J. Elem. s. 1099–1108 DOI: 10.5601/jelem.2014.19.1.294

CONTENT OF PHOSPHORUS AND SELECTED METALS IN BOTTOM SEDIMENTS OF STARZYC LAKE UNDER CONDITIONS OF PULVERIZING WATER AERATION

Hanna Siwek[1], Piotr Wesołowski[2], Adam Brysiewicz[2]

[1]Department of General and Ecological Chemistry
West Pomeranian University of Technology in Szczecin
[2]West Pomeranian Research Centre in Szczecin
Institute of Technology and Life Sciences

Abstract

Artificial aeration of benthic water is a method promoting more intensive phosphorus bonding in bottom sediments. The purpose of this paper was to evaluate changes in the content of phosphorus and some selected metals in the bottom sediments of Starzyc Lake in relation to changes occurring in some quality parameters for the benthic water. During the research, conducted in 2005, 2006 and 2009, the lake water was aerated with a pulverizing aerator. Water and the bottom sediment were sampled in seven sites distributed uniformly throughout the water surface, the inflow area and the area of the lake water outflow to the Krąpiel River. The bottom sediments were analyzed for the total content of P, Ca, Mg and K, while the water samples were tested for pH and the levels of phosphate phosphorus ($P-PO_4$)

In the period covered by the research, the TP content in the bottom sediments of Starzyc Lake decreased only in the inflow area (by a mean of 43%). Additionally, a gradual decrease of the $P-PO_4$ concentration (on average by 42%) in the benthic water was recorded in that period as well as a decrease in the content of Ca, Mg and K in the bottom sediments. The results from the analysed metal content show that the Ca content was most stable, decreasing by an average 21%, whereas the difference for the Mg and K content was 64% and 56%, respectively. The horizontal variability in the content of the analysed elements was found in the bottom sediments collected from various zones of the lake. The lowest content was found in the sediment material collected from the outflow zone of water to the Krąpiel River, and the highest one was recorded in the watercourse inflow zone. The highest variability was observed for the content of Ca and K, which on average was six times higher in the water inflow zone from drainage ditches than in the outflow zone. Throughout the research period, the bottom sediments comprised an indigenous source of phosphorus for the Starzyc Lake waters.

Key words: lake eutrophication, bottom sediment, benthic water, phosphorus, artificial aeration.

dr hab. inż. Hanna Siwek, Department of General and Ecological Chemistry, West Pomeranian University of Technology in Szczecin, J. Słowackiego 17, 71-434 Szczecin, Poland, e-mail: hanna.siwek@zut.edu.pl

ZAWARTOŚĆ FOSFORU I WYBRANYCH METALI W OSADACH DENNYCH JEZIORA STARZYC W WARUNKACH PULWERYZACYJNEGO NAPOWIETRZANIA WODY

Abstrakt

Jedną z metod intensyfikacji wiązania fosforu w osadach dennych jest sztuczne napowietrzanie wód strefy naddanej. Celem pracy była ocena zmian zawartości fosforu i wybranych metali w osadach dennych jeziora Starzyc, którego wody napowietrzano za pomocą aeratora pulweryzacyjnego, na tle zmian wybranych wskaźników jakości wody strefy przydennej. Badania prowadzono w ciągu 3 sezonów wegetacyjnych, w latach 2005, 2006 oraz 2009. Próbki wody i osadu dennego pobrano w 7 punktach rozmieszczonych równomiernie na całej powierzchni jeziora oraz w strefie zasilania i w strefie odpływu wód jeziornych do rzeki Krąpiel. W osadach dennych oznaczono zawartość ogólną: TP, Ca, Mg i K, a w próbkach wody – pH oraz stężenie fosforu fosforanowego ($P\text{-}PO_4$).

W okresie badań zawartość TP w osadach dennych jeziora Starzyc zmniejszyła się istotnie tylko w strefie dopływu (średnio o 43%). Stwierdzono także sukcesywne zmniejszanie się (średnio o 42%) stężenia $P\text{-}PO_4$ w wodzie przydennej oraz zawartości Ca, Mg i K w osadach dennych. Spośród badanych metali najbardziej stabilna była zawartość wapnia, która zmniejszyła się średnio o 21%, a w przypadku Mg i K różnice te wynosiły odpowiednio 64% i 56%. Stwierdzono horyzontalną zmienność zawartości badanych pierwiastków w osadach dennych pobranych w różnych strefach jeziora. Najmniejsze z tych zawartości oznaczono w materiale dennym pochodzącym ze strefy odpływu wód do rzeki Krąpiel, a największe – w strefie dopływu cieków wodnych. Największą zmienność stwierdzono w przypadku zawartości Ca i K, była ona średnio 6-krotnie większa w strefie dopływu wód z rowów melioracyjnych w porównaniu z zawartością w strefie odpływu. Przez cały okres badań osady denne jeziora Starzyc stanowiły autochtoniczne źródło fosforu.

