

**LONG-TERM HYDROCHEMICAL CHANGES
IN A LAKE AFTER THE APPLICATION OF SEVERAL
PROTECTION MEASURES IN THE CATCHMENT**

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Key words: lake, eutrophication, protection techniques, water quality.

Abstract

A study was conducted on Wulpińskie Lake (706.7 ha, 54.6 m), located in north-eastern Poland. In the middle of the twentieth century, the lake began to be subjected to accelerated eutrophication due to excessive pressure from recreation and an inflow of sewage and pollution from leaky septic tanks and putrefactive reservoirs. The protective actions begun in the basin in 1996 resulted in a 77% reduction in phosphorus load and 28% reduction in nitrogen load. In 2008, mineral phosphorus and TP concentrations averaged 0.1 mg L^{-1} and 0.16 mg L^{-1} , respectively, and the TN concentration was 0.84 mg L^{-1} . In addition, chloride and calcium concentrations declined and electrical conductivity subsequently decreased.

**DŁUGOTERMINOWE ZMIANY HYDROCHEMICZNE W JEZIORZE PO ZASTOSOWANIU
ZABIEGÓW OCHRONNYCH ZLEWNI**

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Słowa kluczowe: jezioro, eutrofizacja, techniki ochrony, jakość wody.

Abstract

Badania przeprowadzono na Jeziorze Wulpińskim (706,7 ha, 54,6 m), zlokalizowanym w północno-wschodniej Polsce. Jezioro to od lat 50. XX w. zaczęło podlegać przyspieszonej eutrofizacji z powodu nadmiernej presji turystycznej i rekreacyjnej oraz dopływu ścieków i zanieczyszczeń z nieszczelnych szamb i zbiorników gnilnych. W 1996 r. rozpoczęto działania ochronne w zlewni.

Ładunek fosforu wprowadzany do jeziora zredukowano o 77%, a ładunek azotu o 28%. Spowodowało to bardzo wyraźną i trwałą poprawę jakości wody. W 2008 r. średnia koncentracja fosforu mineralnego wynosiła: $0,1 \text{ mg P} \cdot \text{L}^{-1}$, a fosforu ogólnego $0,16 \text{ mg P} \cdot \text{L}^{-1}$, natomiast azotu ogólnego oscylowała wokół $0,84 \text{ mg N} \cdot \text{L}^{-1}$. Zmniejszało się ponadto stężenie chlorków i wapnia oraz wartości przewodności elektrolitycznej.

Introduction

Lakes with high inflow of minerals and organic compounds from catchments have an elevated risk for eutrophication (JORGENSEN 2001, CARPENTER 2008; FRATERRIGO and DOWNING 2008, ISTVÁNOVICS 2009). The pace of this process can be influenced by many factors, such as the morphometry of the basin and the geological and hydrological systems and features of the catchment (MALMAEUS and HÅKANSON 2004). Under natural conditions, this process will be slow and prolonged. However, human civilization has made a significant contribution to the degradation of water and eutrophication acceleration. Lakes adjacent to urban and agricultural areas, in particular, are usually eutrophicated due to receiving municipal sewage and industrial wastewaters (WANG et al. 2012) and nutrients from leaky septic tanks and agriculture (LI et al. 2007).

Accelerated eutrophication has prompted a search for effective remediation methods, involving the protection of endangered lake basins and reservoirs and the recultivation of those that have already been degraded (JEPPESEN et al. 2007, CASTILLO 2010, FRIESE et al. 2010). COOKE et al (2005) and KLAPPER (2003) provide many solutions for eliminating or reducing external sources of nutrients (protection of lakes) and the technical and chemical methods carried out on the lakes (lakes recultivation). However, many years of experience have shown that the most important and fundamental role in the improvement of the aquatic environment are the protective methods carried out in catchment (FRISK and BILALETIDIN 2001, DUNALSKA 2003, GAWROŃSKA and LOSSOW 2003, REYNOLDS 2003). These activities are arduous, lengthy and not very spectacular, but a reduction in the external load from the catchment can help to prevent the use of expensive recultivation, and improve the efficiency of agriculture and industry by eliminating the leakage of essential nutrients as well as other chemicals and materials.

