*Original Research*

# The Variability and Stability of Water Chemistry in a Deep Temperate Lake: Results of Long-Term Study of Eutrophication

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### Abstract

Temporal and seasonal variability of hydrochemical properties in a deep, highly eutrophic lake was presented. It was shown that the feedback between the biocenosis and abiotic properties was of key importance for the lake environment, especially for features shaped by oxygen content. During vegetation season in a shallow trophogenic zone supersaturated with oxygen, quick depletion of some nutrients (mineral forms of nitrogen, phosphorus, and carbon) were noted. In a tropholytic zone, which constituted the major part of the lake water column, the mineralization of organic matter concentrations of mineral compounds were high. This layer was completely and permanently deoxygenated (anoxia). The reductive conditions intensified the release of biogenic compounds from bottom sediments. Many correlations between abiotic properties of water reflecting the complex interrelationships between biocenosis and biotope were stated. The relationship between photosynthesis and alkalinity and calcium distribution in the water column also was explained. On the basis of historical data (since the 1930s), tendencies of temporal changes in lake water chemistry were discussed as well as causes and effects of eutrophication.

**Keywords:** human impact, effects of eutrophication, hydrochemistry, seasonal and temporal tendencies, bottom sediments, PCA analysis

## Introduction

Each lake ecosystem is composed of abiotic elements and biocenosis, which are related to each other in terms of dynamic feedback [1]. Abiotic features are to a great extent influenced by mineral and organic substances inflowing from the catchment area (whose transportation depends on geological structure and terrain shape), of catchment area management, and hydrogeological and climatic conditions [2-4]. The structure of biocenosis and the activity of hydrobionts are decisive in terms of direction of energy flow and rate of matter circulation in the ecosystem [5]. Except for geographic location determining the intensity of the insolation factor that affects the thermal conditions and depth of the euphotic zone, especially during summer, stagnation is the morphometry of the lake basin [6, 7]. The particularly great significance of solar radiation for energy resources of the lake is observed in small lakes (especially without troughflow) with low alimentation of organic matter and bio-elements from catchment area [8, 9]. The main role of solar energy in a water ecosystem is initializing photosynthesis, biological transformations of matter, and flow of energy. Hence the importance of photic zone depth, along with the abundance of nutrients.

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In nutrient-overloaded lakes photosynthesis significantly influences the abiotic properties of environment. This is noticeable especially in the vegetation season, when development of mass phytoplankton blooms in surface layer occurs. In such conditions the strong reduction of light availability in the water column is noted [10]. The consequence is the elimination of submerged aquatic vegetation and charophytes [11], and also the aquatic organisms connected with them [12, 13]. High primary production causes strong oversaturation of water with oxygen, especially in the shallow layer of the epilimnion. On the other hand, resources of mineral substances are quickly depleted from water. At the same time in the lake, the increase in water pollution with organic products of metabolism is often toxic.

In optimal conditions of eutrophic lake environment the primary production is intensive. However, in the case of a deficit one of the trophogenic components in the production is inhibited and the decomposition processes prevails (aerobic or anaerobic) [14]. With the participation of some animal groups and microorganisms the released mineral compounds and organic metabolites are introduced into the food web and biological cycle. The phases of strong increases and rapid decreases of primary production in the lake are cyclic, which causes seasonal changes of water chemistry. In deep lakes the cause of vertical differentiation of water chemistry is thermal stratification shaped during stagnation periods [5, 7]. In circulation of matter in the lake an important role is played by the cycle of biological and physico-chemical transformations such as dissolving, precipitation, and sedimentation, and dissociation and red-ox reactions.

The dead plankton creates organic material suspended in water, which is deposited in the tropholytic zone, where it decomposes [15]. Because the decomposition of organic material is very rapid it may cause a depletion of oxygen in the subbottom layer, and reductive dissolution of solids. The quality transformation of bottom sediments (which is connected with the processes of sedimentation and acumulation of an excess of organic matter) is a consequence of the process of eutrophication. Organic sediments to a greater extent compared to mineral sediments are responsible for internal phosphorus loading, which may accelerate eutrophication and be a reason for secondary contamination [16]. A specific feature of the organic sediments is higher abundance of phosphorus [17, 18] connected both with organic compounds as well as with metals [19]. In this paper, we document the vertical and temporal variability of abiotic features in the overloaded eutrophic lake. In the example of Góreckie Lake we explain the relationships between biocenosis and biotope, and the key role of biocenosis for lake water chemistry. Additionally, the implications of high photosynthesis and abiotic processes on water properties were analyzed. The problem was considered against the background of historical study of the lake (over a period of 80 years).

## Study Area

Lake Góreckie is one of the most precious hydrographic objects of Wielkopolski National Park (WNP). The lake is partly included in the strict protection area. Góreckie is a typical dimictic ribbon lake whose basin is naturally divided into two sub-basins by a shoal leading to Zamkowa Island (Fig. 1). The southern basin is deep, with a maximum depth of 16.6 m (nearly 1/3 of the bottom lies at a depth of 10-15 m), steep shores, and narrow littoral. The second basin is shallower (5-10 m), its shores are flatter, and the littoral zone is wider. Near the northern edge of the lake there is the second island connected with the land by a belt of rushes. Lake area is 101.63 ha and average depth 8.5 m [20]. The shores are natural at all lengths and there is a protective buffer belt around the lake, formed by forest and rushes. The catchment area of the lake is dominated by forested land (59% of area). About 30% of the catchment area, around the northwestern basin, covers agricultural fields and rural areas. The lake is mainly supplied by groundwater from the upper interloam water-bearing level, and from the Wielkopolska buried valley aquifer as well as to a lesser extent by atmospheric precipitation [21]. The lake is situated away from human settlements, and the northwestern basin also is remote from tourist routes. This isolation makes this part of the lake an attractive destination for many species of water birds, especially for wild geese during winter [22].

