons can be regarded as coastal lakes and the southern Baltic coast is a scarce example where they are very well developed.

Specific features of such depositional environment, affecting lithology and chemical composition of sediments formed therein, are great temporal variation of chemical composition of water, enhanced biological productivity as well as elevated rate of sedimentation (Baltzer, Rivière 1972; Nichols, Allen 1981; Ohtake *et al.* 1982). As a result, closed lagoons and coastal lakes often act as sediment traps. Sediments of coastal basins are composed of mineral and organic matter originating from different sources: river input, marine

washovers, chemical precipitation and increased biological productivity (Nichols, Allen 1981; Andrade *et al.* 2004). Moreover, chemical composition of the sediments is strongly affected by postdepositional processes caused by microbial oxidation of sedimentary organic matter and/or groundwater intrusions of salt water through the permeable barriers (Baltzer, Rivière 1972; Neumann *et al.* 2005; Vaalgamaa, Korhola 2007). Consequently, lagoonal sediments are heterogeneous and reveal considerable spatial lithological and geochemical variability (Levy 1974; Thorbjarnarsson *et al.* 1985; Uścińowicz, Zachowicz 1996; Pustelnikovas 1998; Osadczuk 2004).

Deposits of coastal basins provide reliable proxies for tracking palaeoenvironmental changes in coastal zones, including sea level fluctuations as well as paleohydrological and climatic change (Wojciechowski 1995; Freitas *et al.* 2002; Konotopulos, Avramidis 2003; Garcia-Rodriguez *et al.* 2004; Yum *et al.* 2004; Borówka *et al.* 2005; Cundy *et al.* 2006; Lucchi *et al.* 2006; Woszczyk *et al.* 2008). From that perspective, understanding of local processes that control and modify sediment lithology and geochemistry is of great importance.

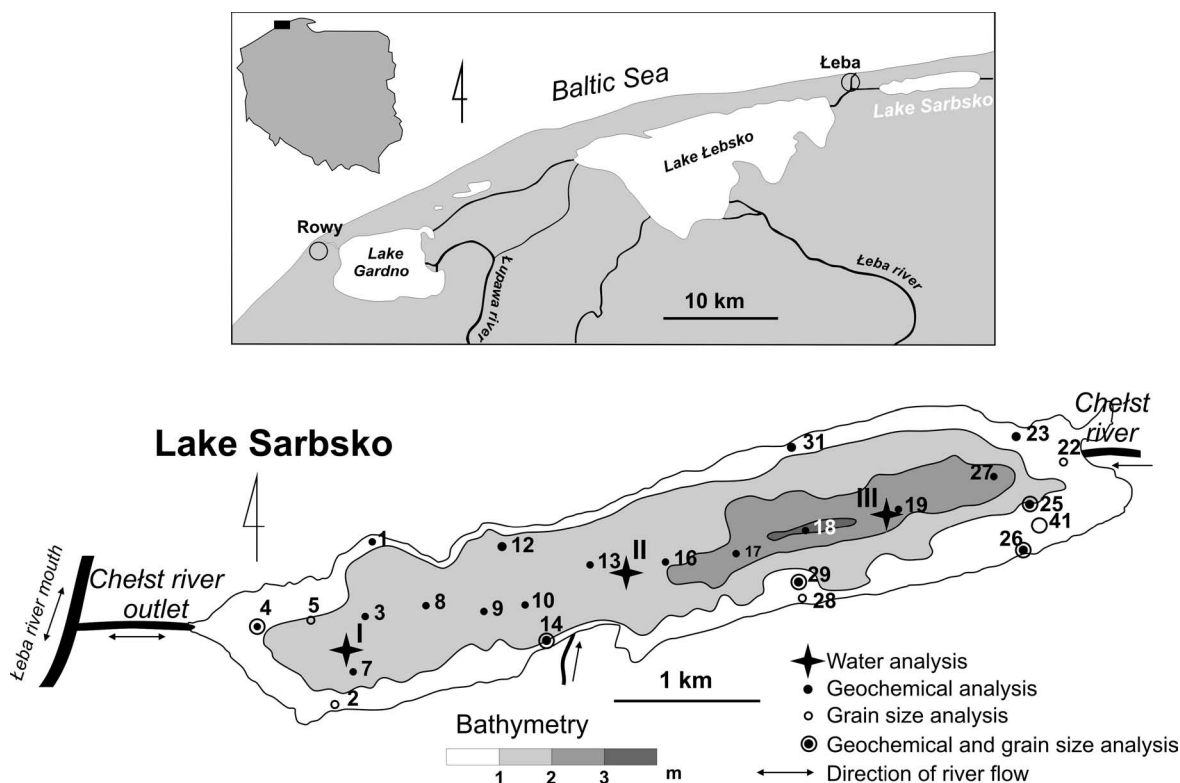


Fig. 1. Location and bathymetric sketch of Lake Sarbsko and distribution of sediment and water sampling points (bathymetry according to the data collected by the Institute of Inland Fishing, Olsztyn, Poland).

The present study aims to outline the spatial distribution of sediments in Lake Sarbsko, Polish Baltic Coast, which is a typical coastal lake. The main objectives of the research was to recognize variability of chemical composition of the lake sediments and to investigate interrelations between chemical composition of water and deposits in the basin.

HYDROGRAPHY OF LAKE SARBSKO

Lake Sarbsko, is located in the eastern part of the Gardno-Łeba Coastal Plain, northern Poland (Fig. 1). The lake area is *ca* 6.5 km² (Jańczak 1997). Lake Sarbsko is elongated parallel to the coastline and is separated from the Baltic Sea by a sand bar (the Sarbsko Barrier) overgrown with pine-wood. Mean water depth in Lake Sarbsko is 1.5 m, and the maximum – 3.2 m (Jańczak 1997) is reached in the central-eastern part of the basin (Fig. 1). Today, mean altitude of lake water table is 517 mm (with regard to sea level in Kronstadt), which is 20 cm higher than the Baltic Sea level in the Łeba gauge station, and during the year it varies from 505 cm to 530 cm following seasonal changes in the sea level (Majewski 1972). Higher lake water levels are observed during winters and late summers, while lowstands occur in springs.

Lake Sarbsko is hydrologically open and displays very short residence time of water, which is completely renewed within as little as 10.7 months (Łukasiewicz 1995). The lake is fed by the Chelst River from the east and a small channel from the south (Fig. 1). The outflow is situated in the western part of the basin and connects Lake Sarbsko with the Łeba river mouth.

As Lake Sarbsko has no direct connection to the Baltic Sea, freshwater inflow has greatest influence on chemical composition of its water (Cieśliński 2004, 2007), which usually is only slightly saline (~0.1‰). On the other hand, during severe winter storms, marine waters may enter the lake, via the Łeba river mouth and the Chelst outflow channel (Fig. 1), raising its salinity up to 3‰ (Szopowski 1962). Despite that salt water intrusions to Lake Sarbsko are relatively infrequent (16% of annual observations acc. to Szopowski 1962), they pump into the lake a lot of clastic material, which is accumulated in the form of a back delta in the westernmost part of the lake (Szopowski 1962).