The first and most important protective method is to cut off the flow of sewage into the lake and redirect its flow beyond the catchment area. In addition, leaky septic tanks and other uncontrolled discharges of pollutants should be identified and eliminated. If lakes are surrounded by agricultural areas, it may be necessary to change the land use practices in the catchment and reduce the amount of arable land in favor of grassland.

Wulpińskie Lake (north-eastern Poland, Olsztyn Lake District) is an example of a water body in which the protective treatments have caused improvements in water quality and other environmental conditions. This lake eutrophicated in the middle of the twentieth century due to excessive nutrient inflow which, in turn, was a result of an increase in wastewater entering the lake due to intensified recreation in the area and the subsequent effect on water quality, including leaks from septic tanks and putrefactive reservoirs.

In 1996, protection actions were started in the basin. In the first stage, the sewerage system was expanded and the localities and recreational centers around the lake were connected to the sewage system. Wastewater was redirected beyond the catchment of the lake. Through this method, the scattered sources of nutrients were eliminated. The next step was to eliminate the discharge of pre-treated wastewater to Wulpińskie Lake. That was done by redirecting the pre-treated wastewaters to the sewage system of Olsztyn, the capital of the region.

Until 1996, before the protective measures in the catchment of Wulpińskie Lake, the lake was affected by $1.6 \text{ tons} \cdot \text{a}^{-1}$ of phosphorus and $> 13 \text{ tons a}^{-1}$ of nitrogen, i.e. $0.24 \text{ g m}^{-2} \text{ a}^{-1}$ of P and $1.99 \text{ g m}^{-2} \text{ a}^{-1}$ of N. As a result, Wulpińskie Lake had high concentrations of P and N, which is characteristic for eutrophic water bodies (HAVENS et al 2001).

This study demonstrated that after reducing external nutrient loading to the lake, essential (apparently long-term) improvements in water quality were achieved.

Material and methods

Wulpińskie Lake ($53^{\circ}42.4' \text{ N}$, $20^{\circ}22.1' \text{ E}$) is situated at a height of 106.04 m. The area of the water body is 706.7 ha and its maximum depth is 54.6 m (Table 1) (CHOIŃSKI 2008). The lake has two basins: eastern – Tomaszowska and western – Barwińska, which have different morphometric features. The basins are inter-connected by a narrow isthmus with a width of 60 m and a depth of 3.8 m. The western basin is a deep, elongated gutter. In this part of the lake bottom there are four distinct hollows. The eastern basin has a wheel-like shape and seven islands. The largest of these are Herta, Mewa and Urbanki. There are a few small inflows to the lake and Gilwa River which flows into the western bay from the SE and flows out in NW. The catchment area of the lake is 82.8 km^2 and the immediate catchment is 7.0 km^2 . Areas bordering the reservoir are mainly barren land (62.4%), forests (16.7%), buildings (10.4%) and arable land (5.7%).

Table 1

Basic morphometric data of Wulpińskie Lake

Morphometric parameter	Value
Surface area	706.7 ha
Maximum depth	54.6 m
Average depth	10.9 m
Relative depth	0.0205
Depth index	0.19
Water volume	76990300 m ³
Maximum length	8321 m
Maximum width	2330 m
Elongation	3.6
Average width	849 m
Length of shoreline	24250 m
Shoreline development	3.4