## History of Lake Eutrophication

The first information about Góreckie hydrochemistry is from 1935-38. In that period in summer Secchi disc visibility reached 4.5 m. The epilimnion was usually 6 m depth, and metalimnion 4 m. The oxygen conditions of water were good – its concentration in the sub-bottom zone of the deeper basin ranged from 4.3 to 5.0 mg $O_2 \cdot L^{-1}$. The pH reaction of surface water was slightly alkaline (pH 8.0). A little worse condition was in the northwestern basin of the lake, which was explained by smaller depth and the influence of bottom sediments. According to a study from the 1930s the lake was mesoeutrophic [23]. Research conducted in the 1950s revealed a significant similarity to the previous period in range of trophy status, light conditions, and oxygen content: water transparency ranged from 3.5 to 4.5 m and

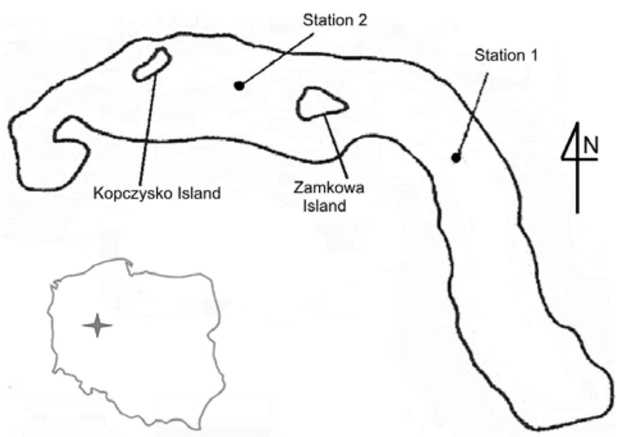


Fig. 1. Map of Góreckie Lake with the sampling stations and location of the lake within Poland.

the oxygen concentration in the sub-bottom zone was 4.3 to 5.7 mg $O_2 \cdot L^{-1}$. In this time *Characeae* were frequently observed in the lake [11, 24]. Significant deterioration of the ecological state of the lake was observed 20 years later when among other factors a large decrease in water transparency was noted (1.9-2.5 m). Relatively large dynamic changes of oxygen concentrations were recorded – in summer of 1974 the smallest content of oxygen was 3.0 mg $O_2 \cdot L^{-1}$, but in next year there was a lack of oxygen near the bottom, and the smell of hydrogen sulphide was detected. At that time the pH and depth of thermic layers did not change. Features of the lake water chemistry were moderate concentrations of nitrogen and phosphorus compounds. The concentrations of nitrates at spring reached 0.4 mg $N_{NO_3} \cdot L^{-1}$, but in the summer were lower (maximum to a hundredth part of a milligram). The concentrations of ammonium did not exceed 0.12 mg $N_{NH_4} \cdot L^{-1}$. Phosphates were not determined in the epilimnion and at the bottom their concentrations reached 0.069 mg $PO_4^{3-} \cdot L^{-1}$ (total phosphorus ranged from 0.13 mg $P \cdot L^{-1}$ to 0.102 mg $P \cdot L^{-1}$, respectively). Calcium was determined in higher concentrations only in the hypolimnion layer. In comparison with studies conducted in the 1930s, a significant increase of water trophy was observed in the lake [25]. What could cause such a change?

The causes of changes are found in lake catchment. In 1941 on the shore of the lake the palace and residential complex were built. It was supplied with mechanical sewage treatments that were then discharged into the lake. From the 1950s the complex was turned into a sanatorium that functioned until 1989. The effectiveness of sewage treatment (Imhoff clarifier, biofilter, and chlorinator) was too weak. The study found that during one day the lake was fed by 6.7 kg $BZT_5$, 0.3 kg $PO_4^{3-}$, 2.4 kg TN, and 2.8 kg of suspensions [26]. The sanatorium was therefore for almost 40 years the sewage release point, and sewage was probably the main cause of lake eutrophication [27].

A second cause of eutrophication at that time was considered recreational use of the lake [28]. In the following years ecological and chemical status of the lake became worse and worse. In summer 1981 in the sub-bottom zone of the lake very small concentrations of oxygen still occurred (0.2 mg $O_2 \cdot L^{-1}$). However, in the next year the water 3 m above the bottom sediment was completely deoxygenated. The concentrations of nitrogen were also significantly higher at spring (in 1981 to 1.9 mg $N_{NO_3} \cdot L^{-1}$), but in the vegetation season it was low (0.2 mg $N_{NO_3} \cdot L^{-1}$). This was similar with phosphates. Only concentrations of ammonium nitrogen were higher (1.98 mg $N_{NH_4} \cdot L^{-1}$). The analyses performed in 1992-93 after closing the sanatorium revealed the constant increase the concentrations of mineral biogenic compounds in lake water. A characteristic feature of the lake since that time has been the large algal blooms from early spring to autumn, and the alkalinity of epilimnion waters (pH 9.0) [29]. In the summer the vertical distribution of ammonium and phosphates were associated with the thermal layers of water – lower concentrations in the epilimnion and higher in the hypolimnion were noted (ammonium 0.0-0.3 mg $N_{NH_4} \cdot L^{-1}$ and 0.1-0.8 mg $N_{NH_4} \cdot L^{-1}$, phosphates 0.02-0.10 mg $PO_4^{3-} \cdot L^{-1}$ and 0.04-0.13 mg $PO_4^{3-} \cdot L^{-1}$, respectively). The nitrates were completely depleted and their detectable concentrations after the vegetation season were detected (to 0.75 mg $N_{NO_3} \cdot L^{-1}$). At that time the lake was eutrophic with a tendency to further eutrophication. The phytoplankton was dominated by species characteristic for hypereutrophy [30, 31].

At the end of the 20th century another hypothesis of lake eutrophication was stated. Since 1980s on the lake wild geese (*Anser fabalis* and *Anser albifrons*) had regular wintering. From unpublished data of the Polish Association of Nature Protection ("Salamandra") in 2004-08, approximately 4-8,000 geese visited lake every day. Numerous assemblages of waterbirds may affect lake water quality and be a source of microbial pollution [32], so due to the fact that the goose pressence lasted for several years and flocks of geese were very numerous, the responsibility for the increase in trophic state of the lake was attributed to them [33, 34]. However, frequently omitted was the fact that during very cold winters (when the lake was totally frozen) geese were not recorded at the lake. The studies on the influence of geese on the bacterial and chemical pollution of the lake did not confirm this hypothesis [22].