METHODS

Hydrochemical analyses of surface and bottom waters were performed in three sampling points (Fig. 1) and in different seasons between the year 2002 and 2006. Dates of measurements are given in Fig. 2. Oxygenation of waters was measured only once in December 2007. In total, 144 water samples were analysed. Surface water samples were taken with a 3-dm³ ladle, and bottom waters were collected using hydrological bottle. Samples were acidified and stored in plastic containers. In the water, electric conductivity, pH and the contents of Cl⁻, SO₄²⁻, HCO₃⁻ and Na⁺, K⁺, Ca²⁺, Mg²⁺ were determined. Conductivity and pH were measured with a WTW 340i Multimeter. Concentration of sulphates was determined using WTW PhotoLab 6 spectrophotometer. In analysis of chloride content, argentometric titration with AgNO₃ with regard to K₂CrO₄ was applied and bicarbonates

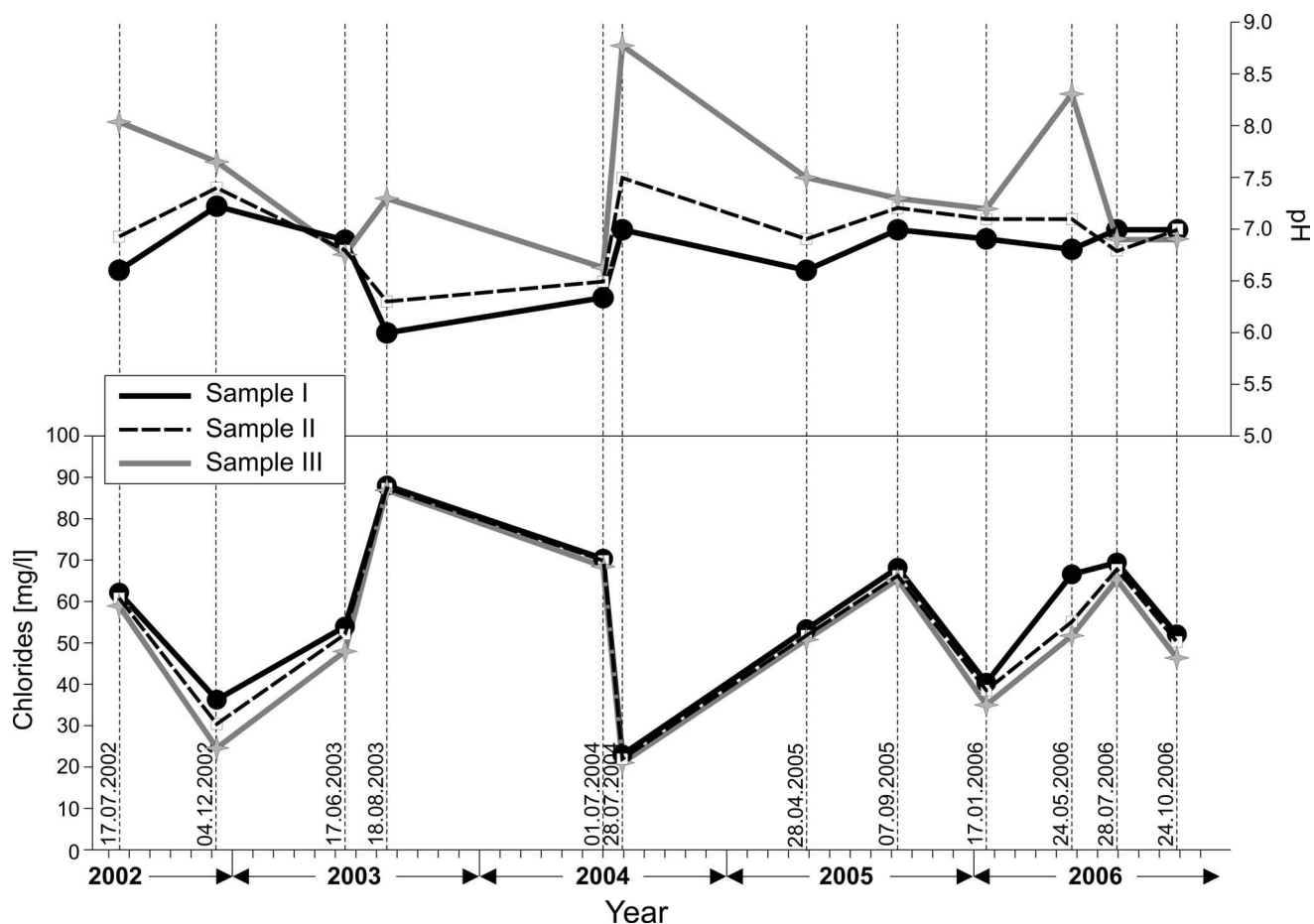


Fig. 2. Temporal changes in pH and chlorides concentration in surface waters of Lake Sarbsko during the study period (for sample location see Fig. 1).

were titrated with a 0.1n HCl solution with regard to methyl orange. Analyses of Na and K were carried out using Sherwood Scientific 410 flame photometry set, and concentrations of Ca and Mg were determined with a method of two-step EDTA titration with regard to murexide in pH = 10 for the sum of Mg and Ca and in pH = 13 for Ca. Oxygen content in surface and bottom water was measured in the field using portable oxygen meter WTW.

Bottom sediments of Lake Sarbsko were recovered with a Russian sampler in 25 points (Fig. 1) in which geochemical (20 samples) and granulometric (10 samples) analyses were made. Due to appreciable vertical homogeneity and possible resuspension of sediments (Uściniowicz, Zachowicz 1996), 5-cm thick samples of "surface deposit" were taken. Geochemical analyses were performed in material dried at 105°C and ground in agate mortar. Organic matter content was determined by combustion of powdered samples at 550°C for 4 h (Heiri *et al.* 2001). CaCO₃ was analysed using carbonate bomb, however when CaCO₃ content was below 5%, loss on ignition at 550°C for 4 h and at 925°C for 2h (Heiri *et al.* 2001) was applied as well to improve the accuracy. Biogenic silica concentration (SiO_{2biog}) was calculated from the weight difference between the total silica content and terrigenous silica percentage (SiO_{2ter}). Total silica was determined after dissolution of acid soluble fractions and organic matter with

H₂SO₄ and H₂O₂ in Hach Digesdahl Digestion Apparatus at 440°C, and the SiO_{2ter}, was the residue after removal of opaline (biogenic) silica from the total silica with 0.5n NaOH in a water bath at 100°C for 2h (Bechtel *et al.* 2007).

