Journal of Elementology ISSN 1644-2296

Potasznik A., Szymczyk S. 2015. *Magnesium and calcium concentrations in the surface water and bottom deposits of a river-lake system*. J. Elem., 20(3): 677-692. DOI: 10.5601/jelem.2015.20.1.788

MAGNESIUM AND CALCIUM CONCENTRATIONS IN THE SURFACE WATER AND BOTTOM DEPOSITS OF A RIVER-LAKE SYSTEM

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Abstract

River-lake systems comprise chains of lakes connected by rivers and streams that flow into and out of them. The contact zone between a lake and a river can act as a barrier, where inflowing matter is accumulated and transformed. Magnesium and calcium are natural components of surface water, and their concentrations can be shaped by various factors, mostly the geological structure of a catchment area, soil class and type, plant cover, weather conditions (precipitation-evaporation, seasonal variations), land relief, type and intensity of water supply (surface runoffs and groundwater inflows), etc.

The aim of this study was to analyze the influence of a river-lake system on magnesium and calcium concentrations in surface water (inflows, lake, outflow) and their accumulation in bottom deposits. The study was performed between March 2011 and May 2014 in a river-lake system comprising Lake Symsar with inflows, lying in the Olsztyn Lakeland region. The study revealed that calcium and magnesium were retained in the water column and the bottom deposits of the lake at 12.75 t Mg year^{-1} and 1.97 t Ca year^{-1}. On average, 12.7±1.2 g of calcium and 1.77±0.9 g of magnesium accumulated in 1 kg of bottom deposits in Lake Symsar. The river-lake system, which received pollutants from an agricultural catchment, influenced the Ca^{2+} and Mg^{2+} concentrations in the water and the bottom deposits of Lake Symsar. The Tolknicka Struga drainage canal, to which incompletely treated municipal wastewater was discharged, also affected Ca^{2+} and Mg^{2+} levels, thus indicating the significant influence of anthropogenic factors.

Keywords: magnesium, calcium, surface water, bottom deposits, river-lake system, anthropopressure.

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INTRODUCTION

The quality and quantity of chemical elements in surface water can be influenced by land relief, geochemical structure, land use, seasonal variations in weather conditions (precipitation-evaporation), plant cover and atmospheric deposition (GROCHOWSKA, TANDYRAK 2009). Magnesium (Mg^{2+}) and calcium (Ca^{2+}) are found naturally in surface water. Also, their presence in water is often closely correlated with the type of land use in the catchment areas (WONS et al. 2012). In addition to being a component of chlorophyll, magnesium participates in enzymatic reactions. Calcium plays various structural roles in plant cell membranes, contributes to oxalate accumulation and regulates water transport as well as metabolic processes. Calcium also induces the coagulation of soil colloids and is responsible for the crumb-like structure of soil (ORZEPOWSKI, PULIKOWSKI 2008, PULIKOWSKI et al. 2006). River-lake systems (RLS) comprise chains of lakes connected by streams that flow in and out of them. River-lake ecotones can act as barriers, where inflowing matter, which is retained in the water column or accumulated in bottom sediments, undergoes numerous physicochemical and biological changes (HILLBRICHT-ILKOWSKA 2005).

The matter originating from the catchment enters a river-lake system (RLS). Therefore, the catchment management may significantly influence the eutrophication of surface waters. A significant share of developed, built-up areas is yet another factor that affects aquatic ecosystems, accelerating the eutrophication process and influencing their functioning. In the following article, the authors will make an attempt to assess the impact of the catchment, including man-made pressure, on water quality in an RLS and its functioning in an area formed during the late-glacial period.

MATERIAL AND METHODS

The study was conducted on a river-lake system located in an area formed during the late-glacial period. The system is composed of Lake Symsar and the Symsarna River, which flows into and out of the lake. The river (57 km in length) flows from Lake Luterskie, into Lake Ławki and Lake Blanki before entering Lake Symsar, which is the last water body through which the river passes before reaching the Łyna River, which then itself flows into the Pregolya River, finally carrying water into the Baltic Sea. The Symsarna River's catchment covers a total area of 276.6 km^2, most of which (229.1 km^2) is situated above Lake Symsar. The catchment is used mainly for agricultural purposes. The river flows through wetlands before feeding water into the lake. The direct catchment of Lake Symsar comprises forest and agricultural land covering 2.2 km2. The lake has a surface area of 135.5 ha and its maximum depth is 9.6 m. In addition to the Symsarna River, three smaller streams, i.e. the Tolknicka Struga and two unnamed streams (I and II), flow into the lake. The Tolknicka Struga, a 9.3-kilometer-long drainage ditch, receives mechanically treated wastewater, which mixes with its water. Stream I (S_I) is 2.5 km in length, and its catchment area is dominated by forest and agricultural land. Its sources are located in wetlands of agricultural areas, whereof the stream flows through a forest and enters the lake in the vicinity of some holiday cottages. Stream II (S_{II}) is almost 1 km in length, and its catchment is dominated by agricultural and afforested land; later on, the stream flows through agricultural areas and a forest.