## Study Methods

The study was conducted in 2008, 2010, and 2011 every month from February to November. Every month, at sampling stations located in the deepest point of the southern basin (52º15'58" N, 16º47'47" E) and in the deepest point of the northwestern basin (52º16'3" N, 16º47'1" E) (Fig. 1) in the vertical profile of the lake the following parameters were measured: temperature (ºC), dissolved oxygen (DO), oxygen saturation (OS), and pH and conductivity (EC) using the multiparameter sonde (Multi 350i, WTW) with a probe with a rotor inducing water movement in the sampling area. Apparent water transparency using a Secchi disk (SD) was analyzed (white, diameter 30 cm). The apparent depth of illuminated zone (ADIZ) was calculated after formulae SD·2. Every 2 m in the whole water column the samples for laboratory analysis (with electric submersible pump, Eijkelkamp) were taken. Water samples for chemical analysis were collected in polyethylene flasks washed in 10% HCl and rinsed several times in distilled water. Water samples were analyzed in the laboratory: total phosphorus (TP, at 850 nm using a spectrophotometer UV-1610 Shimadzu, with molybdate method after mineralization), soluble reactive phosphorus (SRP, at 850 nm using a spectrophotometer Cadas 200 UV-VIS Dr Lange, after filtration thought glass fiber filters GF/F 0.7 μm, with molybdate method), nitrate ($NO_3^-$, with sodium salicylate method), nitrite ($NO_2^-$, with sulphanic acid method), ammonium ($NH_4^+$, with Nessler Method), organic nitrogen ($N_{org}$, with Kjeldahl method), total nitrogen (TN, as sum minerals and organic form), alkalinity (by titration), and calcium (Ca, by EDTA titration) [35, 36]. Carlson's Formulae [37] were used to transform the results into the trophic state index (TSI). The trophic state was estimated using the TSI range proposed by Carlson and Simpson [38]. Statistical calculations were made using

Statistica 8.0 software. Correlation was considered as statistically significant at the $p<0.05$ level.

## Results and Discussion

During the entire study period the thermal conditions of water changed typical for dimictic lakes (Fig. 2). The homothermal phases were short-lasting (in spring – the turn of March and April, in autumn – the turn of October and November) at a relatively low temperature of water. In the shallow basin (station 2) the autumn mixis occurred several weeks earlier than in the deep one (station 1). During summer stagnation a sharp thermocline was formed with a high gradient of temperature (Fig. 2.). During winter the homotermy was observed.

The epilimnion was shallow until July (3-4 m) and later it became deeper (5-6 m). A sharp thermocline isolated the highly over-aerated epilimnion water from cold and completely deoxygenated deeper water. It should be emphasized that the deepening of the epilimnion layer was not accompanied by the improvement of oxygen content in water. During lake stratification the large-scale vertical changeability of oxygen content was observed, a feature of an overloaded lake. We can distinguished three zones: supersaturated with oxygen the epilimnion, metalimnion with sharp gradient of oxygen concentrations (oxycline) and permanently anoxic hypolimnion (Fig. 2). The short-term improvement

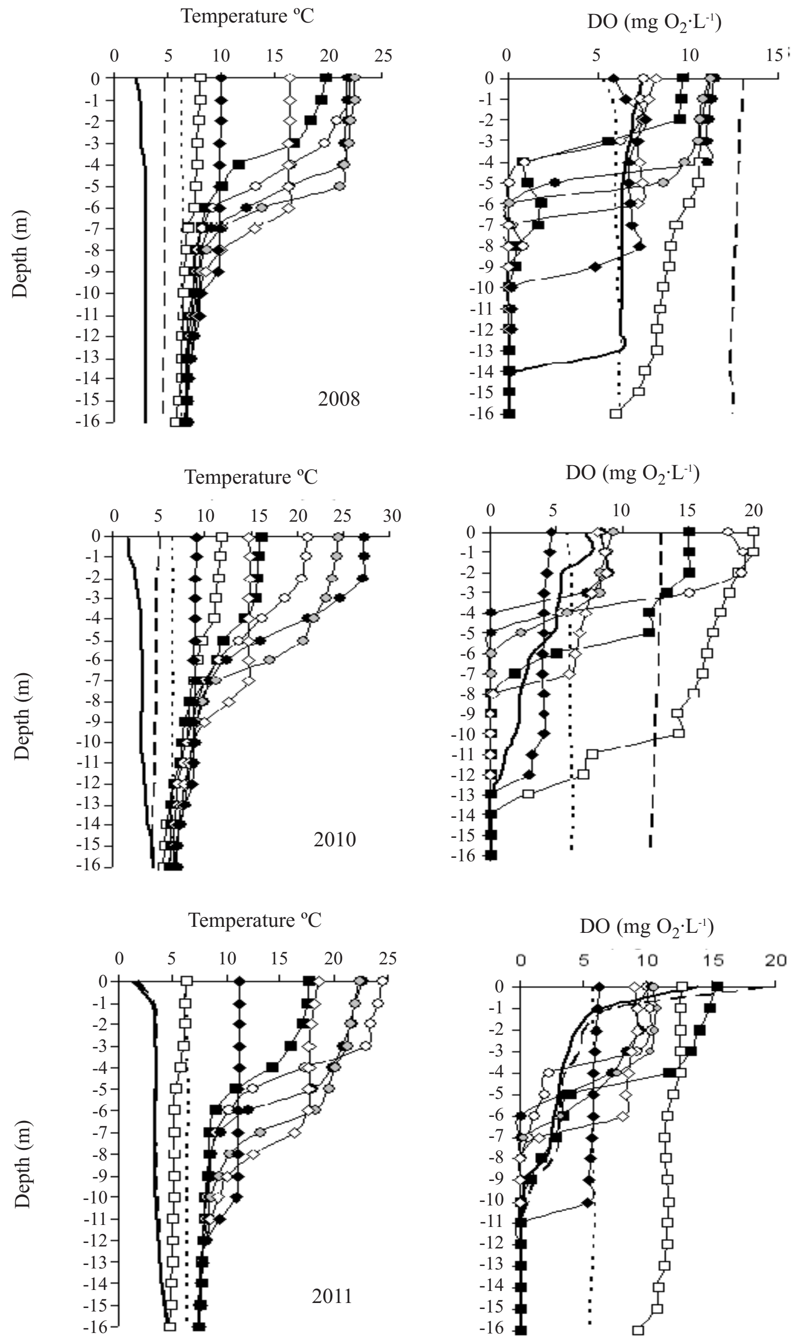


Fig. 2. Vertical water temperature and dissolved oxygen (DO) profiles (marks of months: — February, — — March, □ April, ■ May, ○ June, ● July, ○ August, ◊ September, ♦ Oktober, ····· November).

of sub-bottom water oxygenation occurred during homothermy (mixis). However, it was observed that during the spring the oxygen concentrations in the whole water column of the lake were higher than during autumn.