Słowa kluczowe: eutrofizacja jezior, osad denny, woda przydenna, fosfor, sztuczne napowietrzanie.

INTRODUCTION

Studies on the causes and rates of increased lake eutrophication have shown that the phosphorus content is one of the main factors controlling the development of phytoplankton. Excess phosphorus compounds in aquatic ecosystems are withdrawn by sedimentation mainly to bottom sediments, which constitute an almost inexhaustible source of phosphorus in a water body (Koc, Skwierawski 2003).

One of the methods for decreasing the rate of eutrophication of lakes is artificial aeration of benthic waters, which allows quick improvement of aerobic conditions in near-bottom water layers and limits the release of phosphate ions from bottom sediments to water (Gawrońska, Lossow 2003, Osuch, Podsiadłowski 2012). The efficiency of lake reclamation by artificial aeration is to a large extent dependent on the sorptive capacity of bottom sediments (Gawrońska, Brzozowska 2005). It can be enhanced with chemical methods, which are more often being used along with the artificial aeration of water (Osuch, Podsiadłowski 2012). Water can be aerated using pneumatic aerators, which inject air into water, or pulverizing aerators, which spray water into the air. The latter solution is used more often in lake reclamation. Pulverizing aerators have high specific capacity and their construction allows the use of renewable energy sources. The use of wind-driven pulverizing aerators is the most popular method of lake reclamation in Poland. A pulverizing aerator is characterised by a straightforward design, invulnerability to changing wind direction and high resistance to water pollution (Konieczny, Pieczyński 2006, Osuch, Podsiadłowski 2012).

The purpose of this paper was to evaluate changes in the content of phosphorus and some selected metals in the bottom sediments of Starzyc Lake in relation to changes occurring in some selected quality parameters for the benthic water. During the research, the lake water was aerated with a pulverizing aerator.

MATERIAL AND METHODS

The object of study

Starzyc Lake is a natural lake located in Ińsko Lakeland (Chociwel commune) in West Pomeranian Region. The lake belongs to the Ińsko Nature Refuge (PLB320008) and has the following morphometric parameters:

- water table - 59.2 ha,
- mean depth - 2.7 m,
- maximum depth - 6.1 m,
- maximum length - 1,960 m,
- maximum width - 370 m,
- shoreline length - 5,175 m.

Starzyc Lake is a polymictic lake supplied with influent water from drainage ditches, while the Krąpiel is its effluent river (Figure 1). The ecological state assessment by the Regional Inspectorate of Environmental Protection in Szczecin shows that – according to abiotic typology – Starzyc Lake belongs to category 3b, meaning it is a large, unstratified aquatic ecosystem with a high calcium content (>25 mg Ca dm^{-3}), highly influenced by the basin Shindler coefficient >2 (Bajkiewicz-Grabowska 2010). The assessment of the lake's susceptibility to degradation shows that this lake falls outside any category, i.e. it is characterised by the lack of any resistance to degradation. The town of Chociwel located on the northwest shore of the lake has been operating its own mechanical-biological wastewater treatment plant since 1990. However, in some parts of the town, a combined sewage system is still in use. Both the treatment plant and the combined sewage system need to be modernised and expanded.

The first attempt to rehabilitate Starzyc Lake using a pulverizing aerator with the capacity of 200-800 m^3 day^{-1} was made in 2003, and in May 2004, the first dose of coagulant was used as an experiment (Konieczny,