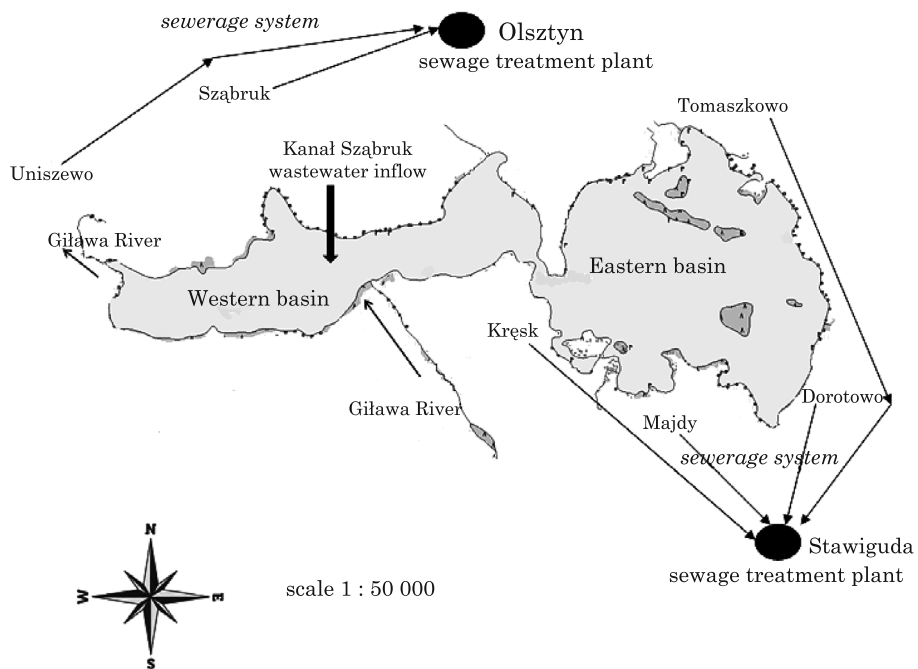


Fig. 1. Research area

Until 2002, Wulpińskie Lake received pre-treated municipal wastewater from the towns of Unieszewo ($26.0 \text{ m}^3 \text{ d}^{-1}$) and Sząbruk ($28.0 \text{ m}^3 \text{ d}^{-1}$). Sewage flowed into the western basin via a stream called Kanał Sząbruk. In order to protect the lake, in 2002, a 20-km collector was built and wastewaters were redirected to sewage treatment plants in Olsztyn.

The lake is surrounded by the towns of Tomaszkowo (population – 584), Dorotowo (population – 391), Majdy (population – 125) and Kręsk (population – 26) (Figure 1). In the catchment of the eastern basin there are also 18 recreational complexes, four holiday resorts and two camp sites. Towns adjacent to the lake and recreation areas were not connected to a sewage system. However, the loading of these sources was eliminated between 1996–1998, when the lake was encircled by a sewerage network and the buildings around the lake were connected to it. Later on, sewage was discharged into a modernized sewage treatment plant in Stawiguda, outside the catchment area of Lake Wulpińskiego (Figure 1).

Water samples for chemical analyses were collected at two stations located at the deepest point of two basins of Wulpińskie Lake. Station 1 was located in the eastern basin (20 m) and station 2 in the western basin (54 m). Samples were taken from a depth of 1 m below the surface and 1 m above the bottom. A chemical analysis was conducted according to the guidelines given in Standard Methods (1999). Electrical conductivity was measured with a WTW MultiLine F/SET – 3, mineral phosphorus was determined with ammonium molybdate and ascorbic acid by a MACHEREY-NAGEL NANOCOLOR UV/VIS spectrophotometer, total phosphorus was determined after digestion with sulfuric acid and potassium persulfate with ammonium molybdate and ascorbic acid by a MACHEREY-NAGEL NANOCOLOR UV/VIS spectrophotometer, ammonium nitrogen was determined by Merck SQ 118 spectrophotometer, total nitrogen was determined by HACH TOC-TN IL 550 carbon and nitrogen analyzer, and calcium, magnesium and chloride were determined by DIONEX DC ICS 5000 ion chromatography.

A one-way ANOVA, $p=0.05$, post-hoc Tukey was used for statistical analyses using Statistica 9.0. The alternative hypothesis tested was based on statistically significant differences of mean concentrations of P and N compounds, Ca, Cl and the values of conductivity between the control year (1992) and the experimental years (1999, 2008), i.e. after application of protection techniques in the catchment.