The difference between 100% and the total sum of organic matter, CaCO₃, SiO_{2ter} and SiO_{2biog} represents ASM. The term ASM was adopted from Wojciechowski (2000) and is assumed to include hot acid extractable compounds excluding carbonates (*e.g.* sulphides, some clay minerals *etc.*), however, its chemical composition was not accurately established.

For analysis of elemental composition of sediments, powdered samples were digested with aqua regia by standing for 16h at room temperature followed by boiling for 2h (Bechtel *et al.* 2007). The element contents were determined using atomic emission spectrometry (AES) for Ca and atomic absorption spectrometry (AAS) for Fe, Mn, Mg, Na and K. Reproducibility of metal determinations was 5–10%.

Mineral composition of seven samples was determined in powdered untreated sediment by X-ray diffraction using VRD6 diffractometer. The diffractograms were recorded by the reflection method using CuK_α radiation. As the XRD detection limit is 5–10% (Kaufhold 2007) and some minerals are difficult to detect by this method due to their amorphous structure (Dean 1993), for four samples (3 samples of black

Table 1

Mean chemical composition of Lake Sarbsko water (in brackets: minimum - maximum values)

Sample	Conductivity [μS/cm]	pH	Dissolved species [mg/l]						
			Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻
ISW	433.0 (310.0 - 551.0)	6.8 (6.0 - 7.2)	39.4 (26.5 - 62.2)	11.8 (5.7 - 15.7)	30.0 (10.8 - 47.5)	3.9 (2.2 - 4.8)	56.9 (23.0 - 87.7)	109.8 (67.1 - 158.6)	43.7 (28.0 - 53.0)
IBW	447.0 (356.0 - 576.0)	7.2 (6.8 - 7.9)	44.7 (27.4 - 65.3)	12.4 (5.7 - 16.2)	30.0 (10.9 - 48.3)	4.0 (2.2 - 5.1)	57.2 (25.0 - 89.7)	134.2 (79.3 - 164.7)	37.9 (21.0 - 47.0)
IISW	421.0 (288.0 - 523.0)	7.0 (6.3 - 7.5)	39.9 (27.1 - 61.3)	11.5 (5.7 - 15.1)	28.8 (10.5 - 46.3)	3.8 (2.1 - 4.6)	54.3 (22.0 - 87.4)	115.9 (79.3 - 164.7)	41.3 (26.0 - 51.0)
IIBW	432.0 (302.0 - 538.0)	7.3 (6.8 - 7.9)	43.3 (28.6 - 63.3)	11.9 (5.7 - 15.8)	29.0 (10.6 - 47.0)	3.8 (2.1 - 5.0)	54.7 (23.0 - 89.0)	140.3 (79.3 - 170.8)	37.6 (20.0 - 48.0)
IIISW	407.0 (268.0 - 501.0)	7.4 (6.6 - 8.8)	40.6 (27.8 - 58.1)	11.1 (5.7 - 15.0)	27.3 (10.3 - 46.0)	3.6 (2.0 - 4.3)	51.9 (21.0 - 87.0)	134.2 (85.4 - 170.8)	38.8 (21.0 - 49.0)
IIIBW	416.0 (275.0 - 516.0)	7.5 (6.5 - 8.5)	42.8 (28.3 - 64.8)	11.5 (5.7 - 16.3)	27.9 (10.4 - 46.6)	3.6 (2.0 - 4.5)	52.5 (21.0 - 88.3)	146.4 (91.5 - 183.0)	37.3 (19.0 - 52.0)

SW – surface water, BW – bottom water

gyttja and 1 sample of olive gyttja) sequential extraction of Fe, Mn and Mg was applied with the aim to distinguish the dominant chemical forms of these elements. This approach was earlier applied to identify Fe and Mn species in sediments by Clark *et al.* (1998), Kaufhold (2007), Ouddane *et al.* (2001) and Overnell (2002). Sequential extraction followed the protocol described by Walna *et al.* (2005). In accordance with Clark *et al.* (1998) and Walna *et al.* (2005) five classes of element associations were defined: 1) exchangeable, 2) carbonates, 3) reducible (adsorbed on Fe and Mn oxides), 4) oxidizable (bound to organic matter and sulphides) and 5) residual. Although sequential extraction was performed on oven dried samples, based on findings of Manning *et al.* (1979) and Clark *et al.* (1998) it is anticipated that the drying procedure caused no significant changes in the speciation of elements.

Grain size distribution in sandy samples was determined by sieving.

Correlations coefficients discussed in the text were calculated using Statistica v 8.0 for total (bulk) sediment and on a terrigenous silica-free basis.

RESULTS AND DISCUSSION

Chemical composition of surface and bottom waters in Lake Sarbsko

Lake Sarbsko water reveals freshwater chemical composition. Ca cations dominate over Na, Mg and K (Ca²⁺>Na⁺>Mg²⁺>K⁺) and bicarbonates dominate over chlorides and sulphates (HCO₃⁻>Cl⁻>SO₄²⁻) (Tab. 1). Bicarbonates and Ca²⁺ ions account for about half of the total dissolved species. Mean pH of Lake Sarbsko waters is 7.2 and mean oxygen content is 13.03 mg O₂ l⁻¹. Surface and bottom waters of Lake Sarbsko are undersaturated with respect to calcite. Saturation index, calculated according to Kelts & Hsü (1978), (SI_{calc} = log(IAP/K_c)) is between -2.26 and -0.40.

Chemical composition of Lake Sarbsko waters shows only minor spatial variability (Tab. 1). However, electric conductivity as well as the contents of Cl⁻, SO₄²⁻, Ca²⁺, Mg²⁺, Na⁺ and K⁺ clearly decrease towards the east together with

increasing pH and enrichment in HCO₃⁻. The differences between surface and bottom waters are insignificant. The latter are slightly enriched in most of dissolved species, except sulfates, and reveal higher pH. The above chemical characteristics indicate that Lake Sarbsko waters become more saline towards the west and from the lake surface to the bottom. At the same time, weakly pronounced chemical gradients argue for very fast and well water mixing in this shallow lake.

On the other hand, between the year 2002 and 2006 chemical composition of water revealed significant temporal changes (Fig. 2). Salinity (expressed as concentration of Cl⁻) varied from 21.0 to 89.7 mg Cl⁻/l with the slight tendency to increase in warmer seasons. The pattern of Cl⁻ fluctuations was the same throughout the lake. Unlike changes in salinity, temporal variations of pH were more irregular and displayed different patterns in the eastern and central/western parts of Lake Sarbsko. In the former, pH fluctuated from 6.6 to 8.8, while in the latter – from 6.0 to 7.5 (Fig. 2).

Sediments of Lake Sarbsko

In the surface sediments of Lake Sarbsko three lithofacies have been distinguished (Fig. 3).

