Introduction

In lakes the bottom sediments are built by mineral and organic substances removed from the water during the processes of precipitation, sorption and sedimentation. They play a significant role in the functioning of the ecosystem, related to the possibility of secondary release of these substances [1-3]. The impact of the biogenic substances accumulated in sediments on water quality depends on the lake basin morphology (especially depth and shape) and on the morphology of the surroundings, determining such factors as the friction of the inflowing air masses causing water movements [4]. The type of water lake mixis determines the relations between sediment and water and their physical-chemical properties. In polymictic lakes in the summer, the water is many times moved down to the bottom, which causes the resuspension of sediments, increasing the water capacity and decreases nutrient content [5]. In dimictic lakes the stable thermal stratification were for short periods disturbed by the homothermic phases, which does not stir the water strong enough to cause a substantial resuspension of the sediment components.

Vertical Changeability of Physical-Chemical Features of Bottom Sediments in Three Lakes, in Aspect Type of Water Mixis and Intensity of Human Impact

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Abstract

Variation of the chemical composition of bottom sediments collected from three lakes with different water mixis, morphometric parameters, catchment areas and anthropogenic pressures was analyzed. Sediment samples were characterized by water content and concentrations of organic matter, nitrogen, phosphorus, calcium, iron and aluminium. Statistically significant correlations between the content of organic matter, nitrogen and phosphorus were found. In a large and deep lake (dimictic) subjected to limited human impact, the tendency changes of chemical composition along the sediment profile indicates a recent considerable increase in water trophy. In a small mid-forest lake (classified as meromictic), the changes in chemical composition of bottom sediments along with depth point to periodical increases in fertility as a result of wastewater inflow. In a large mid-field lake (polymictic), the analogous variation has indicated disturbances in the mechanism of sediment formation.

Keywords: lake, bottom sediments, phosphorus fractions, water mixing, human impact

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The main components of lake sediments are the mineral particles of abiotic origin (produced by weathering and denudation), particles of biogenic origin (carbonates, silica, iron compounds) and auto- and allochthonous organic matter [6, 7]. The formation of bottom sediments is also influenced by physical-chemical processes such as precipitation of insoluble calcium carbonate, iron(II) hydroxide, manganese(IV) and phosphate salts of these metals [8, 9]. The autochthonous matter in the suspended particles (remains of hydrobionts and macrophytes) dissolved in water (metabolites, enzymes) were characterized by high content of nitrogen and phosphorus compounds. In the lakes basin with the high share of forest, important sources of macro- and microelements are plant remains and mineral-organic compounds of humus origin [10].

In the conditions not disturbed by anthropopressure, the vertical profile of the sediment develops according to certain chemical processes. As the process of sedimentation is slow, particular layers differ in age and composition. Analysis of the bottom sediment can provide information about the internal transformations and the history of the ecosystem [11]. The chemical composition of the sediment (e.g. content of heavy metals) reflects the type and intensity of anthropogenic influence on the lake and its catchments [12, 13] and provides information on potential threats of the ecosystem [14]. In the aspect of lake functioning, the most important are the processes of accumulation of nitrogen and phosphorus compounds and the mechanisms of their release to the lake water. From the point of view of primary producers, especially important is the release of bioavailable phosphorus species [8, 15].

The aim of our study was to determine the differentiation of the physical and chemical parameters of bottom sediments in the vertical profile of three lakes of different morphology and basin area character, taking into account the influence of the present and predicted anthropopressure. Of our particular interest was the analysis of nitrogen and phosphorus species in the fractions of different strength of bond to the matrix. The potential possibilities of secondary release of phosphorus bound with metals and organic matter accumulated in the sediment were evaluated. It was assumed that:

1. the increase in anthropopressure leads to eutrophication of water and changes in the vertical gradients of the chemical properties of the sediment, in particular the fraction composition of phosphorus,
2. the bottom sediments of the lakes in the catchment area with forest domination contain greater amounts of nitrogen as a result of greater inflow of natural organic matter in comparison to lakes in the agricultural landscape.