Results

The results showed that the use of protection techniques did not cause any significant changes in P concentrations in the surface layer of Wulpińskie Lake (Table 2). Before and after the protective actions, inorganic P concentrations varied in surface water from <0.05 to 0.108 mg L^{-1} and TP from 0.020 to 0.180 mg L^{-1} . The average values fluctuated around 0.045 mg L^{-1} (inorganic P) and around 0.076 mg L^{-1} (TP) (Figure 2, Figure 3). However, bottom water P concentrations were different before and after measures (Table 2); before the protection measures inorganic P concentrations averaged 0.238 mg L^{-1} and total P 0.384 mg L^{-1} (Figure 2, Figure 3) while five years after the end of protection measures, in 2008, the mineral P concentration was 0.106 mg L^{-1} and TP was 0.157 mg L^{-1} .

Table 2
Results of one – way ANOVA analyses (with Tukey HSD) for investigated variables in Wulpińskie Lake water

Variable	<i>F</i> value	<i>p</i> value	Years which differed significantly from 1984 (before the application of protection techniques in the catchment)
P _{min.} surface	0.931894	0.401273	–
P _{min.} bottom	4.101017	0.023115	1992, 2008
TP surface	0.227555	0.797389	–
TP bottom	4.816231	0.012724	1992, 2008
N _{min.} surface	0.839057	0.438766	–
N _{min.} bottom	4.540644	0.015985	1992, 2008
TN surface	21.43367	0.000000	1992, 1999, 2008
TN bottom	13.52575	0.000025	1992, 1999, 2008
Chlorides surface	1652.200	0.000000	1992, 1999, 2008
Chlorides bottom	1076.976	0.000000	1992, 1999, 2008
Calcium surface	11.58936	0.000087	1992, 1999, 2008
Calcium bottom	43.71172	0.000000	1992, 1999, 2008
Conductivity surface	95.2324	0.000000	1992, 1999, 2008
Conductivity bottom	176.9345	0.000000	1992, 1999, 2008

Along with P, no changes in inorganic N concentrations in the surface water layers (on average 0.056 mg L^{-1}) were found (Figure 4, Table 2), but deep water concentrations decreased from $0.560 \text{ mg} \cdot \text{l}^{-1}$ to 0.165 mg L^{-1} (Figure 4). Correspondingly, before the protective measures in the surface water,

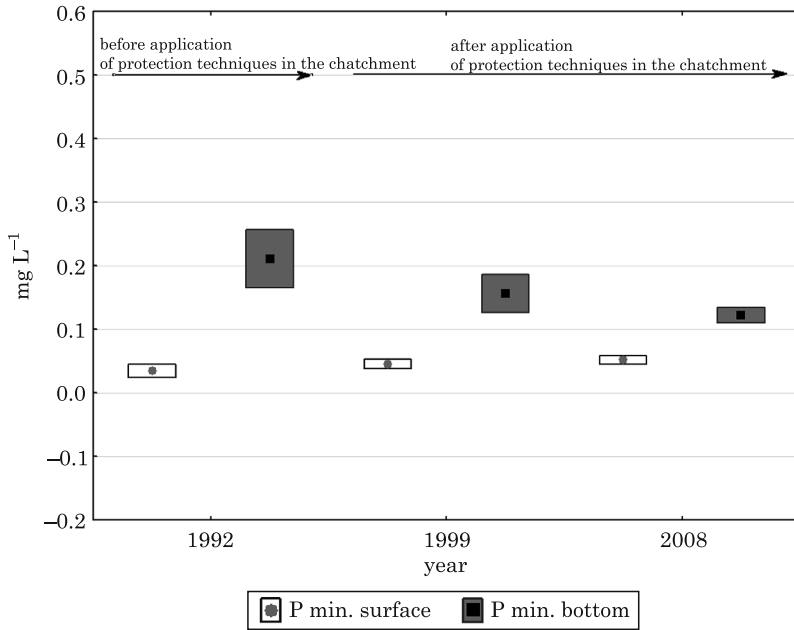


Fig. 2. Mean annual concentrations of phosphate – phosphorus (\pm SEM and SD) in the water of Wulpińskie Lake