The average value of Secchi disk visibility from the entire study period (II-XI) amounted to 2.4 m. In the time of lake summer stratification SD ranged from a low value in 2008 (mean 1.9) to higher in 2010 and 2011 (2.5 m and 3.2 m, respectively). During the study period an unusually large but short-lasting increase of SD (5.05 m) was observed in September 2010. This value was higher than the ones recorded during the first studies of the lake in the 1930s, when the trophy state was much lower [23, 25]. The improvement of light conditions and increase of illuminated zone depth caused an increase of epilimnion depth (Fig. 3). However, at the beginning of 2011 due to early bloom of phytoplankton (early April) light conditions were very bad (SD 1.1 m). The transience of maximum effectiveness of primary production is proven by the fact that as soon as one month later the SD increased by 1 m and in months VII-XI it ranged from 3.0-3.8 m (Fig. 3). A similar state had been recorded in the lake earlier and was defined as the occurrence of the stage of clear water [31]. The increase of SD resulted in the greater range of ATIZ, which in 2011 was much wider than in previous years. A deeper transmission of solar radiation resulted in the increase of water temperature and deepening of the epilimnion.

In the period of spring mixing (usually in March) in the whole water column of the lake oxygen saturation above 100% $O_2$ was noted. However, during the formation of thermal stratification rapid depletion of oxygen occurred, and in May practically only in the epilimnion was noted. In the early summer the oxygen conditions in the lake were stable – the epilimnion was permanently supersaturated with oxygen (maximum 160% $O_2$) while in deep waters the deficit

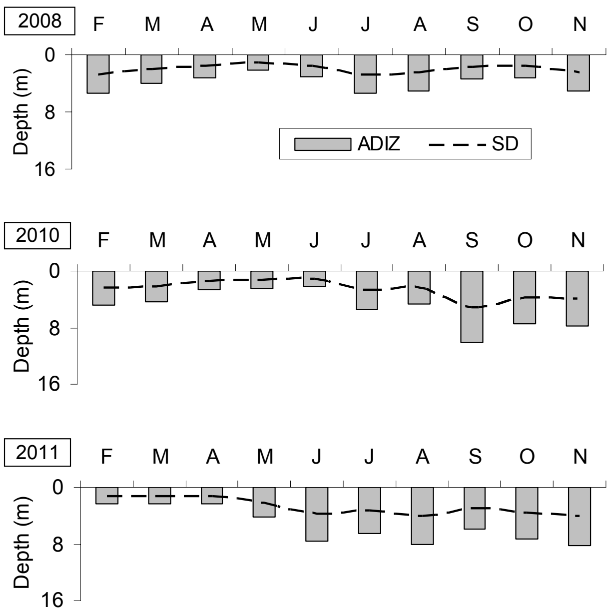


Fig. 3. Annual and seasonal changeability of Secchi disk (SD) and apparent depth of illuminated zone (ADIZ).

or chronically anoxic state was stated (Fig. 4). From July hydrogen sulphide occurred in the hypolimnion. Such an oxygen vertical structure suggest a significance of photosynthesis as the main source of oxygen dissolved in water and major cause the oxygen saturation (or supersaturation) of shallow surface zone. Generally, the concentrations of dissolved oxygen reflected the intensity of production and decomposition processes in different zones of the lake [5].

At the end of the summer the oxygen zone became deeper again and, after the autumn mixis (in November), the whole lake was well oxygenated. The characteristic feature of the lake was relatively low values of oxygen saturation during of autumn mixis (at the level of 50% $O_2$). In the periods of winter (usually from the end of December to the beginning of March) the reach of the anaerobic zone was smaller than in the summer and was limited to the shallow zone over the bottom sediments. This was linked to the low water temperature and inhibition of the processes of biochemical degradation (mineralization) of organic matter due to low enzymatic activity of microorganisms [39]. In 2011 depth of the epilimnion and the trophogenic zone was greater, which slightly improved water oxygenation. The photosynthesis also had a large influence on other abiotic properties of the lake environment, especially on pH of water. The correlation between OS and pH for the entire period of research was high ($r=0.82$, $n=269$) as well as for the vegetation season ($r=0.92$, $n=135$).

In the winter period water pH varied from 7.7 under the ice to 7.0 near the bottom. When the lake was frozen the penetration of light into the water was dramatically small. The light under ice constitutes less than 0.5% of the light on the surface [40]. Immediately after the ice melted (in March 2008 and 2010 and in April 2011) as a result of quick intensification of photosynthesis the alkalization of water was noted. The highest values of water pH were almost always noted in May in the newly formed epilimnion layer, which confirmed the maximum efficiency of photosynthesis. In the summer due to reduction and lack of biologically available nutrients, the production rate decreased as well as pH values. Values of pH in the water column during the summer stratification were variable. The effect of the high efficiency of photosynthesis in the epilimnion was high alkalinity of water related to the depletion of dissolved $CO_2$ and disturbed carbonate balance (Fig. 4). Meanwhile, in deeper waters of the lake (part of the metalimnion and hypolimnion) the pH values were much lower. The confirmation of great differences between biochemical properties of waters in epilimnion and metalimnion was the significant variability of pH values at the borderline of both zones – in 2008 the concentration of $H^+$ ions in the metalimnion was 10 times lower than in the epilimnion ($\Delta pH=1/m$). At the end of vegetation season when in the lake prevailed the processes of mineralization and $CO_2$ release was higher, pH was lower (<7.5).