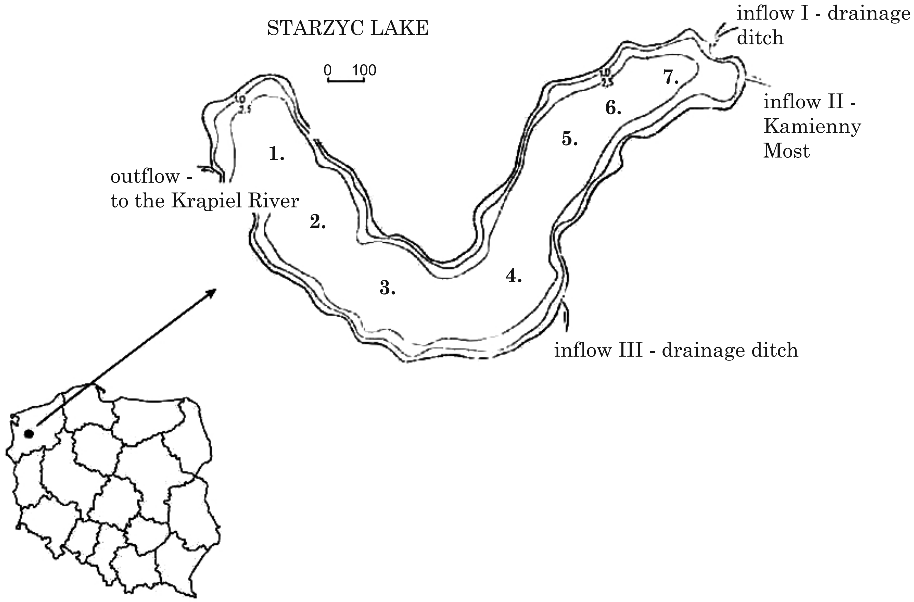

Fig. 1. Arranging of the research points on the Lake Starzyc

PIECZYŃSKI 2006). From 2008 to 2009, PIX1 13 coagulant was used over the whole area of the lake (WESOŁOWSKI et al. 2011).

Field research and chemical analysis

The study was carried out in 2005, 2006 and 2009, and included taking three samples of bottom sediments and near-bottom water each autumn. The measuring stations were located in the zone of the water supply from drainage ditches (point 7), t five sites were evenly distributed in the lake (points 2-6), and one site was located in the zone of effluent waters of the lake to the Krąpiel River (point 1) – Figure 1. The samples of water were obtained with the use of a submersible Gigant pump (Geomor-Technik). The bottom sediment samples were taken using a universal probe, Multisampler (Eijkellkamp), which enables obtaining the maximum 30 cm core sediment sample of intact structure. The sample cores were then split into layers of 10 cm.

The air-dry sediment samples were ground, sifted on a 1-mm mesh size sieve, mineralized in acid mixture of HNO_3 and $HClO_4$ and analysed. The total content of Ca, Mg and K in the prepared samples was determined with the use of atomic absorption spectrometry, while total phosphorus (TP) was assayed with spectrophotometric methods (GOŁACHOWSKA 1977). A hand-held pH-meter CP-401 (Elmetron) was used to measure pH of the samples, and the concentration of phosphate phosphorus ($P\text{-}PO_4$) was determined with the use of a single parameter photometer PC compact (WTW).

Statistical analysis

The results were submitted to statistical analysis. The differences between the mean content of the analysed elements in the layers of core sediment samples and in bottom sediments taken from various zones of the lake were analysed with the use of one-way analysis of variance, following an assessment of the distribution of the analysed content against normal distribution (the Shapiro-Wilk's test) and the test for homogeneity of variance (the Levene's test). The results gave no ground for excluding the hypothesis on normality and homogeneity of the analysed data. The significance of the differences between mean content of the analysed elements was assessed with the Tukey's post-hoc test. The selected parameters of water quality and sediment underwent linear regression analysis; the significance of the Pearson's linear correlation coefficients was assessed with the t test. All statistical processing was conducted at the significance level α=0.05.

RESULTS AND DISSCUSION

The mean TP concentration in the analysed profiles of bottom sediments ranged from 0.97 to 3.43 mg P g^{-1} d.m. (Table 1). The results concerning the content of this element were within the range of concentrations found in bottom sediments of mesotrophic and eutrophic lakes, i.e. from 0.55 to 7.00 mg P g^{-1} d.m. and from 0.63 to 4.72 mg P g^{-1} d.m (Nürnberg 1988). The mean content of the selected metals in bottom sediments of Starzyc Lake during the analysed period amounted to 60.02 mg Ca g^{-1} d.m., 2.39 mg Mg g^{-1} d.m. and 1.88 mg K g^{-1} d.m. These values were within the range of the geochemical background of these elements in the Baltic Sea drainage basin, which is from 0.20 to 110.3 mg Ca g^{-1} d.m., from 0.10 to 21.30 mg Mg g^{-1} d.m. and from 1.90 to 22.50 mg K g^{-1} d.m. The comparison of the mean content of the analysed elements in 10-cm layers of bottom sediment profiles shows no statistically significant differences (Table 2).