Fine- to medium-grained sands – spread along the southern shore of the lake and in its western and eastern margins. Mean diameter of sands varies between 1.49 and 2.40 phi. The facies is characterized by moderate to poor sorting and negative skewness (Fig. 4). Standard deviation and skewness range from 0.38 to 1.40 phi, and from -0.97 to -3.29 phi, respectively (Fig. 4). With respect to chemical composition, the sands are mainly composed of terrigenous silica (quartz) with small admixture of CaCO₃ originated from scarce and fragmented mollusc shells (Tab. 2, Fig. 5). These sediments are poor in Fe, Mn, Na, K, Ca and Mg (Tab. 2).

Olive gyttja – is present in the central part of the lake and laterally passes into fine to medium sands and black gyttjas (Fig. 3). In most samples olive gyttja contains substantial admixture of sand. Consequently, the facies is dominated by terrigenous silica, which content varies between 36.9 and 68.7%. On the other hand, organic matter and CaCO₃ con-

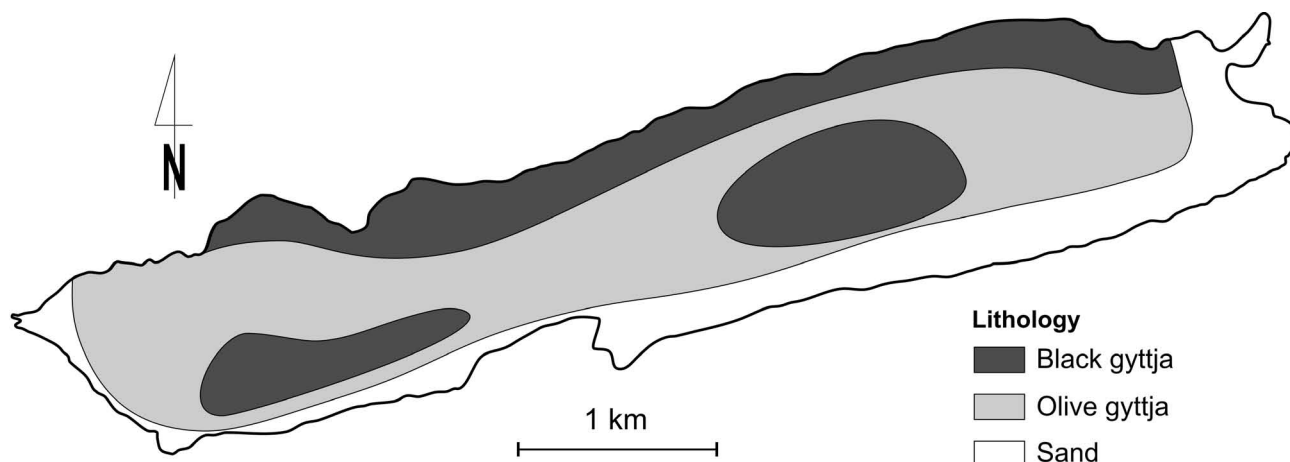


Fig. 3. Spatial distribution of surface sediments of Lake Sarbsko.

centrations are rather small: 14.6–25.6% and 1.6–2.8%, respectively. The olive gyttja is also characterized by elevated contribution of biogenic silica ranging from 9.1 to 34.6% (Tab. 2, Fig. 5).

Nothing more than quartz was identified in olive gyttja by XRD method. Olive gyttja displays very small contents of Mn, Na, K, Ca and Mg but is enriched in Fe which concentration is as high as 1.0–1.8% (Tab. 2). The colour of the gyttja might be explained by the presence of chlorophyll identified by Bechtel *et al.* (2007).

Black gyttja – occurs only locally, in three isolated areas: in a belt extending along the Sarbsko Barrier and in the form of lenticular lithosomes located in south-western and

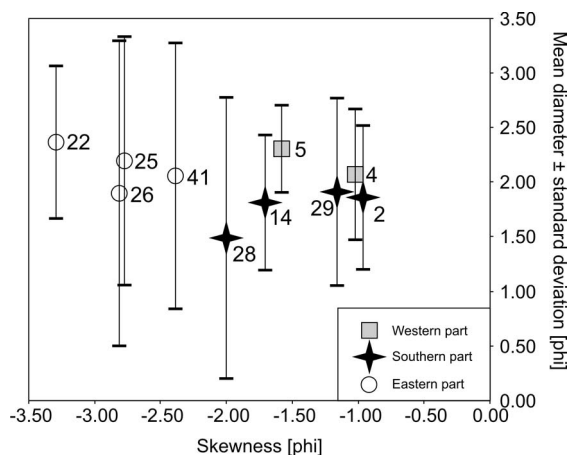


Fig. 4. Grain size distribution of sandy sediments from Lake Sarbsko (numbers indicate sample locations in Fig. 1).

Table 2

Mean chemical composition of lithofacies
 (in brackets: minimum - maximum values)

Element	Black gyttja [%]	Olive gyttja [%]	Fine/medium sand [%]
SiO _{2ter}	50.64 (36.99 - 68.63)	55.35 (36.93 - 68.68)	96.88 (93.30 - 98.01)
SiO _{2biog}	15.93 (8.86 - 25.12)	19.87 (9.12 - 34.65)	0.53 (0.05 - 1.95)
Org. matter	24.90 (15.71 - 33.65)	19.62 (14.57 - 25.61)	0.56 (0.29 - 1.18)
CaCO ₃	14.25 (6.83 - 31.50)	2.18 (1.61 - 2.81)	0.35 (0.07 - 1.00)
Fe	1.968 (1.043 - 2.891)	1.417 (1.044 - 1.780)	0.108 (0.073 - 0.183)
Mn	0.102 (0.057 - 0.126)	0.043 (0.035 - 0.059)	0.005 (0.002 - 0.011)
Ca	5.869 (2.541 - 13.375)	0.562 (0.224 - 0.847)	0.093 (0.070 - 0.309)
Mg	0.242 (0.122 - 0.338)	0.210 (0.148 - 0.285)	0.012 (0.007 - 0.023)
Na	0.041 (0.019 - 0.131)	0.030 (0.020 - 0.040)	0.007 (0.005 - 0.008)
K	0.039 (0.011 - 0.149)	0.016 (0.007 - 0.023)	0.005 (0.002 - 0.008)

central-eastern part of the lake (Fig. 3). The latter coincides with the deepest section of the lake. The black colour of the gyttja as well as reaction of the fresh sediment with HCl (at room temperature), in which H₂S is liberated, indicate the presence of FeS (Berner 1971, Berner *et al.* 1979; Cundy, Croudace 1995; Baumgartner *et al.* 2006), which remains stable under anoxic conditions below sediment – water interface. Accordingly, organic matter content in black gyttja is higher than in olive gyttja varying between 15.7 and 33.6% (Tab. 2, Fig. 5). Nevertheless, terrigenous silica content is again high and ranges from 37.0 to 68.6%. On the other hand, SiO_{2biog} concentration in black gyttja accounts for 8.9–25.1% of the sediment and it is lower than in olive gyttja.