### Study Area

The objects of study were three post-glacial lakes of different surface and morphology of the basins, especially depth: the dimictic Góreckie Lake and Kociołek Lake in the area of Wielkopolski National Park, and the polymictic Strykowskie Lake (Table 1). The basin of Góreckie Lake is naturally divided into two sub-basins: the deep southern one (max. depth 17.2 m) and shallower northwestern one (10.4 m). For over 20 years this lake had been polluted with raw waste from the nearby sanatorium in Jeziory. Although the sanatorium was closed in 1990 and the point sources of pollution were blocked, by the end of the 20th century the lake was hypertrophic [16, 17]. Kociołek Lake is a small, postglacial mid-forest lake (Table 1). Until a few years ago the lake had been polluted with raw waste from the sanatorium in Ludwikowo; at present the inflow of waste is blocked [18]. The lake has for a long time been treated as meromictic, although this opinion has not been corroborated by well-documented study [19]. These two lakes are supplied with underground springs and surface inflow.

The largest and shallowest of the three is Strykowskie Lake. The catchment area of this lake is dominated by agricultural land, while the forest occupies only about ¼ of its coastline. Because of the morphometric features and the agricultural use of the catchment, the lake is highly susceptible to degradation, which is reflected by high eutrophy [20]. The lake is very long and relatively shallow, which at a high value of expose index determines its polymictic character (Table 1). The lake is supplied by a few small watercourses and drainage ditches. The eutrophication results mainly from the agricultural use of the surrounding land, recreational and fishing pressure. The nutrients inflow to the lake with water from the watercourses, surface outflow and ditches (southwestern part of the basin). The water from the lake is used for irrigation of agricultural land and until a decade ago the lake had been polluted with raw waste from nearby villages.

According to the soil-habitat survey, the catchment areas of the lakes are dominated by grey-brown podzolic soils (sand and light loam) and rusty soils (poor loamy and loose sand), transformed from poor quartz sands (unpubl. data). The organic layer is very thin (about 2 cm) and depends on vegetation. The humus layer is shallow and has a thickness of 9-17 cm. Its composition is characteristic of sandy dusts. The upper levels of soil profile are either acid or faintly acid.
Methods

The examination of the physical-chemical features of bottom sediment were carried out in July 2008 at the deepest places of each lake. The samples of the sediments (4 cores in each lakes) were collected by a Limnos sampler with direct core cutting into 5-cm-thick layers. The cores collected from Góreckie Lake were 35 cm long, while those from the other two lakes were 40 cm long. In as-collected sediment sample the water content was determined and phosphorus was fractionated by sequential extraction, according to the Psenner procedure [21, 22]. The fractions were:

1) NH₄Cl-P – loosely bound and extractable with a water solution of NH₄Cl,
2) Fe-P – bound with iron, extractable with water solution of sodium hydrocarbonate and sodium thiosulphate,
3) NaOH-P – bound with aluminium and organic matter and extractable with a water solution of NaOH,
4) HCl-P – bound with calcium and extractable with a water solution of HCl and
5) Res.-P – residual, permanently bound with the matrix after complete mineralization.

In the air dry samples the following determinations were made: organic matter (OM) as loss on ignition at 550°C, total nitrogen (TN) according to Kjeldahl’s method, total phosphorus (TP) by the molybdate method after mineralization (with a mixture of HNO₃ and H₂SO₄), calcium (Ca), iron (Fe) and aluminium (Al) by means of the AAS method in acid concentrate. Determination of aluminium from the acid extract permitted isolation of the acid-soluble fraction. Statistical analysis was made using Statistica 7.