In the analysed profiles of bottom sediments, the relative content of the selected metals can be expressed as Ca>K>Mg. The bottom sediment profiles taken from the effluent zone were an exception, with the concentrations in the order of Ca>Mg>K, and the Mg content was on average four times higher than that of K. The K compounds are characterized by higher solubility than the compounds of P, Ca or Mg. Additionally, K ions as well as other monovalent cations do not form complex bonding with organic matter. The smallest content of Mg in the central zone of the lake can be attributed to the development of phytoplankton biomass, which uses Mg as a building block in the chlorophyll structure.

The study indicates horizontal variability in the total content of the analysed elements in the bottom sediments (Table 1). The lowest content

Table 1

Content of the tested metals in bottom sediments sampled in different zones of Starzyc Lake

Element	Zone of lake	Content of the elements in sediment (mg g^{-1} d.m.)					
		inflow		centre		outflow	
		mean	SD	mean	SD	mean	SD
P	2005	2.73	0.67	1.43	0.42	1.03	0.15
	2006	3.43	0.15	1.7	0.26	1.17	0.15
	2009	1.9	0.1	1.43	0.21	0.97	0.06
	all the years	2.69^{a}	0.31	1.52^{b}	0.30	1.06^{b}	0.12
Ca	2005	97.9	0.71	86.6	1.22	24.7	1.71
	2006	78.1	0.92	78.4	0.33	58.1	1.62
	2009	64.2	2.01	26.4	0.31	25.7	0.42
	all the years	80.07^{a}	1.21	63.80^{a}	0.62	36.17^{b}	1.25
Mg	2005	4.17	0.01	2.60	0.01	2.40	0.03
	2006	4.10	0.01	2.50	0.02	2.47	0.02
	2009	1.37	0.02	1.20	0.01	0.70	0.01
	all the years	3.21^{a}	0.01	2.10^{b}	0.01	1.86^{c}	0.02
K	2005	4.53	0.04	2.83	0.05	0.63	0.03
	2006	3.53	0.01	2.07	0.05	0.43	0.02
	2009	1.33	0.02	1.13	0.01	0.40	0.01
	all the years	3.13^{a}	0.02	2.01^{b}	0.04	0.49^{c}	0.02

Table 2

Average content of elements in examined layers of bottom sediments, 0-10, 10-20 and 20-30 cm thick

Layer of sediment (cm)	Content of the elements in sediment (mg g^{-1} d.m.)							
	P		Ca		K		Mg	
	mean	SD	mean	SD	mean	SD	mean	SD
0-10	1.99^{a}	0.95	58.9^{a}	29.9	1.87^{a}	1.42	2.33^{a}	0.79
10-20	1.71^{a}	0.76	65.1^{a}	38.2	1.84^{a}	1.29	2.37^{a}	0.67
20-30	1.57^{a}	0.82	56.0^{a}	22.3	1.92^{a}	1.31	2.47^{a}	0.70

was found in sediments taken from the effluent zone to the Krąpiel River, and the highest content was determined in sediments sampled from the watercourse influent zone. The biggest differences between the levels of the analysed macroelements in bottom sediments were determined for Ca and K. The content of these metals in bottom sediments taken from the influent zone from drainage ditches was six times higher than the content found in samples obtained from the effluent zone.

During the five-year long period of pulverizing aeration of Starzyc Lake, there was a significant decrease in the TP content, on average by 43%, in bottom sediments taken from the influent zone (Figure 2). No significant differences were determined in the mean TP content in bottom sediments taken from the other parts of the lake. The content of all the analysed metals in bottom sediments of the lake decreased gradually during the analysed period (Table 1). The content of Ca was most stable and decreased on average by 21% in the analysed period. As for Mg and K, the differences were comparable: 64% and 56%, respectively. The $P\text{-}PO_4$ concentration in near-bottom water layers decreased significantly (Figure 2): the mean content in 2005 was 0.19 mg P dm^{-3}, and fell down to 0.11 mg P dm^{-3} in 2009. The concentration was also characterized by horizontal variability: in the influent zone it