In black gyttja FeS coexists with CaCO₃, which amounts to 14.2% on average, but varies between 6.8 and 31.5% (Tab. 2, Fig. 5). Within the facies the presence of quartz, albite, calcite and bassanite was demonstrated by X-ray diffraction (Fig. 6). Bassanite (2CaSO₄·H₂O) was hardly ever reported from temperate freshwater lake sediments (Last 2001) and in black gyttja it may originate from oxidation of sulphides. With respect to element composition black gyttja is characterized by elevated values of Ca, Mn and Fe, while Mg, K and

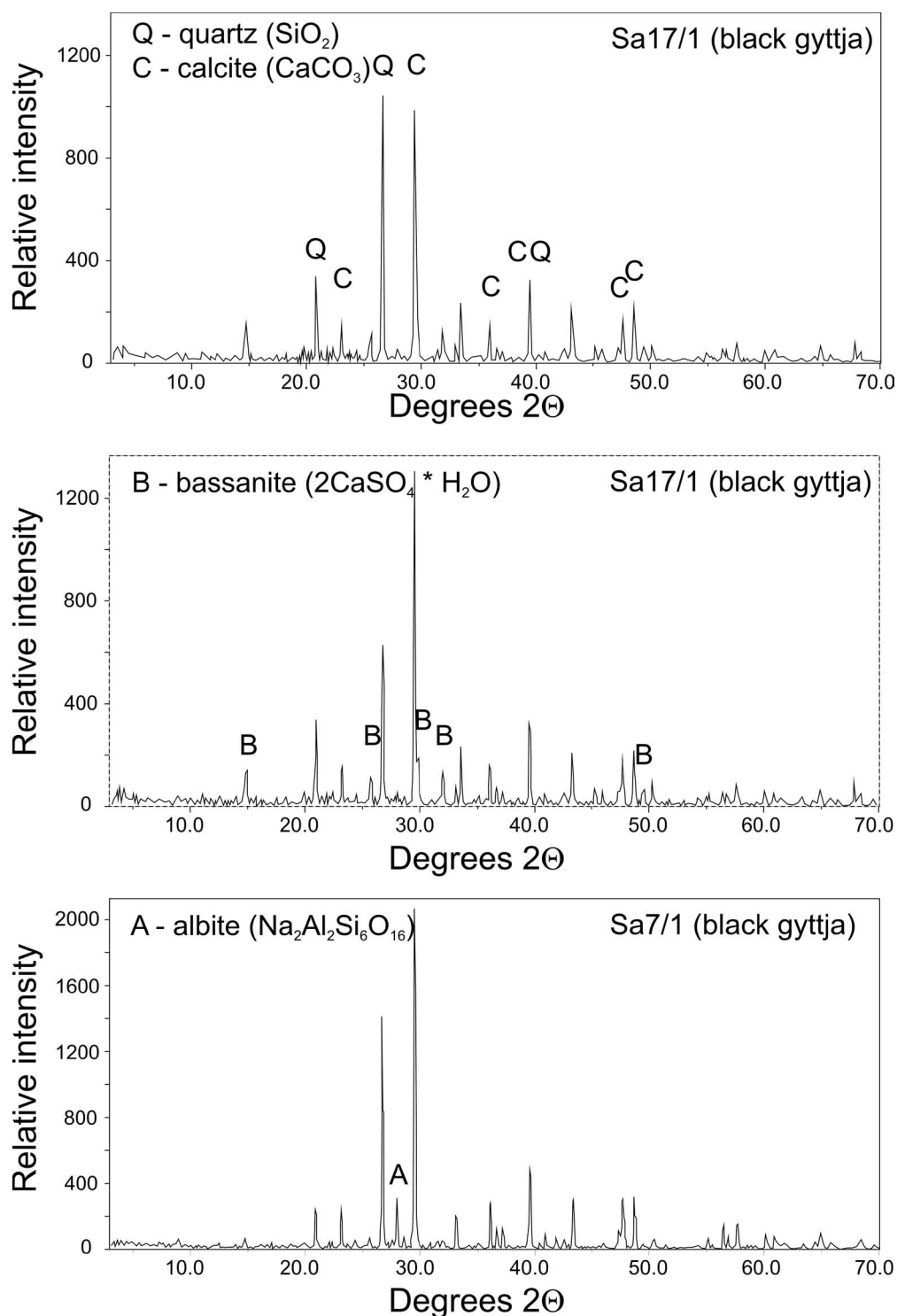


Fig. 6. X-ray diffraction patterns of black gyttja samples from Lake Sarbsko.

each case CaCO_3 coexists with FeS . The only determined carbonate mineral in Lake Sarbsko sediments was calcite (Fig. 6), however, as indicated by sequential extraction analyses, minor amounts of Mn-enriched carbonates are present as well (Fig. 7). Spatial distribution of carbonates in Lake Sarbsko does not coincide with physical/chemical variability of the bottom waters in the basin. Moreover, as it was stated in the previous section, calcium carbonate can not precipitate from the lake waters because of too low values of saturation

index. Hence, it is anticipated that CaCO_3 in Lake Sarbsko was formed below the sediment-water interface.

Co-occurrence of carbonates and FeS has been earlier reported by Sternbeck & Sohlenius (1997), Clark *et al.* (1998) and Eusterhues *et al.* (2005), who related it to microbial oxidation of organic matter at the expense of sulphates as well as to reduction of Fe and Mn oxides under anoxic conditions. According to Clark *et al.* (1998) the process is represented by the formula:

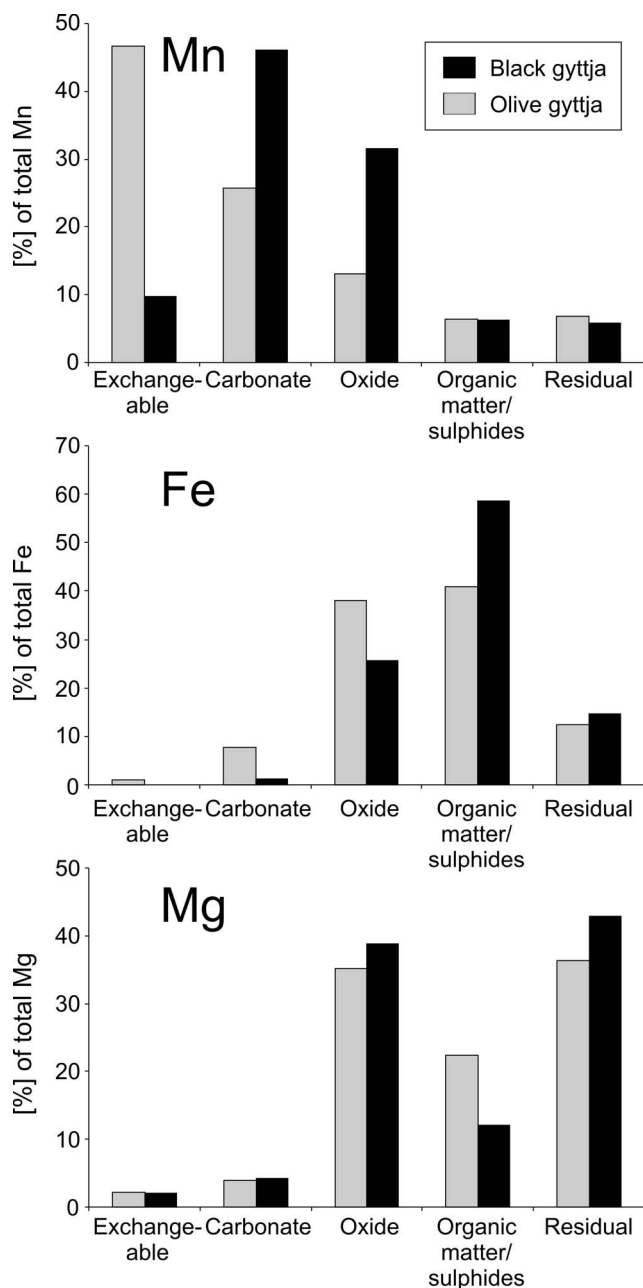
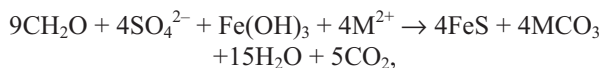


Fig. 7. Speciation of Fe, Mn and Mg in black and olive gyttjas from Lake Sarbsko.



where M – any divalent metal (*e.g.* Ca). On the other hand, Aller & Rude (1988), Calvert & Pedersen (1993) and Sternbeck & Sohlenius (1997) point out that in the deposits containing FeS, mixed Ca-Mn carbonates are likely to form when MnO₂ settling from the oxygenated water column is rapidly reduced in the sediment. The Mn speciation analysis showed that in Lake Sarbsko in black gyttja 38–59% of total Mn occurred in the form of carbonate (Fig. 7). Thus, the above mechanism is postulated as the most prominent explanation of genesis of carbonate sedimentation, however, unresolved problem remains why carbonates precipitate only in some parts of Lake Sarbsko.

Elemental composition

In the analysis of the elemental composition of Lake Sarbsko deposits, the focus was put on the levels and spatial distribution of six elements: Ca, Mg, Na, K, Fe and Mn (Fig. 8), owing to their most frequent occurrence in the deposits. Apart from rates of supply from the catchment, concentrations of Ca, Mg, Na, K, Fe and Mn in coastal lakes depend basically on salinity (Liss 1976), the levels of Fe and Mn being additionally affected by water oxygenation (Engstrom, Wright 1984; Boyle 2001).

In terms of Fe, Mn, Ca, Mg, Na and K percentages, sediments of Lake Sarbsko differ from those in the other lagoons of the southern Baltic coast. The concentrations of all the analysed elements are generally lower here than those observed in the deposits of Szczecin Lagoon, Vistula Lagoon, or Curonian Lagoon (Uściniowicz, Zachowicz 1996; Pustelnikovas 1998; Osadczyk 2004). The differences can be explained by the absence of a major tributary, which is the main input path of those metals into coastal water bodies (Liss 1976).

The most abundant elements are calcium and iron. It was observed that in olive gyttjas and sands Fe exceeded Ca in quantity, while in black gyttjas Ca levels were 2 to 6 times higher than those of Fe. Those differences are due to the fact that Ca in the sediments of Lake Sarbsko mainly occurs in carbonate form. This is corroborated by a high correlation coefficient between Ca and carbonates, both in bulk sediment ($r = 0.99$) and on SiO_{2ter}-free basis ($r = 0.71$) (Tab. 3, Tab 4). Moreover, the contents of Ca and CaCO₃ in the sediments of Lake Sarbsko are very close to their stoichiometric relation in a particle of calcium carbonate (Fig. 9).

In sands and olive gyttjas the CaCO₃ content does not exceed 1.0 and 2.8%, respectively, whereas in black gyttjas it reaches 31.5% (Fig. 5).

Quantitative relations among the elements in the deposits (Ca>Mg>Na>K) are somewhat different than those in the lake water (Ca>Na>Mg>K). Depletion of Na in sediment can be explained by less effective sorption of the former with respect to Mg (Gornitz 1972). On the other hand, concentrations of potassium lower than sodium, with a dominant role of Ca in the sorption complex, is a diagnostic feature of deposits formed in lagoonal basins with considerably freshened waters (Vu Ngoc-Ky *et al.* 1981). In typical fresh-water sediments the situation is as a rule reversed, *i.e.* levels of K are higher than those of Na (Vu Ngoc-Ky *et al.* 1981; Robinson 1994; Virkanen 2000; Borówka *et al.* 2005; Vaalgamaa, Korhola 2007). In the surface sediments of Lake Sarbsko sodium and potassium are correlated at the level of $r = 0.95$ in bulk sediment (Tab. 3) and $r = 0.92$ on a SiO_{2ter}-free basis (Tab. 4). As K is usually associated with clay minerals (Berner 1971; Kretz 1972; Lopez-Buendia *et al.* 1999), the relationship may indicate that Na is mainly adsorbed or bound in the structure of the latter.

The ratio of Na/K in sediments is highly dependent on salinity. In freshwater environments values of Na/K are generally <1, while in conditions of elevated salinity concentration of sodium is greater than potassium, and usually Na/K >>1 (Vu Ngoc Ky *et al.* 1981; Lopez-Buendia *et al.* 1999; Barjaktarovic, Bendell-Young 2002). In the deposits of Lake