This study, which investigated the effect of a river-lake system on changes in magnesium and calcium concentrations in surface water and bottom deposits, was carried out between March 2011 and May 2014. Changes in Mg^{2+} and Ca^{2+} concentrations in surface water, their accumulation and distribution in the surface layer of bottom deposits in Lake Symsar, the Symsarna River and the smaller streams supplying the lake were analyzed.

Samples of surface water were collected for chemical analysis from the lake's inflows, the lake itself and the lake's outflow once a month in two research periods: from March 2011 to April 2012, and from November 2012 to May 2014 (Figure 1). Samples were collected from seven sites situated at the lake's inflows, the lake itself and the lake outflow:

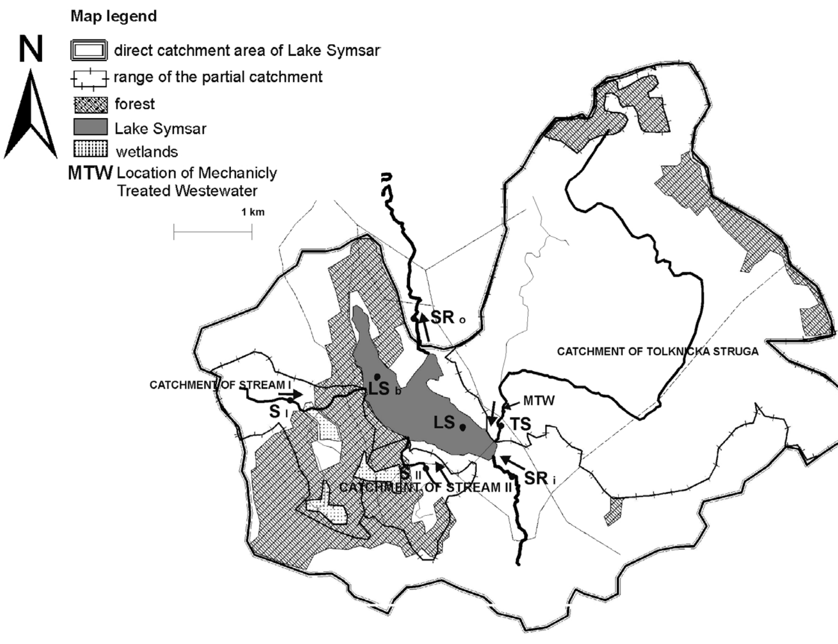

Fig. 1. The direct catchment of Lake Symsar and the location of water sampling sites: SR_i – Symsarna River flowing into the lake (part of the catchment between Lake Blanki and an outflow from Lake Symsar).; TS –Tolknicka Struga drainage ditch; S_I – Stream I (forest-agricultural catchment; S_{II} – stream II (agricultural-forest catchment); SR_o – Symsarna River exiting the lake (part of the cachment between Lake Symsar and the inflow of Kierwińskia Struga)

- the Symsarna River flowing into Lake Symsar – SR $_i$;
- the Tolknicka Struga drainage canal – TS;
- stream I with a catchment area covered by forests and agricultural land – S $_I$;
- stream II with a catchment covered by agricultural land and forests (from January 2013) – S $_{II}$;
- Lake Symsar, the main basin – LS;
- Lake Symsar's bay (from November 2012) – LS $_b$;
- the Symsarna River flowing out of Lake Symsar – SR $_o$.

Water was sampled into 5 L polyethylene containers. The samples were analyzed in the laboratory of the Department of Land Reclamation and Environmental Management of the University of Warmia and Mazury in Olsztyn, in line with standard methods.

Magnesium concentrations were determined colorimetrically with the use of titanium yellow, and calcium levels were measured by Atomic Absorption Spectrometry (AAS). Mg and Ca loads in inflows and outflows from the lake were determined by measuring the flow rate with a Valeport current meter. Flow intensity was calculated based on the area of the stream's cross-section.

The flow rates during the plant growing and non-growing season were calculated as an average momentary water flow (monthly, m^3) in winter and summer. The flow unit was calculated as a quotient of the average flow rate in and outside the growing season (in dm^3 s^{-1}) to the area of the partial catchment (km^2). Seasonal loads were calculated in the same manner as the flow rate, i.e. as the ratio of elemental concentrations and the average flow rate during the season (average momentary flows - once a month).

The distribution of Mg and Ca in the bottom deposits of Lake Symsar was analyzed by collecting samples from the surface layer (an average thickness of 10 cm) of bottom deposits in six transects, at two to three sampling sites each (the number of sampling sites varied subject to the width and shape of the lake bed). Deposits were also sampled from the bottom of the Symsarna River (inflow and outflow sections) and the Tolknicka Struga drainage canal (Figure 2). Samples were collected with an Ekman grab over a sampling area of 225 cm^2. Air-dried deposits were ground and analyzed to determine their Mg and Ca content. The samples were mineralized in a mixture of HNO_3 and $HClO_4$. The content of MgO and CaO was determined by titration with $C_{10}H_{14}N_2O_8Na_2$ (disodium versenate 0.01 M) in the presence of erichromium black and murexide. The content of Mg and Ca was expressed in terms of mg kg^{-1} DM by multiplication by 0.603 (Mg) and 0.715 (Ca).