Results and Discussion

In the core samples from all lakes the hydration level decreased with depth. In lakes Góreckie and Strykowskie in the whole vertical profile hydration was at >80%, and in Kociołek Lake the hydration suddenly decreased in the deepest layer and did not exceed 40% (Table 2). In Góreckie Lake, in which the inflow from the catchment area (in some periods with the raw waste) was distributed over a large area, the maximum content of OM was found in the top layer of the sediment (33.6% d.w.) and decreased with depth (Fig. 1). These data indicate the abundant and stable supply of organic detritus related to high trophy and primary production [17]. The content of organic matter was the highest in sediments of Kociołek Lake with maximum in layer 10-15 cm. These data testify to a period of greater inflow of OM, together with nitrogen and phosphorus, as proved by the high coefficient of determination (r²=0.99, p<0.000 and r²=0.84, p<0.001, n=32). Taking into regard the rate of sediment increase established for Gościąż Lake in central Poland by Ralska-Jasiewiczowa et al. [11] as 1-2 mm per year, the period of the increased inflow of organic matter to Kociołek started about 75 years ago. So shortly after opening of the sanatorium in Ludwikowo, however, an

<table>
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<th>Parameter</th>
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<td>Water content</td>
<td>Góreckie</td>
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<td>Kociołek</td>
<td>93.7</td>
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<td>Strykowskie</td>
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<td>Ca [g kg⁻¹ d.w.]</td>
<td>Góreckie</td>
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<td>Kociołek</td>
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<td>Fe [g kg⁻¹ d.w.]</td>
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<td>Kociołek</td>
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<td>Residue* [% d.w.]</td>
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<td>Kociołek</td>
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<td>Strykowskie</td>
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* components insoluble in acids.
important source of OM is also the catchment area about 15 times greater than the lake. In deepest sediments the content of OM quickly decreased (Fig. 1).

In bottom sediments of polymictic Strykowskie Lake the content of organic matter was the lowest from all the lakes, with maximum at 15-25 cm. The vertical changeability of OM content indicates variations in its supply, which suggests that the high trophy of the lake water and strong anthropopressure changed in time. In this lake a high correlation was found between OM and phosphorus and nitrogen (in turn $r=0.78$, $p<0.022$ and $r=0.74$, $p<0.037$; $n=32$). In the shallow layers the content of these two elements decreased (Fig. 1), which probably can be related to the reduced use of artificial fertilizers used in agriculture, and regulation of water supply and sewage disposal.

The content of calcium in the bottom sediments of lakes Góreckie and Strykowskie was much higher (in turn mean concentration 11.5 g kg$^{-1}$ d.w. and 24.8 g kg$^{-1}$ d.w.) than in Kociołek Lake (1.1 g kg$^{-1}$ d.w.). In the vertical profiles of all lakes the variability of Ca was similar. The highest content was stated in the youngest sediments and in deep layers the concentration was lower (Table 2). In Góreckie Lake below 15 cm the content of Ca was unchanged. The increasing content of Ca in the younger layers of bottom sediments indicate the effect of the primary production of phytoplankton. As a result of inorganic carbon assimilation in the process of photosynthesis, the water-soluble calcium bicarbonate is converted into insoluble calcium carbonate and undergoes sedimentation [8, 11]. According to statistical analysis, Ca was supplied to Góreckie Lake together with organic matter ($r^2=0.85$, $p<0.003$, $n=28$), similarly as in Kociołek Lake ($r^2=0.81$, $p<0.002$, $n=32$). The OM from Góreckie Lake was biogenic-substances rich, and illustrated the high correlations with nitrogen ($r=0.96$, $p<0.001$) and phosphorus ($r=0.85$, $p<0.015$, $n=28$). In Kociołek Lake the analogous correlation was greater for phosphorus ($r=0.94$, $p<0.001$) than for nitrogen ($r=0.88$, $p<0.004$, $n=32$), while in Strykowskie Lake similar correlations were not found.