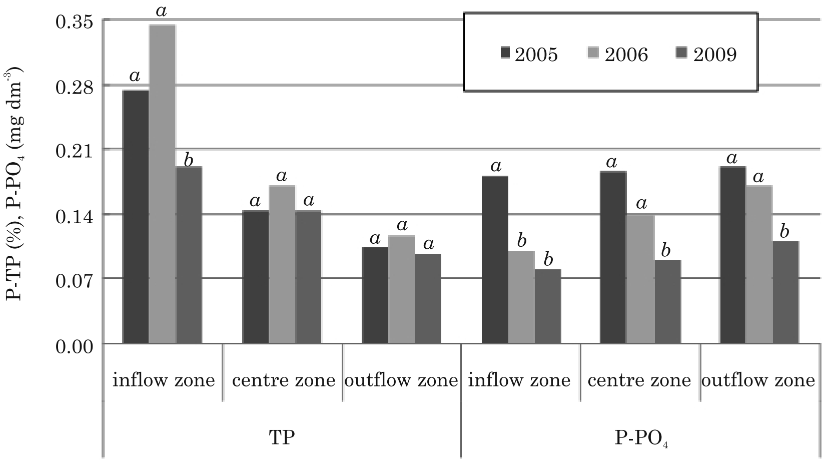

Fig. 2. Changes of the content of TP in the bottom sediments surface layer and $P\text{-}PO_4$ in benthic water during the research period

was on 0.12 mg P dm^{-3} and in the effluent zone it reached 0.16 mg P dm^{-3} on average The results indicate that the bottom sediments were the source of $P\text{-}PO_4$ for the lake during the analysed period. This process is dependent on many other factors and in flow-through lakes the prolonged retention time in the central basin favours mineralisation of organic matter in bottom sediments (Gajewski, Chróst 1995).

A significant positive linear correlation between the Ca content and TP in bottom sediments (Figure 3) and a decrease of the $P\text{-}PO_4$ concentration in near-bottom water layers together with an increase in pH (Figure 4) indicate that in the central zone and in the zone of effluent waters phosphorus was binding with Ca. Two significant functions of linear regression were calculated for the relationship between pH and the $P\text{-}PO_4$ concentration in the near-bottom water layers. The first function includes the results obtained prior to the use of PIX coagulant, while the second includes the results obtained in 2009, after the chemical reclamation began. The decrease in pH and the $P\text{-}PO_4$ concentration in the lake's near-bottom water layers observed during the analysed period indicates that the phosphorus content in the near-bottom layers of water could have been affected by the chemical binding of phospho-