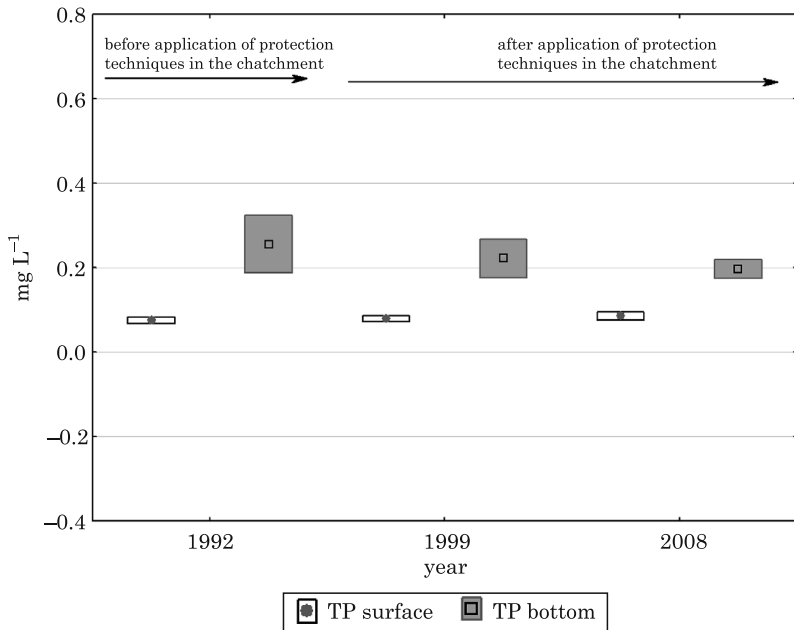


Fig. 3. Mean annual values of total phosphorus content (\pm SEM and SD) in the water of Wulpińskie Lake

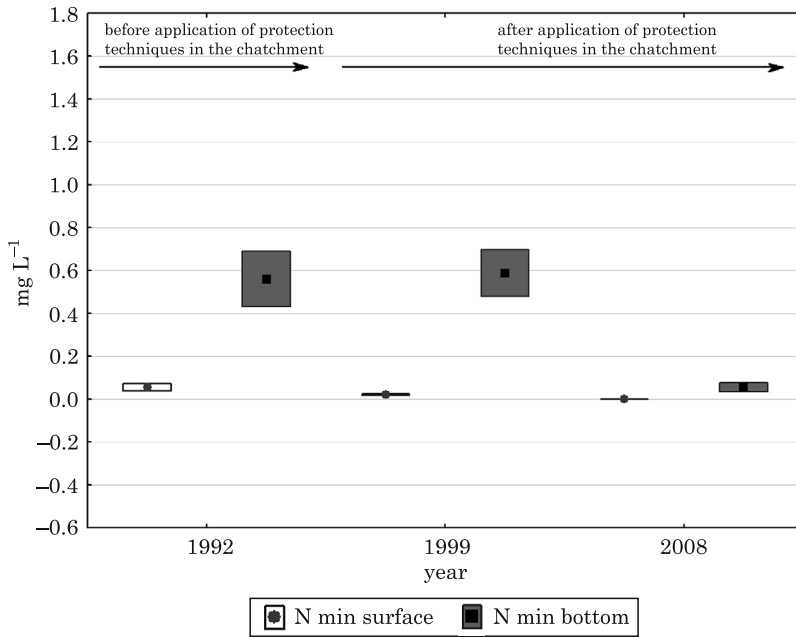


Fig. 4. Mean annual values of mineral nitrogen content (\pm SEM and SD) in the water of Wulpińskie Lake