Due to differences in the direction and intensity of the processes observed in the aquatic environment, the results for the growing season (April-September) and for the remaining months of the year (October-March) are discussed separately.

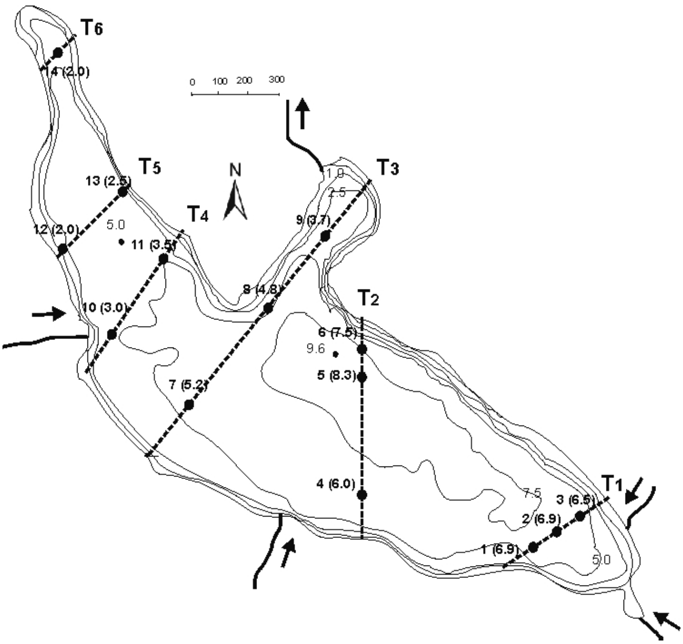

Fig. 2. A bathymetric map of Lake Symsar with the location of transects (Tx) and sediment sampling sites: 1 (1.1) – depth of bottom sediments (m)

The laboratory data were processed with a Statistica pl v. 10 application (StatSoft 2010). The data were submitted to student's *T*-test to check normal distribution, and to the Shapiro-Wilk test as well as one-way analysis of variance (Levene) with a post hoc test (the Schefeě and Tukey's test) to check differences between average Mg and Ca concentrations in surface water of the Lake Symsar's catchment relative to the season and to the land-use type in partial catchments.

RESULTS AND DISCUSSION

Seasonal changes in the water flow rate and biological activity contribute to differences in the chemical composition of surface water (Augustyn et al. 2012). In the inflows supplying Lake Symsar, flow intensity differed considerably between the analyzed periods. In the growing season, the average flow intensity ranged from 0.019 m^3 s^{-1} in stream S_{I}, whose catchment was covered mostly by a forest, to 1.172 m^3 s^{-1} in the Symsarna River (Table 1). The lowest flow intensity was reported in streams S_{I} and S_{II}, which could be attributed to the small area of their catchments (270 ha and 140 ha, respectively) and a high water uptake by trees in forest catchments; the latter additionally led to a seasonal loss of water from the stream beds. Outside of the growing season, the average water flow ranged from 0.017 $m^3 s^{-1}$ (stream II with its catchment covered by agricultural land and forests) to 0.674 $m^3 s^{-1}$ in the Symsarna River.

Table 1

Seasonal variation of flow and drainage unit from the catchment of Lake Symsar

Sites	Catch-ment area (km^2)	Q ($m^3 s^{-1}$)		q ($dm^3 s^{-1} km^{-2}$)		Average ± SEM	
		G	N	G	N	Q ($m^3 s^{-1}$)	q ($dm^3 s^{-1} km^{-2}$)
SR_i	33.4	1.172	0.674	35.09	20.18	0.923±0.51	27.60±10.54
TS	19.2	0.090	0.074	4.70	3.85	0.082±0.13	4.89±0.60
S_I*	2.7	0.019	0.037	7.01	13.67	0.028±0.035	10.10±4.71
S_{II}*	1.4	0.063	0.017	44.65	12.34	0.040±0.06	35.42±4.08
SR_o	22.9	1.309	0.884	57.16	38.59	1.096±0.57	48.22±13.13

G – growing season; N – no-growing season; Q – flow of water; q – drainage unit; * – selected streams are characterized by a significant difference between the means flow in the growing and nongrowing season (Tukey test, p <0.05)

The average total inflows into the lake during the growing season reached 1.344 $m^3 s^{-1}$ and were 2.67% higher than the outflows. Outside of the growing season, the average total inflows were 9.2% lower than outflows and were 40.3% lower than during the growing season. The annual volume of water carried to the lake by the Symsarna River accounted for approximately 86.0% of total surface inflows. Past the outflow from the lake, the flow intensity in the Symsarna River increased by 11.67% during the growing season and by 39.09% outside the growing season, which could be attributed to the fact that both the lake and the river were also supplied by surface runoffs from its catchment characterised by varied land relief, as well as by rainwater and water that had evaporated in periods of high ambient temperature, lowered water levels and decreased outflows.