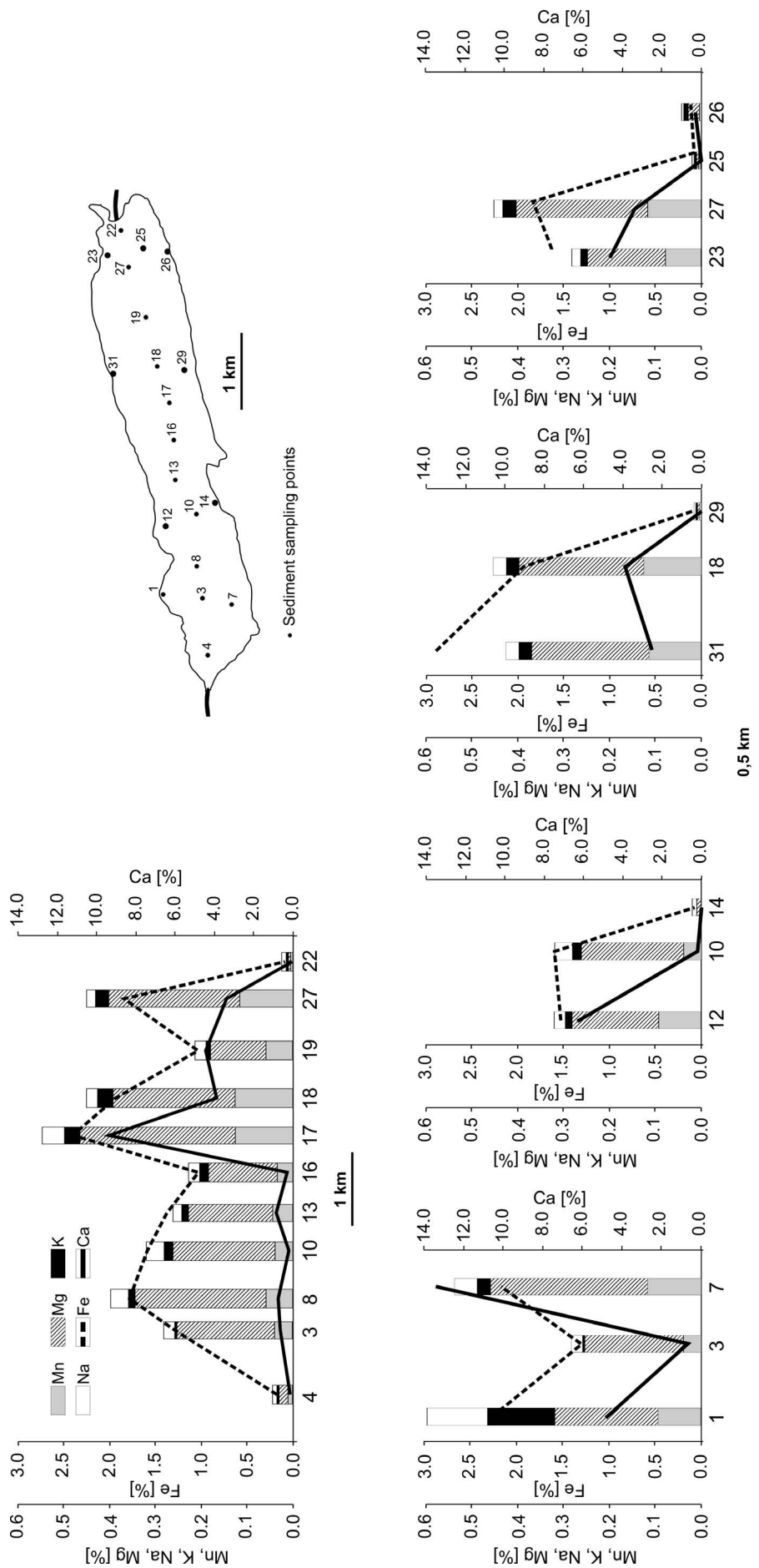


Fig. 8. Spatial distribution of Fe, Mn, Na, K, Ca and Mg in surface sediments of Lake Sarbsko.

Table 4

Correlation coefficients between chemical components of Lake Sarbsko surface sediments on terrigenous silica free basis (values statistically significant at $p < 0.01$ are marked in bold)

SiO _{2bio}	Org. mat.	CaCO ₃	Fe	Mn	Ca	Mg	Na	K	
1	-0.31	-0.81	-0.30	-0.43	-0.40	-0.16	-0.21	-0.17	SiO _{2bio}
	1	-0.04	0.42	0.37	-0.19	0.36	0.27	0.19	Org. mat.
		1	0.08	0.26	0.71	-0.07	0.06	0.06	CaCO ₃
			1	0.82	-0.24	0.95	0.91	0.91	Fe
				1	0.08	0.80	0.65	0.70	Mn
					1	-0.23	-0.28	-0.24	Ca
						1	0.87	0.88	Mg
							1	0.92	Na
								1	K

Sarbsko the Na/K ratio varies from 0.6 to 3.4, which is indicative for a low level of salinity in a depositional environment. In the western part of the lake Na/K values (from 1.5 to 3.5) were higher than in the east-central section of the basin (< 1.5). This is in agreement with the eastward decline in salinity of the bottom and surface waters of Lake Sarbsko (Tab. 1).

The total contents of Fe, Mn, Ca, Mg, Na and K in the sediments of Lake Sarbsko are strongly negatively correlated with the proportion of SiO_{2ter} (Tab. 3) which is understandable because detritic quartz has very low sorption capacity and its accumulation in deposits can contribute to the dilution of authigenic components. On the other hand, the concentrations of the analysed elements in Lake Sarbsko deposits increase with the proportion of organic matter. Especially strong correlations with the organic matter content are shown by Fe, Mn and Mg (Tab. 3). The highest concentrations of those metals are observed in the northern and central parts of the lake, where organic-rich sediments occur, and the lowest, in the lake margins dominated by sands. This relationship indicates that Fe, Mn and Mg are accumulated in conditions of restricted water dynamics, which also facilitates sedimentation of organic matter. As a rule, increased concentrations of organic compounds and associated metals are found in the

deepest sections of lakes or in parts sheltered from wind and wave action (Engstrom, Wright 1984). In such circumstances iron may occur in complexes with organic matter and in a form of sulphides, however, Fe-oxides may be also present (Engstrom, Wright 1984). In Lake Sarbsko deposits, large part of Fe is bound in oxidizable fraction (associations with organic matter and sulphides) (41% in olive gyttja and 58% in black gyttja, Fig. 7). On the other hand, contribution of oxide-Fe is 38% and 25% in olive and black gyttja, respectively (Fig. 7).

It should also be noted that because the quantity of organic matter was determined using the loss-on-ignition method, it might be a bit overestimated, since some clay minerals undergo dehydration and dehydroxylation when samples are heated at 550°C (Boyle 2001). Consequently, the LOI figure is not only an indicator of the organic matter level, but to some extent, also of clay minerals (Boyle 2001).

In the sediments of Lake Sarbsko the content of residual iron (bound in the crystal lattices of clay minerals) is relatively small (14.5% in black gyttja and 12.4% in olive gyttja), however, high correlation coefficients between Fe and K, Na and Mg in SiO_{2ter}-free sediments (Tab. 4) indicate that clay minerals concentration might partially control the distribution of Fe throughout Lake Sarbsko.

Diversified speciation of iron might explain a weak correlation coefficient between Fe and organic matter contents calculated for SiO_{2ter}-free sediment (Tab. 4).