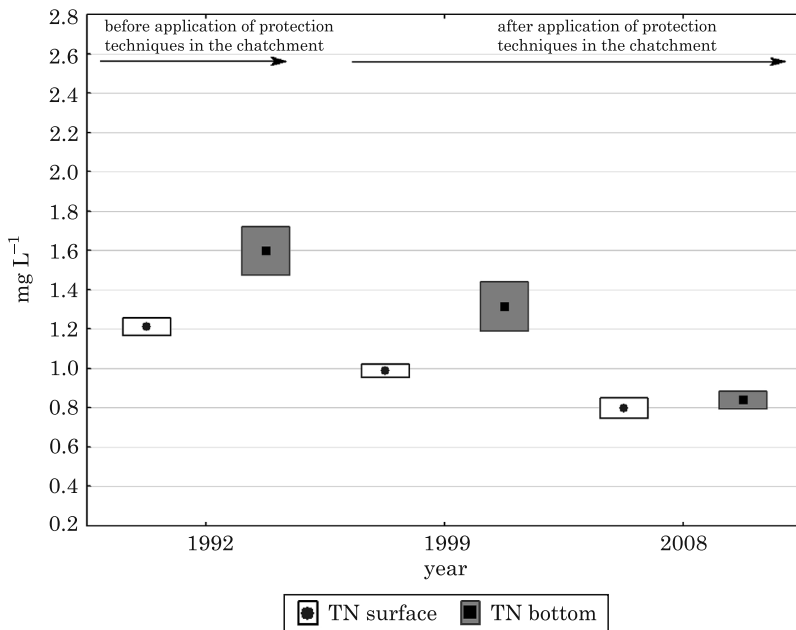


Fig. 5. Mean annual values of total nitrogen content (\pm SEM and SD) in the water of Wulpińskie Lake

the mean concentration of TN was 1.21 mg L^{-1} and above the bottom 1.60 mg L^{-1} , respectively, while after the end of the measures the concentrations were significantly lower, i.e. 0.80 mg L^{-1} and 0.84 mg L^{-1} (Figure 5).

The results revealed a clear change in chloride concentration as well (Table 2); before the protection measures the average concentration was 33.8 mg L^{-1} (Figure 6), and after it was 16.8 mg L^{-1} . Five years after the end of the measures, a further reduction was found – the concentrations varied between 14.5 mg L^{-1} to 14.3 mg L^{-1} (Figure 6). Clear differences in calcium concentrations were also found (Figure 7). In parallel with the above results, significant differences in electrical conductivity were found (Table 2). Before the protection measures, the mean value on the surface was $284 \text{ }\mu\text{S L}^{-1}$ and above the bottom it was $315 \text{ }\mu\text{S L}^{-1}$, respectively. In 2008, the respective values were $201 \text{ }\mu\text{S L}^{-1}$ and $210 \text{ }\mu\text{S L}^{-1}$ (Figure 8).