The specific runoff rate per 1 km^2 of catchment area in the section of the river between Lake Blanki and Lake Symsar was determined at 35.09 $dm^3 s^{-1} km^{-2}$ in the growing season and 20.18 $dm^3 s^{-1} km^{-2}$ outside the growing season. Diffuse runoffs are also responsible for the inflow of biogenic substances, which - particularly in the growing season - may be accumulated in wetlands, acting as a biogeochemical barrier to water flow (SZYMCZYK, GLIŃSKA-LEWCZUK 2007).

Out of all the sources supplying Lake Symsar, the lowest specific runoff rate of 4.89±0.60 $dm^3 s^{-1} km^{-2}$ on average was reported in the catchment of the Tolknicka Struga drainage canal. Despite the data above, the ditch could still be a significant source of pollution because its direct catchment is occupied by agricultural land, farm buildings and a housing estate, all served by a mechanical wastewater processing plant with insufficient capacity.

Magnesium and calcium, which occur naturally in water bodies, are among the most highly available alkali metals in the environment (Grochowska, Tandyrak 2009). Magnesium salts are found naturally and in high concentrations in surface and ground water, and the only other elements that occur in greater abundance are sodium and calcium cations. Magnesium and calcium concentrations in ground and surface waters increase as those elements are washed out from bedrock (Gałczyńska et al. 2013). Calcium compounds occur naturally in surface water, and their concentrations are determined mainly by the carbonate balance (Gałczyńska et al. 2013). Grochowska and Tandyrak (2009), determined the calcium content of lake water in the range of 14.9-67.8 mg Ca dm^{-3}.

In this study, the magnesium content of surface water ranged from 6.9±2.25 mg dm^{-3} in stream S_I to 12.0±4.1 mg dm^{-3} in the Tolknicka Struga, while the calcium content varied from 55.4±11.5 mg dm^{-3} in the Symsarna River above the lake to 74.0±20.8 mg dm^{-3} in the Tolknicka Struga, which receives wastewater from a local wastewater treatment plant, a plant with insufficient processing capacity (Table 2). In the latter case, the magnesium and calcium levels in surface water could be significantly influenced by organic compounds supplied with the wastewater (Kolanek, Kowalski 2002). Relatively low Mg and Ca concentrations in runoffs from the catchment covered by forests and agricultural land (S_I) could be attributed to their accumulation by trees.

This observation was confirmed by low levels of Mg in spring and summer, when plants have the highest water requirements. Mg and Ca concentrations were lower in the outflow than in the inflow to the lake (Figure 3).

Large quantities of magnesium are released to groundwater from sedimentary rocks, mainly dolomite – $CaMg(CO_3)_2$ (Wons et al. 2012). The influence of anthropogenic factors on the outflow of magnesium and calcium

Table 2

Variations in Ca and Mg concentrations and the Ca:Mg ratio in surface water in and outside growing seasons

Location	Growing season			Outside growing season			Mean±SEM		
	Ca (mg dm^{-3})	Mg (mg dm^{-3})	Ca:Mg	Ca (mg dm^{-3})	Mg (mg dm^{-3})	Ca:Mg	Ca (mg dm^{-3})	Mg (mg dm^{-3})	Ca:Mg
SR_i	35.14*	11.25	3.12:1	50.05*	10.99	4.55:1	55.4±11.5	11.0±1.8	5.0:1
TS	50.84	12.96	3.92:1	66.24	11.09	5.97:1	74.0±20.8	12.0±4.1	6.2:1
S_I	43.88*	6.45	6.80:1	53.55*	7.00	7.65:1	61.8±17.7	6.9±2.3	8.9:1
S_{II}	58.23	8.67	6.72:1	62.77	8.03	7.81:1	60.5±8.8	8.3±2.7	7.3:1
LS	69.47	9.68	7.17:1	48.46	9.51	5.09:1	68.5±69.6	9.7±2.7	7.1:1
LB	35.65*	10.63	3.36:1	52.71	10.64	4.96:1	49.9±12.3	10.4±2.4	4.8:1
SR_o	33.85	10.51	3.22:1	52.05	11.06	4.71:1	56.8±12.9	10.8±1.8	5.3:1

* – selected average concentrations differed significantly between the remaining watercourses (Tukey's test, $p < 0.05$)

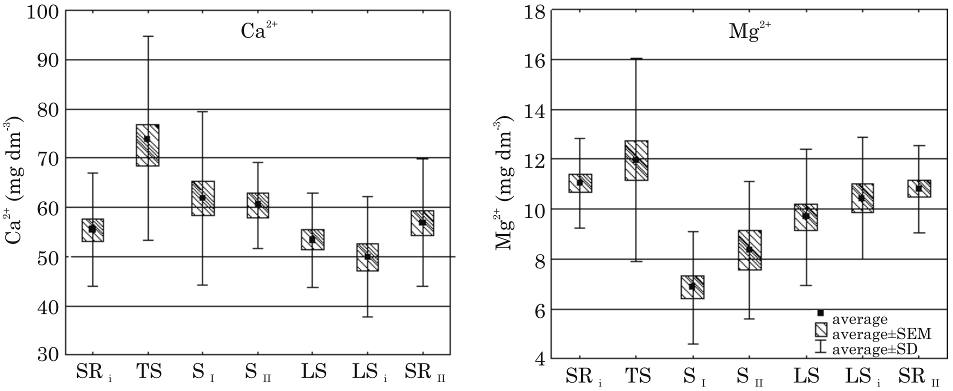

Fig. 3. Variations in Ca and Mg concentrations in the catchment area of Lake Symsar