Alkalinity of the water fluctuated from low and similar values in the whole water column before and after vegetation season (especially in winter) to high and extremely differentiated values in vertical profile during summer stratifi-

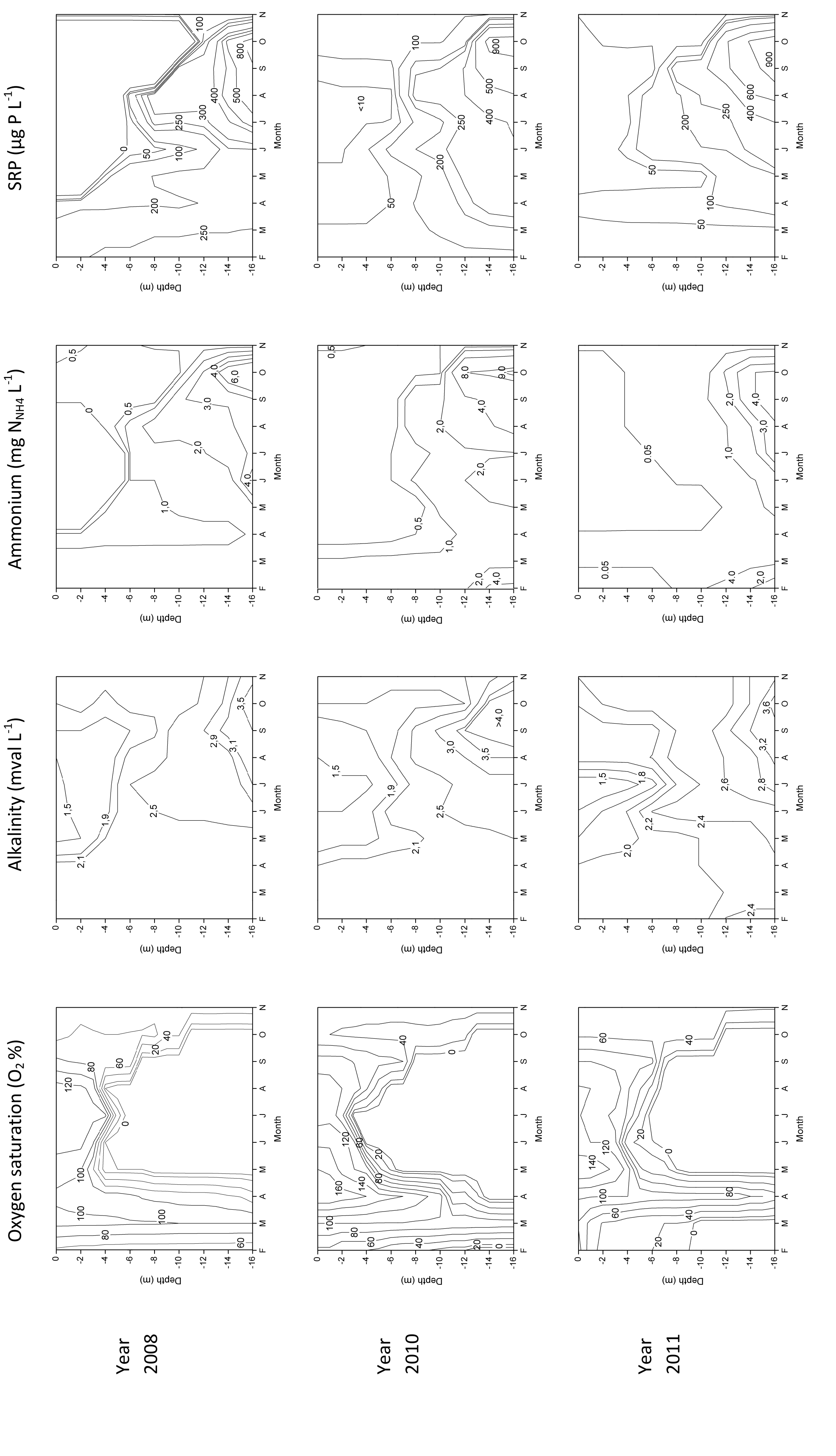


Fig. 4. Vertical distributions of oxygen saturation, alkalinity, ammonium, and soluble reactive phosphorus concentrations in all years of study.

cation (high photosynthesis). The negative and high correlation between the water oxygen saturation and alkalinity indicated the crucial influence of photosynthesis on the decrease of alkalinity – for the entire study period the Pearson coefficient was r=-0.55 (n=269), and exclusively for the vegetation season was r=-0.69 (n=135). The intensive depletion of $CO_2$ from water disturbed the carbonate balance, which shifted toward carbonates precipitated in the form of insoluble calcium carbonate. This phenomenon intensified during the following summer months. The calcium carbonate sedimentation resulted in the increase of alkalinity in the deeper water of the lake with maximum over the bottom in the period before the autumn mixis. This was confirmed by the high correlation between alkalinity and calcium (r=0.67, n=179).

This meant that the direct result of intensive primary production was an increase of calcium carbonate content in bottom sediments. Scientific research of sediment cores confirmed it [40]. However, it should be underlined that higher content of Ca was noted only in the surface (youngest) layers of sediment, which were formed during the period of intensified eutrophication of the lake during sewage inflow [41, 42].

A great influence of photosynthesis on the formation of water chemistry (especially in the case of seasonal and vertical variability of concentrations of mineral forms of nitrogen and phosphorus) was recorded. The predominant form of nitrogen was ammonium nitrogen. With respect to the entire research period of Góreckie Lake, a gradual decrease of $NH_4^+$ concentrations was observed. The average annual concentration in 2008 amounted to 1.26 mg $N \cdot L^{-1}$, in 2010 1.38 mg $N \cdot L^{-1}$, and in 2011 it decreased by half to 0.75 mg $N \cdot L^{-1}$. Relatively high and homogenous in vertical profile content of ammonium ions occurred in winter (Fig. 4), when low water temperature inhibited the processes of biochemical oxygenation of ammonium nitrogen to nitrites and nitrates. Seasonally higher concentrations of $NH_4^+$ were found before the vegetation season. During summer its total depletion, especially in the photic zone, was noted. The statistical analysis for the entire period of study showed a negative and only average relationship between the OS and $NH_4^+$ (r=-0.45, n=269), and higher for the vegetation period (r=-0.55, n=135).