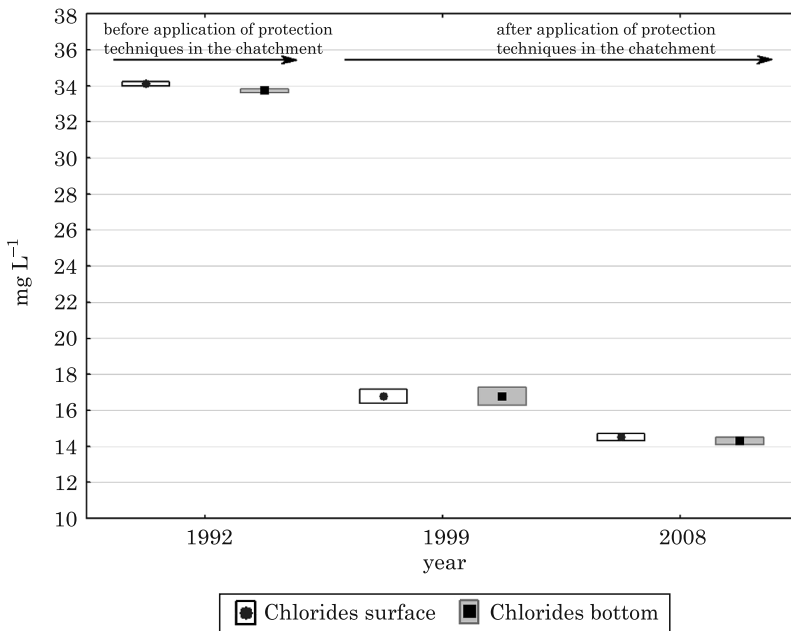


Fig. 6. Mean annual values of chloride content (\pm SEM and SD) in the water of Wulpińskie Lake

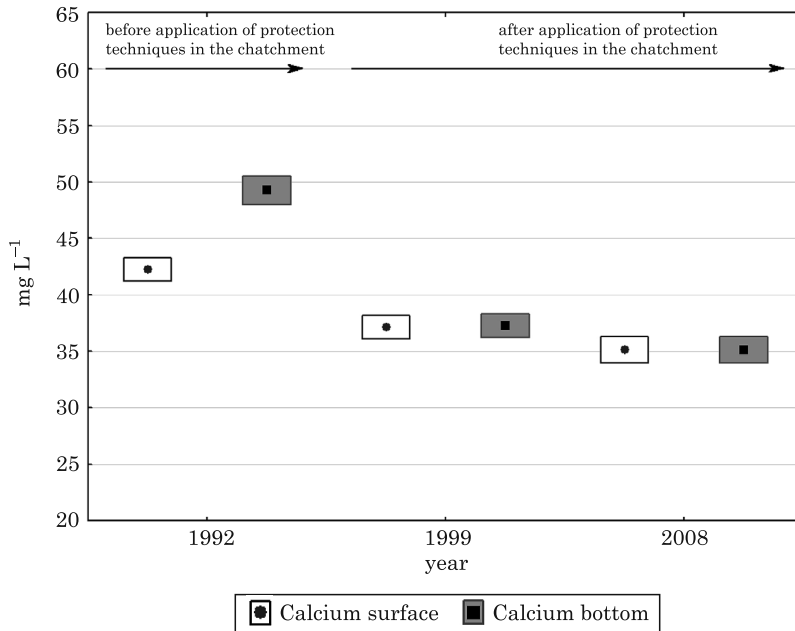


Fig. 7. Mean annual values of calcium content (\pm SEM and SD) in the water of Wulpińskie Lake

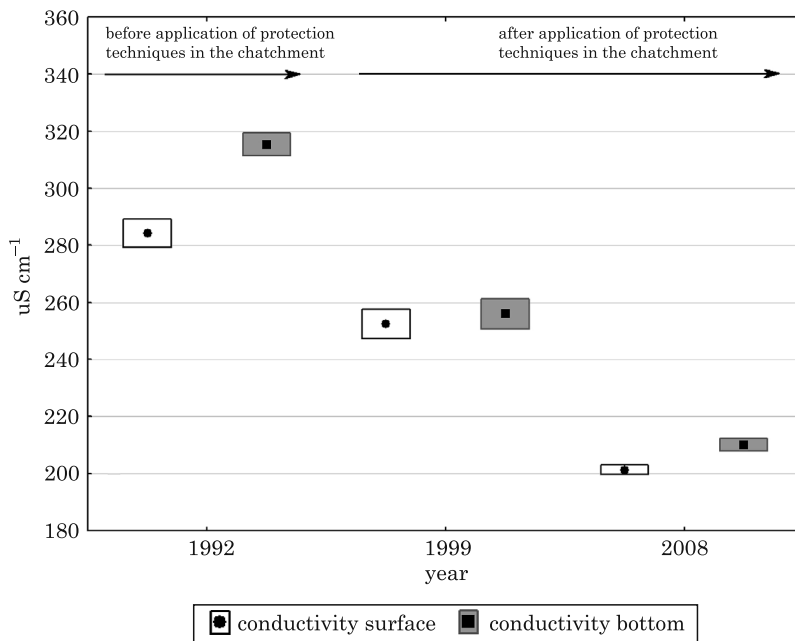


Fig. 8. Mean annual values of water conductivity (\pm SEM and SD) of Wulpińskie Lake