clearly manifested itself in two catchment areas drained by small streams (S_I and S_{II}). Magnesium and calcium concentrations were somewhat higher in the catchment featuring mostly drained farmland, and exposed to increased human activity (S_{II}), than in the catchment occupied mostly by forest. The above observations indicate that the concentrations and loss of Mg and Ca in water drained by canals from agricultural land are determined mainly by weather conditions (significant seasonal variations), the type of drainage system, soil compactness and mineral fertilization rates. In comparison with drainage ditches, drain pipes contribute to a much greater loss of magnesium and calcium from the soil and an increase in Mg and Cu concentrations in the outflows (Gałczyńska et al. 2013, Koc, Szymczyk 2003, Treder, Kowalczyk 2010).

Magnesium and calcium concentrations in surface water differed considerably between the analyzed periods. During the growing season, magnesium levels were higher (except for stream S_I which drains the catchment covered by forests and agricultural land), while calcium concentrations were significantly lower (excluding the main lake basin – LS). Magnesium levels were significantly lower in the outflow from the lake (SR_o) than in the inflows (excluding streams S_I and S_{II}) during the growing season, which was also characterized by the lowest calcium concentrations (33.85 mg dm^{-3} on average) in the lake outflow. The decrease in Mg and Ca levels in the outflow could have resulted from their bioaccumulation and deposition at the bottom of the lake. A decrease in magnesium levels and a significant increase in calcium concentrations were observed in most bodies of water outside the growing season. The above could have been caused by the reduced absorption by plants as well as the release of calcium from partially uncovered bottom deposits, especially in streams where calcium levels increased with a rise in the water supply and flow rate (desorption from sediments).

The lowest volume of water with relatively high calcium concentrations was reported in the Tolknicka Struga drainage canal, which was additionally polluted by the incompletely treated municipal effluents from a local housing estate. Wastewater contributed to the highest (>30%) increase in calcium levels in water outside the growing season.

Similarly to stream S_I, the lowest magnesium concentrations in the Symsarna River were observed during the growing season (11.25 mg dm^{-3} above the lake and 10.51 mg dm^{-3} below the lake). The highest magnesium levels were noted in summer (14.84 mg dm^{-3}) in the Tolknicka Struga supplied with mechanically treated wastewater. Magnesium is a component of chlorophyll, was found in higher concentrations (by 6.7% on average) in the bay of Lake Symsar, characterized by more intensive plant growth (Table 2) than in segments intersected by flowing streams. According to SZYPEREK (2005), the solubility of magnesium in the surface water of ponds is determined by the degree of contamination with biogenic compounds.

The reduction in calcium and magnesium concentrations in the Symsarna River flowing through Lake Symsar could be due to their retention by macrophytes and their accumulation in bottom deposits of the lake. The above processes lowers the purity of lake water, but improves water quality in the river and minimizes the transport of ca and mg outside the catchment area.

The calcium to magnesium ratio in the analyzed water bodies ranged from 4.8:1 (the lake's bay) to 8.9:1 (S_I). An increase in the mineral content of water leads to a greater abundance of magnesium ions than calcium ions and a low Ca:Mg ratio. In water with low levels of mineralization, the Ca:Mg ratio can range from 4:1 to 2:1. The Symsarna River (lake inflow and lake outflow) and the bay of the lake were characterized by low mineral concentrations in the growing season (Table 2).

The Ca:Mg ratio was broader in the surface waters of the remaining water bodies, which could be due to anthropogenic pressure, particularly in the catchment areas of small streams. In lakes situated in catchment areas that have not been transformed by human activity, the ca:mg ratio ranged from 2:1 to 4:1. In a study by GROCHOWSKA and TANDYRAK (2009), the Ca:Mg ratio in Lake Pasłęk was determined in the range of 4:1 to 13:1 due to the presence of forests in the catchment. In Lake Symsar, the Ca:Mg ratio ranged from 5.1:1 outside the growing season to 7.2:1 in the growing season.

Based on the obtained data, it can be concluded that the average concentration of calcium in the waters of the symsarna river and the tolknicka struga varied significantly in response to anthropogenic factors. The vicinity of built-up areas and the type of agricultural land use could have added to the contamination of surface water from the analyzed system. The average magnesium concentrations were lowest in the waters of the two temporary streams, and they were significantly lower than in the other examined surface waters (Table 3).