During summer stratification of water the concentrations of $NH_4^+$ were strongly vertically differentiated. In the epilimnion they were totally depleted, while in the metalimnion (and especially in the hypolimnion) its content was very high. The dramatic increase of $NH_4^+$ concentrations was observed in the sub-bottom zone (maximum 9.6 mg $N \cdot L^{-1}$ in October 2010) (Fig. 4). At the same time, a similar phenomenon was observed in the shallow basin of the lake. The quantitative scale of the phenomenon of releasing the ammonium nitrogen to water suggests that it may have a significant influence on the content of TN (highest always in October).

Nitrate as well as nitrite was noted in higher concentrations in autumn and spring when the water was warmer and oxygen content was highest. Maximum content of $NO_3^-$ amounting to 1.6 mg $N \cdot L^{-1}$ were observed in spring 2011, despite the fact that the content of dissolved oxygen in water was low. Lack of nitrates during vegetation season and strong intensification of primary production was stated. The statistical analysis did not show any significant relationship between the oxygen saturation of water and the concentration of nitrate nitrogen. Meanwhile, the year-long study of littoral water chemistry revealed the presence of nitrate ions [43, 44]. This shows that a catchment area has a significant impact on lake water chemistry in a coastal zone, which is difficult to confirm in a pelagial zone.

During the following years of study the content of organic nitrogen in lake water increased slowly – average annual concentrations amounted to 1.56 mg $N \cdot L^{-1}$ in 2008, 1.66 mg $N \cdot L^{-1}$ in 2010, and 2.09 mg $N \cdot L^{-1}$ in 2011. However, in the following years high seasonal fluctuations of maximum concentrations were stated. In the first year the maximum values were recorded at the end of the vegetation season when algae bloom was dying. In spring at the very beginning of the phytoplankton bloom the concentrations of $N_{org}$ were low (0.71 mg $N \cdot L^{-1}$). In the next years the highest concentrations were stated in early spring during the period of high intensity of algae blooms (IV-V). In summer the concentrations were lower, and the second increase occurred as early as the end of summer. The average annual concentrations of TN amounted to 2.82 mg $N \cdot L^{-1}$ in 2008, 3.10 mg $N \cdot L^{-1}$ in 2010, and 3.26 mg $N \cdot L^{-1}$ in 2011.

The mean annual content of bioavailable soluble reactive phosphates (SRP), which stimulate the growth of autotrophic algae in waterbodies, during our research period fluctuated in a small range, from 0.18 mg $PO_4^{3-} \cdot L^{-1}$ in 2008 to 0.16 mg $PO_4^{3-} \cdot L^{-1}$ in 2010 and 0.17 mg $PO_4^{3-} \cdot L^{-1}$ in 2011. Seasonally higher concentrations in winter and early spring were stated (Fig. 4). At the beginning of the vegetation season SRP were fast assimilated by phytoplankton and their concentrations, especially in photic zone, where they decreased to the undetectable level. During summer stratification the higher concentrations were stated in the metalimnion and hypolimnion, where the decomposition of organic matter was intensive. The significant influence of primary production on the SRP content is illustrated by the negative correlation with oxygen – for the entire study period r=-0.48 (n=269), and in the period of highest intensity of photosynthesis r=-0.62 (n=135). The large increase of SRP concentrations as well as ammonium nitrogen and water alkalinity in the second half of summer in the sub-bottom zone was stated. Similar tendencies were observed in other eutrophic lakes [45]. The cause of such a state may be the influence of bottom sediments from which, at the concentration of oxygen below 1 mg $O_2 \cdot L$-1 (in reductive conditions), mineral nutrients are intensively released [46-48], including phosphorus in the exchangeable fraction (chemically bound with iron) and organic compounds [27, 49, 50]. During the autumn mixis of the lake, content of SRP in the whole water column was averaged over. The increase of phosphate concentrations in the surface layer during late autumn was wrongly attributed to the influence of wild geese wintering on the lake [23, 34].

The mass occurrence of phytoplankton (algae blooms) for many years caused the dramatic worsening of organoleptic properties of lake water. This forced the restoration decision to use commonly used methods [51-53]. In 2010 the restoration was carried out on several levels that involved phosphorus inactivation by iron coagulant. The direct effect was a slight decrease of SRP concentrations but also, significantly, changes of vertical stratification of concentrations. In comparison to the earlier years in the summer, higher concentrations were observed in the epilimnion (Fig. 5). Unfortunately, in the next year the concentrations were again higher.

Share of SRP in the pool of total phosphorus was generally low (Fig. 5), and in relation to the entire study period it did not exceed 5% in the epilimnion, 20% in the metalimnion, and 30% in the hypolimnion. The differences were higher in particular years – in the first and last year the participation of SRP reached 20% TP, while in 2010 it increased to 43%. The rise of SRP participation in TP in 2010 resulted from the decreasing of TP concentration due to coagulation and sedimentation to the bottom sediments (after lake restoration). The average annual concentrations of TP in 2008 and 2011 were similar (respectively 0.31 mg $P{\cdot}L^{-1}$ and 0.29 mg $P{\cdot}L^{-1}$), and decreased by around half in 2010 (to 0.16 mg $P{\cdot}L^{-1}$). In the vertical profile of a lake the concentrations were lower in the epilimnion and much higher in the hypolimnion. This resulted from the sedimentation of organic suspension (living and dead biologic material) in the form of detritus containing high concentrations of organic phosphorus, as well as trypton containing adsorbed polyphosphates [16, 49].

The vertical differentiation of water chemistry related to the influence of biocenosis and bottom sediments in the electrolytic conductivity of water also was reflected.