In the case of manganese, the relation between this element and organic matter in bulk sediment ($r = 0.89$, Tab. 3) is in fact an indirect correlation as the r value between Mn and organic matter on SiO_{2ter}-free basis is much lower and statistically insignificant (Tab. 4). In the Lake Sarbsko deposits the amount of this element bound to organic matter is much smaller than that of iron and equals 6% in both, black and olive gyttjas. Still, Mn occurs in the analysed samples largely in the form of carbonates (Fig. 7), which develop below the bottom water-sediment boundary in the conditions of restricted oxygenation, and is held by surfactants (*e.g.* clay minerals), which is supported by 46.7% contribution of extractable Mn in olive gyttja (Fig. 7) as well as strong positive correlations between Mn and K, Na and Mg contents calculated on a SiO_{2ter}-free basis (Tab. 4). Both, Mn-enriched carbonates and clay minerals are accumulated in low energy environ-

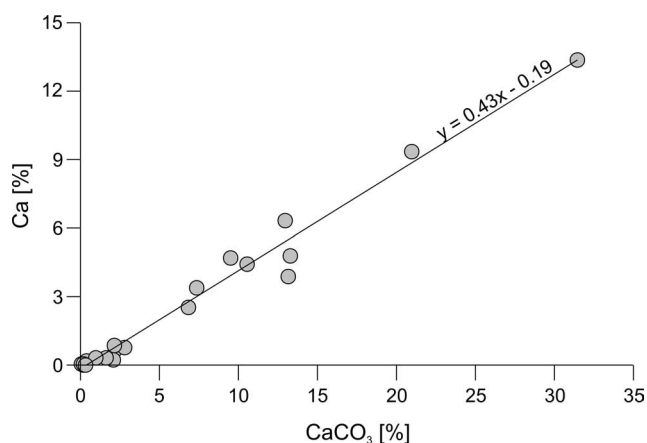


Fig. 9. Relation between the contents of Ca and CaCO₃ in the sediments of Lake Sarbsko (note nearly stoichiometric relation of the species)

ments favourable to the preservation of organic matter as well. On the other hand, a close relationship between Mn and Fe (Tab. 3 and Tab. 4) argues for coprecipitation of these elements in hydrated Fe/Mn oxides (Engstrom, Wright 1984). The content of oxide-Mn in the sediments of Lake Sarbsko is between 13.1% in olive gyttja and 31.5% in black gyttja (Fig. 7).

Notwithstanding very strong correlation between organic matter and Mg contents in total sediment (including $\text{SiO}_{2\text{ter}}$) of Lake Sarbsko ($r = 0.96$) the binding of Mg in mineral-organic compounds seems to be of lesser importance here because in this form only 12% of Mg occurs in black gyttja and 22.5% in olive gyttja (Fig. 7). Moreover, the correlation between Mg and organic matter contents after subtraction of terrigenous silica is as low as $r = 0.36$ (Tab. 4). Of greater significance is the occurrence of Mg in the residual fraction, *i.e.* in clay minerals (Berner 1971) which, like organic matter, accumulate in conditions of restricted environmental dynamics (de Groot *et al.* 1976; Sly 1978; Osadczuk 2004). Residual Mg makes up 43% of total Mg in black gyttja and 36% in olive gyttja (Fig. 7). The binding of Mg by clays in the deposits of Lake Sarbsko is also indicated by positive correlation of Mg and K in $\text{SiO}_{2\text{ter}}$ -free sediments (Tab. 4).

Strong positive correlation of Fe, Mg and organic matter may further explain a positive relationship between these elements and biogenic silica in bulk sediment (Tab. 3). As $\text{SiO}_{2\text{biog}}$ and organic matter in the deposits of Lake Sarbsko display very similar spatial distribution, co-occurrence of Fe, Mg and $\text{SiO}_{2\text{biog}}$ may arise from their tendency to accumulate in conditions of low environmental dynamics.

Biochemical fixation of oxide-Fe and Mg as a protective film on diatoms' frustules (Berner 1980, Peinerud 2000) seems to be of secondary importance as indicated by missing correlation between $\text{SiO}_{2\text{biog}}$ and Fe and Mg in $\text{SiO}_{2\text{ter}}$ -free sediment (Tab. 4). Relationship between Fe and biogenic silica in sediments looks different in each lake and lagoonal basin. Jones & Bowser (1978) reported co-precipitation of iron and biogenic silica in lakes. Osadczuk (2004) obtained a slight tendency towards increasing concentration of Fe with increasing biogenic silica content in the sediments of Szczecin Lagoon, albeit with rather low correlation coefficient. On the other hand, Vaalgamaa & Korhola (2007) showed that there were no correlation between the contents of Fe and $\text{SiO}_{2\text{biog}}$ in the deposits of Pieni Pernajanlahti Bay estuary (Finland).

The levels of Ca, Mn, Fe, Na, K and Mg are also positively correlated with the proportion of carbonates (Tab. 3). However, it is only in the case of Ca that correlation coefficient remained high after subtraction of $\text{SiO}_{2\text{ter}}$ (Tab. 4). In the case of Ca, the carbonate is the most frequent and widespread form of this element in lacustrine deposits (Kelts, Hsü 1978).

CONCLUSIONS

The deposits of Lake Sarbsko are characterized by appreciable spatial lithological and geochemical variability. They are mainly composed of terrigenous silica (quartz) indicating enhanced input of mineral matter from the watershed and/or increased dynamics of the lake waters.

Strong negative correlation coefficients between $\text{SiO}_{2\text{ter}}$ and $\text{SiO}_{2\text{biog}}$, organic matter as well as element contents argue for diluting effect of the former towards authigenic components of sediments. This, in turn obscures interpretation of sediment composition with regard to chemical processes in lakes.

Nevertheless, environmental factors controlling sedimentation of chemical elements in Lake Sarbsko can be inferred from the analysis of correlations calculated for terrigenous silica free sediments.

It was shown that spatial distribution of Fe, Mn, Ca, Mg, Na and K within the sediments of Lake Sarbsko is governed by their geochemical affinities to organic matter, sulphides, clay minerals and carbonates. Fe is mainly bound to organic matter and sulphides. Mn is fixed by clays and Fe/Mn oxides as well as co-occurs with carbonates. Mg, K and Na are adsorbed by clay minerals and Ca precipitate with carbonates.

As surface and bottom waters in Lake Sarbsko are highly undersaturated with respect to calcite, carbonate precipitation in the lake can occur only below the sediment-water interface and results from microbial decomposition of sedimentary organic matter at the expense of sulfates as well as iron and manganese oxides.

Acknowledgments

The authors greatly appreciate thorough reviews by Prof. T. Madeyska, dr B. Łącka and Prof. T. Goslar. M.Sc. Michał Kubiak (Institute of Geology, AMU, Poznań) is acknowledged for conducting XRD analyses of Lake Sarbsko sediment samples and interpretation of the results.

This study was made possible due to financial support of the Polish Ministry of Science and Higher Education (grant no. NN306 3543 33).

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