Magnesium retention in the water and bottom deposits of Lake Symsar was estimated at 4.33 t season^{-1} during the growing season, being twice as high (at 8.52 t season^{-1}) outside the growing season. A total of 12.75 t Mg year^{-1} was retained in the water and bottom deposits of Lake Symsar throughout the

Table 3

Results of one-way Anova and post-hoc test (Schefĕ) investigating differences in calcium and magnesium concentrations resulting from land-use types in the partial catchment

Sites	Average (mg dm^{-3})	SR- i	TS	S I	S II
Ca^{2+}					
SR_i	55.5				
TS	74.0	*			
S_I	61.8	0.7026	0.1053		
S_{II}	60.5	0.9286	0.1978	0.9996	
SR_o	56.8	0.9987	*	0.8542	0.9772
Mg^{2+}					
SR_i	11.0				
TS	11.9	0.8101			
S_I	6.9	*	*		
S_{II}	8.4	0.0827	*	0.6351	
SR_o	10.8	0.9987	0.6536	*	0.1439

study. The Symsarna River carried approximately 324.31 t Mg $year^{-1}$ of magnesium into the lake and evacuated 349.65 t Mg $year^{-1}$ of magnesium outside the catchment. In the growing season, approximately 63.25 t Ca $season^{-1}$ was evacuated from the lake, and a similar amount was retained in the lake water and the bottom deposits in the remaining months of the year. Approximately 1.97 t Ca $year^{-1}$ was retained in the water and bottom deposits of Lake Symsar throughout the year, and the largest part of the load (1.62 t Ca $year^{-1}$) was supplied by the Symsarna River. Relatively high Mg and Ca loads in the lake were associated with the type of land use in the catchment area, which contained mostly drained farmland (Koc, Szymczyk 2003).

In the bottom deposits of the lake, magnesium concentrations ranged from 0.96 g kg^{-1} DM (near the deepest part of the lake intersected by the Symsarna River) to 3.59 g kg^{-1} DM (near the inflow of the Symsarna River). Magnesium levels in the river bed sediments were determined at 0.76 g kg^{-1} DM (Figure 4).

A positive magnesium balance was observed in the lake throughout the year, which implies that the analyzed element could have been retained in bottom deposits, mostly in the part of the lake intersected by the Symsarna River (which explains lower magnesium levels in the river bed below the lake), whereas higher magnesium concentrations were reported near the inflow to the lake. Lake Symsar retained magnesium in bottom deposits and prevented its spread outside the catchment. The magnesium concentrations in the bottom deposits of the lake bay were determined at 1.72 g kg^{-1} DM on average. Lower magnesium levels in the bay, which is unaffected by the

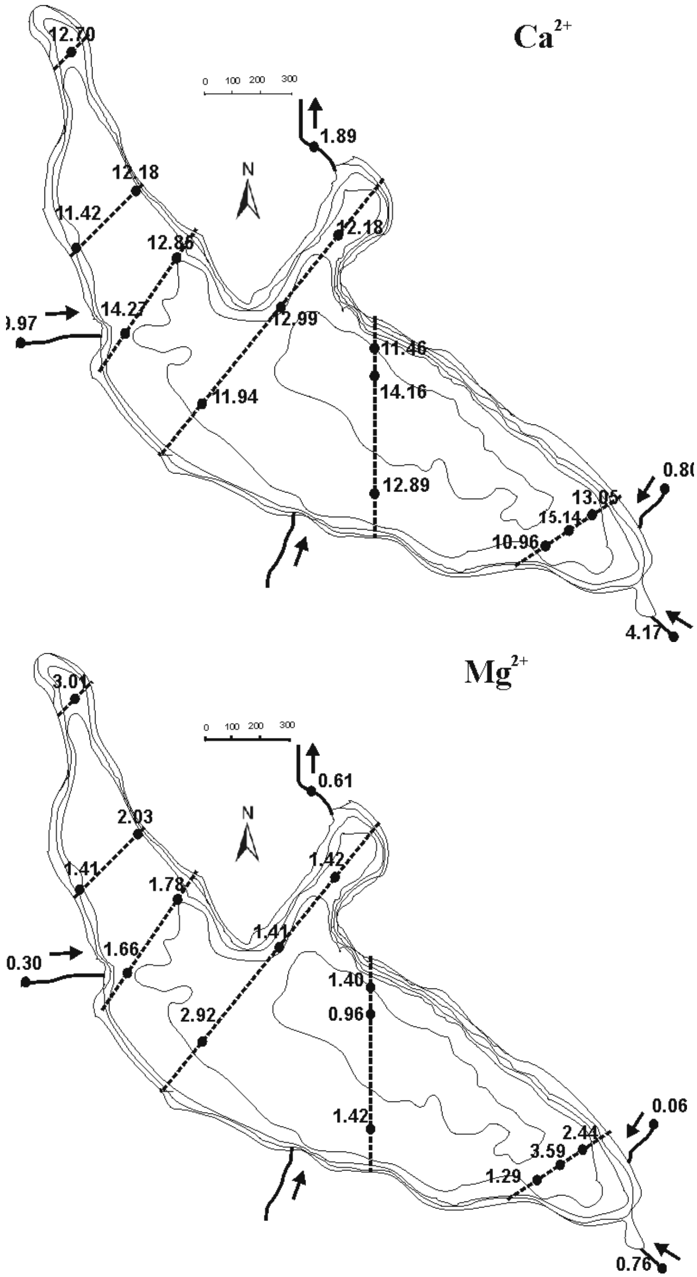

Fig. 4. Spatial distribution of calcium and magnesium in the bottom sediments of Lake Symsar