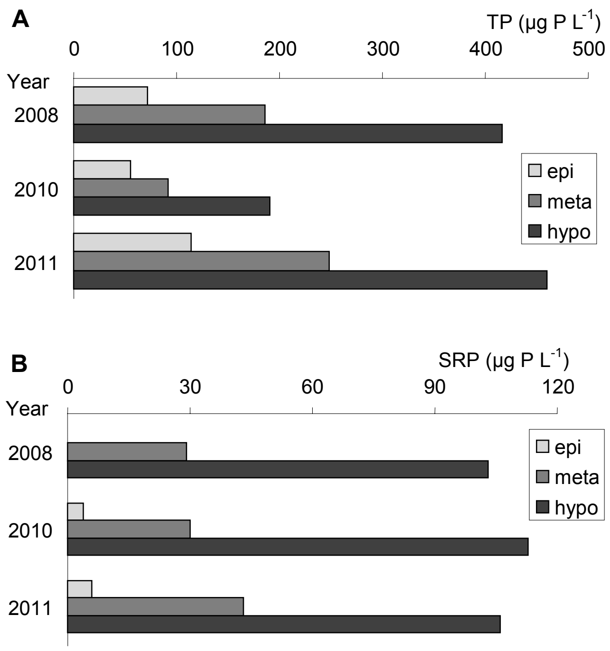


Fig. 5. Vertical variability of total phosphorus (A) and soluble reactive phosphorus (B) concentrations in thermal layers of lake (mean values).

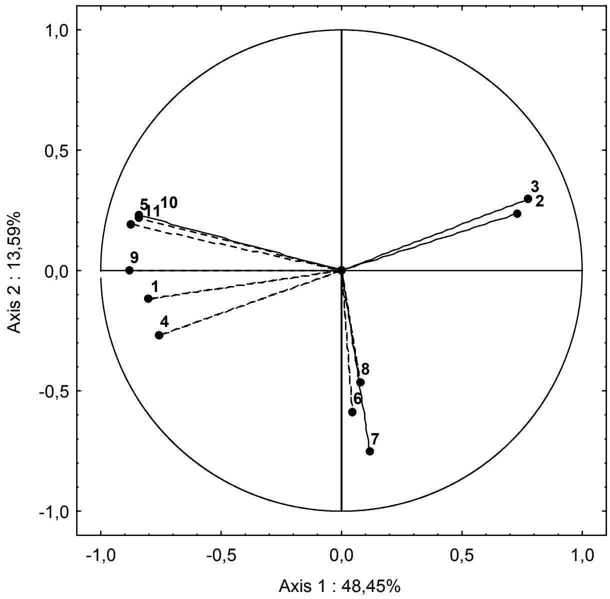


Fig. 6. Principal component analysis of lake and water properties for the entire time of study (symbols: 1 – depth, 2 – oxygen saturation, 3 – pH, 4 – EC, 5 – $NH_4^+$, 6 – $NO_2^-$, 7 – $NO_3^-$, 8 – $N_{org}$, 9 – alkalinity, 10 – TP, 11 – SRP).

From late autumn to early spring (a period of low primary production) values of EC were low and aligned in the whole water column. During that time mineral biogenic elements in dissociated forms dominated in the lake. However, since the beginning of the vegetation season due to assimilation of mineral elements by phytoplankton the EC was significantly lower, especially in the epilimnion. Statistical analysis revealed moderately high negative correlation between EC and oxygen saturation – for the entire study period $r=-0.53$ ($n=269$), and for the vegetation period $r=-0.60$ ($n=135$). In the deeper waters of the lake the EC was higher. A significant increase, especially in the tropholitic zone in the second half of the summer, was observed. This was caused by detritus decomposition and migration of mineral forms of nitrogen and phosphorus from the trophogenic zone. The factor which to a great extent influenced the decrease of EC in the epilimnion was the precipitation of calcium carbonate. In turn a very high increase in EC in the sub-bottom zone, observed at the end of summer and in autumn, was undoubtedly caused by the influence of bottom sediments.

In order to better and more accurately define the correlations between the studied parameters a principal components analysis was conducted. PCA showed that part of physico-chemical properties such as $NH_4^+$, SRP, TP, and alkalinity were closely related. First they were connected through photosynthesis, which caused a decrease in their values and shows the position of the vector of oxygen saturation and pH, revealing the negative correlation with the above components. In turn, their increase was connected with influence of the bottom sediments that show a correlation with depth (Fig. 6).

The photosynthesis was very intensive from May to September. For that period PCA showed stronger than for the whole year, relationships between $NH_4^+$, SRP, and TP

(Fig. 7A). During wintertime when the mineralization of organic matter and the photosynthesis were weaker due to low temperature and less access to sunlight, these relationships also were much weaker (Fig. 7B). Only average correlation of oxygen saturation with $NH_4^+$ and SRP was a consequence of intensive assimilation of both compounds through primary producers. Due to their deficits the primary production and photosynthesis slowly decreased. Oxygen conditions of the lake under the influence of mineralization processes (which eliminate large amounts of oxygen) also were formed. The daily fluctuations of water oxygenation observed in the epilimnion also were of certain importance.