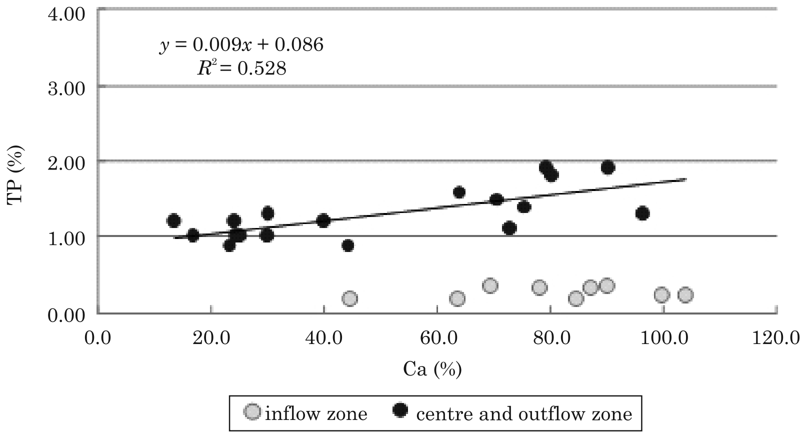

Fig. 3. Relation between the content of TP and Ca in the bottom sediments

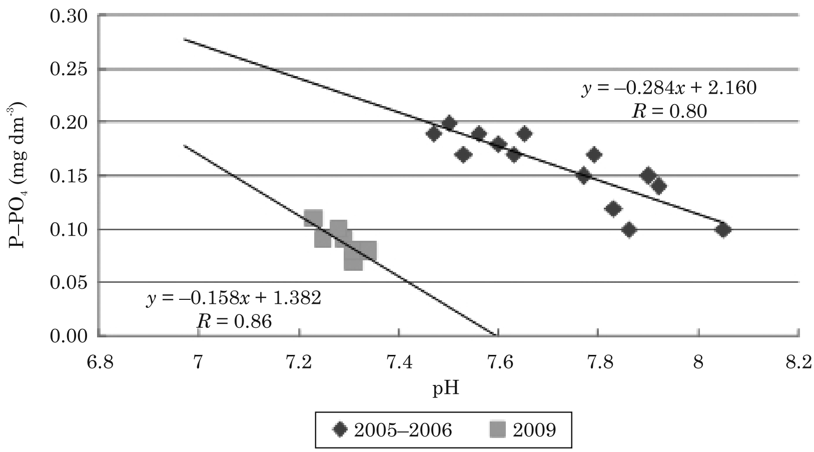

Fig. 4. Relation between pH and P-PO_4 concentration in benthic water

rus which occurred in 2008 and 2009 in response to the use of PIX 113 coagulant, which includes strong acidic electrolytes: 43% $Fe_2(SO_4)_3$ and 1% H_2SO_4.

Monitoring studies conducted on Starzyc Lake in 2010 by the Regional Inspectorate of Environmental Protection in Szczecin show small efficiency of reclamation with the use of a pulverizing aerator. After the completion of a seven-year long period of aeration, the ecological state of the lake was classified as poor. Such classification was due to the high content of phytoplankton, deoxygenation and high total phosphorus in the near-bottom layers of water. The fact that the reclamation conducted with the above method has failed can be explained by inadequate protective actions pursued in and around Starzyc Lake. Reclamation measures will not improve water quality unless it is possible to eliminate the excessive inflow of biogenic compounds to the lake (Lossow 1998).

SUMMARY

During the five-year long period of pulverizing aeration of Starzyc Lake, no significant differences in the annual content of total phosphorus in bottom sediments were found. The only exception was the sediment sampled from the influent zone, where a decrease in total phosphorus by an average 43% was observed. The results show a gradual decrease of the content calcium, potassium and magnesium (by 21, 56 and 64% respectively), as well as a decrease in phosphate phosphorus in the near-bottom layers of water (on average 0.19 mg P dm^{-3} in 2005, and 0.11 mg P dm^{-3} in 2009). The horizontal variability in the content of the analysed elements was found in bottom sediments collected from various zones of the lake. The lowest content was found in sediment material collected from the zone outflow water to the Krąpiel River, and the highest content was recorded in the watercourse inflow zone. It has been found that bottom sediments constituted an indigenous source of phosphorus during the reclamation processes conducted on Starzyc Lake.

REFERENCES

Bajkiewicz-Grabowska E. 2010. *Assessment of the ecological state of lakes as proposed by the Polish Limnological Society*. Limnol. Rev., 10(3-4): 105-116.

Gajewski A.J., Chróst. R.J. 1995. *Production and enzymatic decomposition of organic matter by microplankton in a eutrophic lake*. J. Plankton. Res., 17: 709-728.

Gawrońska H, Lossow K. 2003. *Possibilities of a saprotrophic lake recultivation exemplified by Lake Długie in Olsztyn*. Pol. J. Environ. Stud., 12(3): 301-307.

Gawrońska H., Brzozowska R. 2005. *Influence of a multi-year artificial aeration of a lake using destratification method on the sediment-water phosphorus exchange*. Arch. Environ Prot., 31(3): 71-88. (in Polish)

Gołachowska J., 1977. *A fast and simple metod for determination of total phosphorus in lake bottom sedmiments*. Rocz. Nauk Rol., H 98(2): 27-37. (in Polish)

Koc J., Skwierawski A. 2003. *Phosphorus in the waters in rural areas, effects and prevention.* J. Elementol., 3(8) (Suppl): 123-141. (in Polish)

Konieczny R., Pieczyński L. 2006. *Reclamation possibility of West Pomerania Region lakes using pulverizing aeration technology*. Acta Agroph., 7(4): 947-957.

Lossow K. 1998. *Protection and recultivation of lakes - theory and practice*. Idee Ekolog. Ser. Szkice, 13(7): 55-71. (in Polish)

Nürnberg G.K. 1988. *Prediction of phosphorus release rates from total and reluctant soluble phosphorus in anoxic lake sediments.* Can. J. Fish. Aquat. Sci., 45(1): 453-462.

Osuch E., Podsiadłowski S. 2012. *Efficiency of pulverizing aeration on Lake Panieńskie*. Limnol. Rev., 12(3): 139-14.

Wesołowski P., Brysiweicz A., Pawlos D. 2011. *Physicochemical properties of waters in Lake Starzyc aerated by means of a pulverising aerator*. Water-Environ.-Rural Areas, 11(33): 315-330. (in Polish)