Symsarna River, and higher magnesium concentrations in the bottom deposits of the main lake basin indicate that the river is chiefly responsible for the supply and accumulation of this essential mineral in the lake. In a study by Obolewski et al. (2011), sodium, magnesium and potassium were significantly better absorbed from surface water by reed, whose growth in the shallow part of the lagoon is affected by other conditions than in the main part of the water body. In bed sediments of the river above the lake, the magnesium accumulation reached 0.76 g kg^{-1} DM, and the magnesium levels were 20% lower than below the lake. The above resulted from the retention of magnesium in the bottom deposits of Lake Symsar near the river's outflow, which was estimated at 1.42 g kg^{-1} DM. In the analyzed period, Lake Symsar accumulated magnesium in bottom deposits, thus preventing its distribution outside the catchment. Magnesium can reach the lake by routes other than surface runoffs, which implies that the overall balance could be completely different. The average magnesium concentrations in the bottom deposits of the lake bay were estimated at 1.72 g kg^{-1} DM. Lower magnesium levels in bottom deposits of this lake's zone and higher Mg concentrations in the main basin of the lake imply that the discussed element in the lake originates from waters of the Symsarna River as well as from atmospheric precipitations, groundwater and surface runoffs.

The calcium concentrations in the bottom deposits of Lake Symsar ranged from 10.96 g kg^{-1} DM at the point where stream S_{II}, with a predominantly agricultural catchment, feeds into the lake on its left shore bordering forests, to 15.14 g kg^{-1} DM in bottom deposits near the inflow of the Symsarna River (Figure 4). Obolewski, Glińska-Lewczuk (2013) pointed to the influence of accumulation (resulting from a lower flow rate) and erosion on concentrations of mineral elements in bottom deposits. Attention was also paid to the different set of habitat conditions that favoured biodiversity and the role of surface waters, flowing and standing, which function as a filter, e.g. different conditions in the water of a meandering river and an oxbow lake, which has been separated from a river (Glińska-Lewczuk, Burandt 2011). It is precisely that contact zone of flowing and standing surface waters, i.e. the riverbed and oxbow lakes (Obolewski et al. 2009) that is a critical factor affecting the diversity and abundance of molluscs in thewater body and that may also reflect the diversity of other properties (physical properties and chemical composition) of the tested ecotone zone. Mineral levels can be significantly affected by the carbonate balance. Depending on the physicochemical parameters of the local environment, calcium can be precipitated or transferred from bottom deposits to water (Gałczyńska et al. 2014). Mineral elements released from bottom deposits can pollute surface water (Szymczyk, Glińska-Lewczuk 2007). Bed sediments in the Symsarna River were rich in calcium (4.17 g kg^{-1} DM), and the highest Ca concentrations were noted in bottom deposits of stream S_{I}, whose catchment is covered mostly by forests (9.97 g kg^{-1} DM). Calcium levels were 55% lower in the river bed below the lake, which indicates that calcium, similarly to magnesium, was retained in the lake's bottom deposits.

The Ca:Mg ratio of bottom deposits in Lake Symsar ranged from 4.2:1 near the inflow of the Symsarna River (where Mg and Ca concentrations were high) to 14.75:1 near forests (along the western shore of the lake where Ca levels were low at 0.96 g kg^{-1} DM). The Ca:Mg ratio was determined in the range of 3.1:1 in the Symsarna River (outflow) to 32.8:1 in stream S I (inflow).

DISCUSSION

The influence of natural and antropogenic factors is manifested by the presence of cations such as calcium and magnesium. The effect of the geological structure stands out among the natural factors. Based on the research carried out by Katz, Nishri (2013) on the circulation of ions like Ca^{2+} and Mg^{2+} in Lake Kinneret, Israel (a stratified lake with high water hardness), it was found that the main source of these components was calcite, which was dominant in the catchment. Calcite crystalized in the epilimnion, then the cation Ca^{2+} and Mg^{2+}, precipitated together with Ca^{2+}, moved in the water column as a result of the mixing process. In consequence, cations were partly dissoved in the hypolimnion. As a result of the exchange of water between the epilimnion and hypolimnion (mixing) the cations were moved in the whole volume of lake water. In addition, Correll (1998) emphasized that prevailing anaerobic conditions can induce the release of components that were originally associated with the bottom sediments. In turn, Bhat et al. (2014) mentioned anthropogenic pressure, like land use and inflows of wastewater, as factors which could cause high concentrations of cations in water.