In all lakes the content of Fe and Al showed large variation. In lakes Góreckie and Kociołek, elevated levels of Fe were found in the middle part of the deposit cores and its content in the deep layer was twice lower. In Strykowskie Lake the concentration of Fe increased with increasing depth, but iron content in sediments from this lake were lowest (Table 2). It is supposed that the concentration of Fe was related to the periodically increased anthropopressure (inflow of domestic sewage from nearby villages) and increased trophy of the water. A consequence is a drop of oxygen concentration in the subbottom water layer. In such conditions Fe(III) forming water-insoluble hydroxide was reduced to Fe(II), whose species are water-soluble and are released to lake water [8]. The differences of Fe and Al contents in the lake deposits, much lower in Strykowskie Lake, could be related to a greater content of these metals in the soils of forest catchment than in the agricultural. A special role for solubility and migration of these metals is taken by dissolved humic substances (DHS) [23]. The chelates formed by DHS and mineral components were of great significance, because their easy movement and sorptive capacity exert a strong influence on migration of chemical elements across ecotone systems [10].

Although the mean concentrations of nitrogen in sediments of all lakes were similar (12.2 g kg$^{-1}$ d.w. in Góreckie, 12.7 g kg$^{-1}$ d.w. in Kociołek and 13.6 g kg$^{-1}$ d.w. in Strykowskie), the vertical changeability of concentration...
was different. In the small Kociołek Lake the maximum was noted in layer 10-15 cm, and below 30 cm it abruptly decreased. In Góreckie Lake the maximum content was found at a depth of 0-5 cm, while at 5-10 cm the concentration was by almost 6 g kg⁻¹ d.w. lower. In Strykowskie Lake the vertical variation of nitrogen was very small (SD 0.7 g kg⁻¹ d.w.) (Fig. 1). In the sediments of lakes Góreckie and Kociołek the content of nitrogen was exactly correlated with the content of OM, while in Strykowskie Lake correlation was lower (r=0.74, p<0.037, n=32).

The content of phosphorus in the sediment samples studied was not high. A mean concentration in Strykowskie Lake was 1.204 g kg⁻¹ d.w., similar in Góreckie Lake at 1.126 g kg⁻¹ d.w., and only 0.67 g kg⁻¹ d.w. in Kociołek Lake. The vertical differentiation of concentration suggests that sedimentation of phosphorus species has changed over time. In Góreckie Lake the maximal concentration was found in surface layer, and decreased in deeper deposits. Under 20 cm depth high fluctuations in the content of phosphorus were observed (Fig. 1). Statistical analysis revealed a strong correlation between the content of phosphorus and organic matter (r²=0.81, p<0.006, n=28). In Kociołek Lake the concentration of phosphorus decreased with increasing depth of deposits. In the third lake it increased to the depth of 10-15 cm, which means that not long ago this lake absorbed much greater amounts of phosphorus than now. The greater absorption of phosphorus should be related to the release of domestic sewage from nearby villages, as such waste usually has high phosphorus content. Despite significant differences in the lake morphology and catchment character, the content of phosphorus in the top sediment layers in these two lakes was similar: 0.9 and 1.1 g kg⁻¹ d.w., respectively. For Kociołek Lake this result suggests poor inflow of phosphorus from the catchment area, while for Strykowskie Lake – high efficiency of phosphorus species release to the lake water as a result of polymixis. Easy release of phosphorus to the lake water was a consequence of a great contribution of the loosely bound fraction of NH₄Cl-P (Fig. 2).

The vertical distribution of the phosphorus fraction in lakes Góreckie and Kociołek was similar: increasing depth content of mobile phosphorus in the loosely bound fraction, iron bound fraction and organic matter bound fraction decreased (Fig. 2). The contribution of the fraction bound with calcium, especially in Kociołek sediments, increased with depth, in other words with age, which was probably the result of biogeochemical transformations (e.g. mineralization of organic matter, reduction of Fe(III)). In Strykowskie Lake no significant trends in the phosphorus fractional composition were noted. The chemical composition of the sediments from this lake, and especially low concentrations of phosphorus in the surface layer (0-5 cm), was a consequence of frequent water movements reaching the lake bottom and sediment rinsing. The investigations of the release of phosphorus from bottom sediments in the lakes with high water trophy (experimental and field) demonstrate that release resulting from the resuspension is 8-10 times more effective than in unmixed sediments [5]. The soluble reactive phosphorus, which is released from deeper

![Fig. 2. The percentage share of phosphorus fractions in vertical profile of deposits of Góreckie Lake (A), Kociołek Lake (B) and Strykowskie Lake (C).](image-url)
sediments through diffusion, is the most prone to rinsing from the surface layer (to 8 cm depth) of bottom sediments [24].