Discussion

According to KUBIAK and TÓRZ (2005) and GROCHOWSKA and TANDYRAK (2007), the quantity of nutrients in an aquatic ecosystem depends not only on their external load, but also on long-term accumulation to sediments. SCHINDLER and FEE (1974) have stated that lake sediments act as nutrient „trap” until their sorption capacity is depleted. In lakes with high trophic state and oxygen depletion in the near-bottom zone, sediments may act as a significant P source and become the cause of secondary pollution (HICKEY and GIBBS 2009, LIM and CHAI 2011). The substances stored in sediments may have a harmful impact on lake water for a long time. The wastewater inflow to Wulpińskie Lake and the bottom water oxygen depletion may be conducive to the removal of P to the bottom sediments. The anoxic conditions may also limit the nitrification of ammonia, which was produced in the decomposition of organic matter.

In moderately eutrophic lakes, P and N cycles are regulated largely by phytoplankton and during its maximum development, inorganic P concentration may decrease below to the detection limit of standard analytical methods (GOLTERMAN 1975). The results showed that despite the external load, P was lowered by 77% and N by 28%, in the surface water layers there was no clear change in total phosphorus or total nitrogen concentrations relative to the time-period before the treatments. The decrease in TP was caused mainly by the decrease in inorganic P concentration. Micro-organisms play a key role in the transformation of N compounds; their activity depends on many factors, and ammonification, for example, can take place under both aerobic and anaerobic conditions across wide pH and temperature ranges (DUNALSKA et al. 2012). The intensity of the process ultimately depends on the activity of microbes. According CERCO (1989) and HÖHENER and GÄCHTER (1994), the release of ammonium-N from lake sediments is correlated with temperature. As already stated, $\text{NH}_4\text{-N}$ concentrations in Wulpińskie Lake were very high before the protection measures (up to 1.5 mg L^{-1}). Improving the oxygen conditions in deeper waters resulted in $\text{NH}_4\text{-N}$ oxidation to $\text{NO}_3\text{-N}$ and a rapid decrease in $\text{NH}_4\text{-N}$ concentration.

Non-contaminated Polish surface water typically has up to 15 mg L^{-1} of chlorides (PASCHALSKI and OLSZEWSKI 1959), which is < 50% of the level found in Wulpińskie Lake prior to 1992. However, in 2008 Cl concentrations were only c.a. 13 mg L^{-1} (Figure 6). Respectively, calcium concentrations usually vary in Polish lakes between $25\text{--}75 \text{ mg L}^{-1}$ (KOLADA et al 2005), and we found very similar concentrations in Wulpińskie Lake as well. KOWALSKI (1997) suggested that Ca concentrations in surface waters are influenced by processes occurring in the presence of organic pollutants introduced with sewage. In the

surface layer, there was a distinct minimum of calcium during the summer stagnation, which coincided with the highest concentrations of chlorophyll *a* and the lowest water transparency. This relationship seems to be associated with the biological decalcification of water during high photosynthesis and the absence of free carbon dioxide (HÅKANSON et al 2005). The resulting calcium carbonate falls to deeper layers of the lake, causing an increase in metal ions at the bottom. After cutting off the external load, calcium concentrations decreased substantially (Figure 7). In good agreement with Ca and Cl results and the results of MARSZELEWSKI (2005), electrical conductivity values decreased significantly after the protection measures in Wulpińskie Lake (Figure 8), which strongly suggests essential improvements in water quality.

Conclusions

The results showed that a radical reduction in external loading resulted in a decrease in nutrient (P, N, Cl and Ca) concentrations in lake water. At the same time, the results indicate that nutrients were released from the bottom sediments of the lake. Along with the above, electrical conductivity decreased substantially relative to the prior water protection measures.

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