Based on the assessments made in this study, it was demonstrated that the average calcium concentrations in the analyzed surface water samples were 50.92 mg Ca dm^{-3} and the average magnesium concentrations equalled 9.89 mg Mg dm^{-3}. The highest Ca^{2+} and Mg^{2+} levels were reported in the Tolknicka Struga drainage canal supplied with incompletely treated wastewater (55.45 mg Ca dm^{-3}, 11.04 mg Mg dm^{-3}) and in the Symsarna River fed by outflows from an agricultural catchment (74.0 mg Ca dm^{-3}, 11.96 mg Mg dm^{-3}). Low concentrations were observed in the waters of streams, whose catchment areas are partly overgrown by forest, i.e. stream I: 61.82 mg Ca dm^{-3}, 6.86 mg Mg dm^{-3} and stream II: 60.5 mg Ca dm^{-3}, 8.35 mg Mg dm^{-3}, which according to Jeziorski et al. (2014) was due to the inlfux of humic acids from forest areas, as well as result of the hauling wood was performed in these areas. The cation concentrations in Lake Symsar were about 68.45 mg Ca dm^{-3}, 9.68 mg Mg dm^{-3} in the main basins, and 49.9 mg Ca dm^{-3}, 10.44 mg Mg dm^{-3} in bay's water. In research on water quality in the Great Lakes in the US, the averaged concentrations were as follows: 13.62 mg Ca dm^{-3} and 2.83 mg Mg dm^{-3} (Lake Superior), 35.95 mg Ca dm-3 and 11.28 mg Mg dm^{-3} (Lake Michigan), 26.4 mg Ca dm^{-3} and 7.46 mg Mg dm^{-3} (Lake Huron), 32.1 mg Ca dm^{-3} and 8.89 mg Mg dm^{-3} (Lake East Erie) and 33.55 mg Ca dm^{-3} and 8.61 mg Mg dm^{-3} (Lake Ontario). Chapra et. al. (2012)

observed a reduction of the concentration of calcium in the Great Lakes, which the authors contributed to the introduction in 1970 of *Dreissena* mussels to the aquatic ecosystem, the weathering of rocks in the basin and the presence of dolomite along the southern shore of Lake Eire, causing high magnesium concentrations in Lake Michigan and Lake Eire. Apart from the geological structure and acidity, the literature emphasizes the impact of climate change on the formation of cation concentrations in surface waters, but these changes are often elusive (Bhat et al. 2014).

The magnesium and calcium balance in the inflows to Lake Symsar indicates that both elements were retained in the water column and bottom deposits at 0.89 kg Ca and 5.80 kg Mg per 1 ha of the total catchment area, respectively. In the research carried out by Rafałowska and Sobczyńska-Wójcik (2012) concerning Lake Dobskie (a moraine water body, covering 52.98 ha, with the depth of about 3.66 m and the total catchment area is 17 km^2, composed mostly of farmland), total loads accumulated reached 704.0 kg Ca and 5.6 kg Mg per 1 ha of the catchment. Lake Symsar, which receives about 14.78 t Mg and 2.79 t Ca per 1 ha of the lake's area. In turn, Lake Dobskie (whose only inflow is a drainage ditch) receives loads of components equal 89.0 kg Ca and 11.6 kg Mg per 1 ha of the lake (Rafałowska, Sobczyńska-Wójcik 2012). An average of 12.7±1.2 g of calcium and 1.77±0.90 g of magnesium were accumulated in 1 kg of bottom deposits in Lake Symsar in the analyzed period. The Ca:Mg ratio was determined at 7.75:1, on average. Calcium and magnesium accumulation patterns varied considerably in the analyzed water bodies. The highest Ca and Mg levels in the bottom deposits of the lake were noted near the inflow of the Symsarna River, suggesting a significant role of the river in the distribution of nutrients at the bottom. In a study by Sheikh et. al. (2014), the concentrations of the analyzed elements in the sediments had a tendency to decline in the direction opposite to the shoreline. This trend was attributed to the geochemical processes in the contact zone between the direct catchment and the lake's littoral zone.

CONCLUSIONS

1. The highest Ca and Mg levels were reported in the Tolknicka Struga drainage canal supplied by incompletely treated wastewater (55.45 mg Ca dm^{-3}, 11.04 mg Mg dm^{-3}) and in the Symsarna River fed by outflows from an agricultural catchment (74.0 mg Ca dm^{-3}, 11.96 mg Mg dm^{-3}), which indicated that additional material introduced to aquatic ecosystems due to human activity could threaten their life.

2. The magnesium and calcium balance in the inflows to Lake Symsar indicates that both elements were retained in the water column and bottom deposits at 12.75 t Mg year^{-1} and 1.97 t Ca year^{-1}.

3. Calcium and magnesium accumulation patterns varied considerably in the analyzed water bodies. The highest Ca and Mg levels in the bottom deposits of the lake were noted near the inflow of the Symsarna River, which indicates that the river is largely responsible for the quality of lake water and bottom deposits. Bottom deposits in the lake's bay and near the inflow of stream S_I contained relatively lower levels of Ca and Mg.

4. The river-lake system which received pollutants from an agricultural catchment influenced Ca and Mg concentrations in the water and bottom deposits of Lake Symsar. The Tolknicka Struga, the recipient of incompletely treated municipal wastewater, also affected Ca and Mg levels, which points to the significant influence of anthropogenic factors.

FINANCING

KAPITAŁ LUDZKI
NARODOWA STRATEGIA SPÓJNOŚCI

UNIA EUROPEJSKA
EUROPEJSKI
FUNDUSZ SPOŁECZNY

Supported by the European Union within the European Social Fund.

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