The deposits from all researched lakes were characterized by similar values of the N/P index, indicating a similar genesis of the sediment material. In lakes Góreckie and Strykowskie the mean values of N/P were of 11 and 12, which correspond to the proportion of N/P characteristic for plankton [8]. High vertical stability of the N/P index suggests a large contribution of organic matter formed as a result of the metabolism of organisms. According to the results of the statistical analysis, in Góreckie Lake the content of phosphorus in the sediment was moderately correlated with nitrogen (r=0.79, p<0.033, n=28), while in Strykowskie Lake no similar correlation was found. In Kociołek Lake the N/P index was higher, on average 18, and in its vertical profile the value increased from 17 (layer 0-5 cm) to 26 (25-30 cm). The phosphorus and nitrogen in the sediments of this lake correlated exactly (r=0.91, p<0.002, n=28), which indicated deposition of material in specific proportions of components with a majority of nitrogen. The explanation of the origin of the sediment material probably leads to the forest character of the catchment area. The lake is surrounded by pine-oak forest (Pino-Quercetum) with old and high trees of Quercus petraea and Q. robar along the coastline. The plant waste falling into the lake is mostly oak leaves, found in a state of considerable decomposition in the profundal sediments as deep as 20 cm. They contain up to 10.8 g N kg⁻¹ and 1.6 g P kg⁻¹, while the pine needles contain up to 6.5 g N kg⁻¹ and 0.5 g P kg⁻¹. The concentration of nitrogen in the autumn leaves is greater in dry years and increases with the age of the trees [25]. The inflow of the biogenic compounds into the lake is enhanced by high inclination of the lake banks, favouring surface outflow. The genesis of these formations is determined by the role of migrating humic acids (mainly fulvic) washed out from the level of ectohumus [26]. In the upper part of the soil profile the acids are engaged in the formation of organic-mineral compounds with nutrients and metal ions, whose stability depends on pH value [27]. Strong migration of DHS to lakes leads to nutrition restrictions of macrophytes and phytoplankton [28, 29]. However, the chelates undergo bacterial decomposition, which leads to mass development of bacterioplankton [15], mainly the photo- and chemoheterotrophic bacteria [30]. In Kociołek Lake the abundant presence of bacterioplankton was found in the subbottom layer, although its presence was manifested in whole vertical profile of water in the form of mucilage originating from bacteria sheet. The content of nitrogen in the sediment from this lake can be a result of bacterial decomposition of soil colloids and sedimentation of chelates.

Conclusions

The high contribution of forests in the lake catchment area create conditions favouring isolation of the bottom sediments from external interactions, capable of causing their mechanical disturbance. Unfortunately, in Poland the localization of lakes in the National Parks has not protected them from the deteriorating effects of anthropopressure in the form of wastewater. In large Góreckie Lake the inflow of the wastewater has not brought significant changes in the vertical profile of the deposit chemistry, but in small Kociołek Lake the introduction of waste has resulted in high concentrations of organic matter correlated with the content of nitrogen and phosphorus compounds. Another factor having a significant effect on the sediments of this lake is the abundant inflow of the organic matter from leaf-fall and soil colloids with the high content of organic-mineral complexes formed by humic compounds. The high chemical activity of these substances have an especially strong negative influence on phytoplankton as it chemically binds phosphates and life-essential elements (among others calcium and iron) into colloidal complexes which are difficult to decompose. Deposition of large amounts of dissolved organic matter in the bottom sediments favours the development of bacterioplankton. Reserves of energy chemically bound with organic-mineral complexes can be partly made available by the organisms of the microbial loop. The vertical changeability of Strykowskie Lake deposits has pointed to a greater role of the specific morphological features of the lake basin, responsible for the oft water mixis and mixing of sediments, in their formation.

Acknowledgements

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