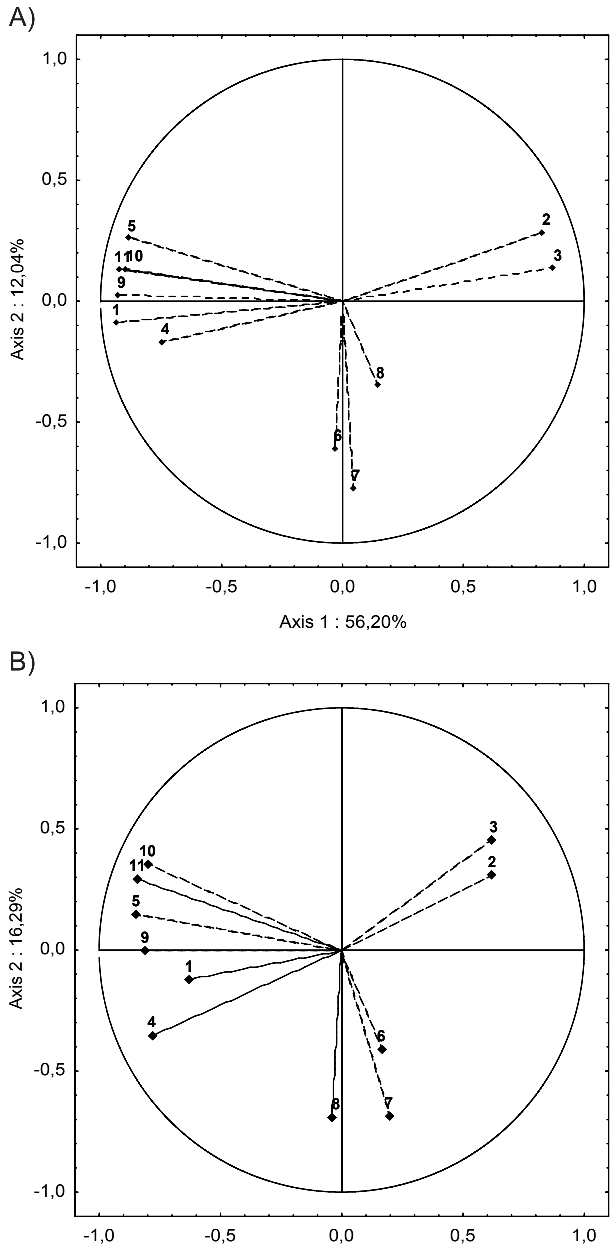


Fig. 7. Principal component analysis of lake and water properties for the vegetation season (A) and for wintertime (B) (symbols: see Fig. 6).

The trophy of Lake Góreckie changed slightly during the research period. The mean value of TSI ranged from 58 in 2008, through 55 in 2010, to 56 in 2011. This means that Góreckie was eutrophic [38]. A comparison of our results with historical data [23, 25, 26, 28, 29, 33] show that a large increase of content of ortophosphates occured, total phosphorus and ammonium nitrogen occurred, plus a decrease of nitrate. The reason is probably the permanent occurrence during summer stagnation, the extensive anaerobic zone, and reduced conditions in the sub-bottom zone, which promotes the release of labile phosphate fractions and ammonium nitrogen from the bottom sediments [48]. Therefore, it is possible to change factors limiting phytoplankton production. Analysis of N:P ratio at the vegetation season (V-IX) revealed high variability of mean annual values and a clear downward trend (from 43 in 2008, 37 in 2010 to 18 in 2011). In 2008 the scatter of N:P ratio was much greater (9-126) than in 2010 and 2011 (28-47 and 15-21, respectively). The lower value of N:P ratio indicates the increasing role of nitrogen in limiting primary production [54].

In the 1970s the lake had significant higher concentrations of calcium. At that time average concentration of calcium in the water column was 38.0 mg $Ca\cdot L^{-1}$, and during our research 48.2 mg $Ca\cdot L^{-1}$. Is is highly probable that the increase in concentrations of calcium was the result of intensive photosynthesis, which intensified together with the trophy increase. This also is suggested by vertical distributions of oxygen content and strong alkalization of the surface water layer. The source of calcium could not be the catchment poor in nutrients and calcium, grey-brown podzolic soils (sand and light loam), and rusty soils (poor loamy and loose sand) transformed from poor quartz sands. The organic layer is very thin (about 2 cm) and depends on vegetation. The humus layer is shallow and has a thickness less than 20 cm. Its composition is characteristic of sandy dusts. The upper levels of soil profile are either acid or faintly acid [27]. The lake is surrounded by pine-oak forest (Pino-Quercetum) and on the areas closer to the lake (more humid and fertile loam soil) grows an oak-hornbeam forest. The agricultural areas situated in the catchment are separated from the lake by a natural buffer zone that minimizes their influence (uptake of surface runoff).

Due to very bad oxygen conditions a restoration was conducted in the lake in 2010. This procedure involved the aeration of the hypolimnon zone (in deepest spot in the southern basin), coagulation of phosphates by the addition of small amounts of ferric coagulant, and removing 3 tons of plankton-eating fish [21]. In the same year the improvement of the lake state was not found. The above-mentioned increase in water transparency in 2011 suggests the improved quality of the lake water, most probably connected with the influence of biomanipulation. The reduction of the fish population decreased eating pressure on zooplankton, which could more efficiently control the phytoplankton [55]. Higher concentrations of mineral forms of nitrogen and phosphorus in the euphotic zone also was stated. However, water oxygenation was not better.

## Conclusions

1. Abiotic features of water in a eutrophic lake, especially bioavailability of mineral nutrients, provide good conditions for functioning of the lake biocenosis. However, a key significance for seasonal and vertical changeability of water chemistry had primary production via photosynthesis. Intensive assimilation of mineral compounds (C, N, P) during the period of highest spring intensity of photosynthesis caused a decrease of their concentrations to the trace level.
2. Intensive photosynthesis disturbed the carbonate balance. The result of depletion of the carbon dioxide was bicarbonate transformation into carbonates, precipitated in the form of sparingly soluble calcium carbonate. This caused alkalization, decalcification, and a decrease of alkalinity of the epilimnion zone and, simultaneously, an increase of calcium concentrations and alkalinity in the sub-bottom zone. This confirm the studies of bottom sediments that indicated the higher content of calcium in the surface zone of sediments in comparison to deeper sediments formed during the period of lower trophy of the lake.
3. The consequence of abundant primary production was a strong shading of water and shallowing of the illuminated zone. In vegetation season, the epilimnion was oversaturated with oxygen due to intensive photosynthesis. In metalimnion and hypolimnion of dissolved oxygen deficits (anoxia) were almost always noted, which indicated a high consumption by deposited organic matter and/or by reduced substances released from the bottom sediments. After depletion of nutrients in epilimnion the depth of light zone was increased, but this did not result in improvement of oxygenation of water in deeper layers of the lake.
4. Before the autumn mixis the highest concentrations of ammonium nitrogen and phosphates in the sub-bottom layer of the lake were stated. A common explanation of this phenomenon is intense sedimentation and mineralization of fresh organic material (mainly the dead phytoplankton). In the case of Góreckie Lake, which is supplied mainly from groundwater, this may partly result from inflow of interstitial waters rich in mineral compounds, introduced into the lake with groundwaters passing through the bottom sediments. However, this hypothesis requires further research.

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