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Evaluation of Selected Physicochemical Indicators of the Waters of Rudnickie Wielkie Lake after Reclamation

Krzysztof Berleć[*]*, Katarzyna Budzińska, Magdalena Michalska*
University of Technology and Life Sciences in Bydgoszcz, Poland
[*]*corresponding author's e-mail: kberlec@wp.pl*

1. Introduction

Eutrophication manifests itself in many adverse phenomena for the natural environment and for the husbandry of phenomenon. The factors accelerating the process of eutrophication in the lakes affect numerous changes which are causing an increase of nutrition salts, mainly mineral form of nitrogen and phosphorus, which contributes greatly to the more intensified development of aquatic plants. The excess of organic substance falls to the bottom and creates organic deposits (Jezierska-Madziar & Pińskwar 2008). In aerobic conditions sediment works like a "phosphate trap", while in anaerobic conditions it becomes the most important source of phosphorus for the developing algae (Siwek et al. 2009). The organic substance logged at the bottom is disposed by aerobic bacteria which are using significant amount of oxygen to deplete it. Oxygen deficits in the bottom layers of the water are causing degradation of the organic compounds accumulated at the bottom as a result of anaerobic bacteria action. Incomplete degradation is leading to the release of hydrogen sulphide and methane. Mineral phosphorus (under aerobic conditions bound to the bottom with iron and aluminium compounds) in anaerobic conditions is excreted into the water causing further intense growth of algae (internal enrichment of water in phosphorus) and consequently blooms (Jezierska-Madziar & Pińskwar 2008).

The consequence of the progressing eutrophication is its poor quality, which is one of the most serious threats to water (Soszka 2009). This problem is often and widely discussed in the European Union's water policy.

Many EU directives contain a requirement to assess this phenomenon and give a range of protective measures which can limit its intensity (Soszka 2009).

Nowadays, both its causes and effects are well known and they are comprehensively described in the limnological literature.

Eutrophication is defined in the Act of "Water Law" as "enrichment of water with biogens, in particular compounds of nitrogen or phosphorus, which are causing accelerated growth of algae and higher forms of plant life, and as a result activating undesirable disturbances of biological relations in the water environment and deterioration of these waters" (Dz.U. 2017, poz. 1566). In natural conditions, eutrophication occurs over the period of almost thousand years causing intensive growth of algae and cyanobacteria in the water reservoirs, especially in spring and autumn. It leads to the cloudiness of water and finally to the loss of biological life (Kowalik et al. 2014).

Small kettels are mostly endangered by it opposite to the ribbon lakes, which are resisting best. This natural process has been significantly accelerated since the mid-18th century as a result of changes in the catchment management, forest burning and cutting, and arable areas increase. Another source of acceleration can be linked to the usage of artificial fertilizers, the transition from breeding to large-scale farming and land drainage. Intensification was also caused by the urbanization, which resulted in the flowage of sewage into the lake (Sondergaard & Jeppsen 2007, Lossow & Gawrońska 2000).

The intensity of eutrophication is determined by the phosphorus, which in comparison with other elements usually occurs in small amounts. The concentration of just about 20-30 $\mu g\ P\cdot dm^{-3}$ can cause water blooming. In addition to phosphorus, nitrogen is another factor contributing to the process of eutrophication. It's compounds dissolved in both surface and underground water are reflecting quality of the natural environment. Therefore, it is very important to analyse and control the concentration of nitrogen in the water, especially in the era of the more and more intensive development of agriculture in Poland (Jekatierynczuk-Rudczyk et al. 1997).

Location of the lakes in the low-lying area makes them natural settlers, in which suspension sediments and compounds dissolved from the catchment or formed in the lake inflow. This process can be observed in all types of lakes, and depends on the age and individual morphometric characteristics of the reservoir. As a result, the lake disappears due to filling the bowl with crumbly and organogenic deposits (Choiński 1995).

In environmental protection methods of preserving lakes are not identical with the methods of their reclamation. The protection depends on good organization and rational water and sewage management in the catchment of the reservoir. Reclamation on the other hand, happens when there are treatments carried out within reservoir's bowl to improve the cleanliness of both the water and reservoir's bowl itself. The purpose of reclamation is to undo, stop or slow down the lake eutrophication processes, and sometimes even to remove its negative consequences.

The purpose of this study was to assess the effectiveness of the reclamation of the Lake Rudnickie Wielkie on the basis of analysis of selected physical and chemical indicators of water quality.

2. Material and methods

2.1. Description of the object

The object of the research was the Rudnickie Wielkie lake located in the Grudziądzka Basin, in the Vistula River basin, in the Kuyavian-Pomeranian Voivodeship, about 3km south from the city of Grudziądz. Rudnickie Wielkie lake, because of origination of it's bowl, is classified as a kettle. It is a flow-through lake, that stores on an average $6.7 \cdot 10^6$ m^3 of water. It has a tributary, the Marusza river in the eastern part, and an outflow, the Rudniczanka river in the south-western part. The Rudnickie Wielki lake catchment is a typical agricultural area (Table 1) (WIOŚ Bydgoszcz, 2001).

Table. 1. Morphometric data of the Rudnickie Wielkie Lake

Parameters	Value
Area (ha)	160.9
Maximum depth (m)	11.9
Average depth (m)	4.4
Shoreline length (m)	6585
Schindler's coefficient	18.4
Volume (10^6 m^3)	6.7
Catchment area (km^2)	127.6

In the studied lake since 1982 there were 2 pipelines exploited (1 more was added in 1991), which are pumping out extremely fertile deep water from two depths, instead of spontaneous outflow of surface waters. This treatment is much easier and cheaper than removal of bottom sediments, and can be use in flow lakes. Thanks to the use of the "Olszewski siphon", water from the hypolimnion, instead of surface water, is flowing out of the lake (Żbikowski & Żelazo 1993). Before proceeding, it is necessary to calculate how much water will be drained and how will the concentration of nutrients change, after what time the entire hypolimnion will be replaced, considering continuous though decreasing inflow of bottom sediments in the outflow. The only disadvantage of this method is the pollution of the watercourse flowing out of the lake (in the watercourse these pollutants are to some extent subject to the self-cleaning processes) by high concentrations of phosphorus and nitrogen, usually also hydrogen sulphide and other substances accumulated in deep water. This method can be used only in specific situations where such contamination is acceptable. In the process of the deep water removal, which is in chemical balance with the bottom sediments, they also diminish themselves and become less and less threatening to the secondary pollution of the reservoir. This process can take many years. Relatively low cost and ease of this treatment, including automatic runoff which does not require energy inputs, encourage its usage wherever possible (Mientki 1994).

2.2. Research methodology

Water was collected once a month from October to April 2018, from three points at the depth of 20 cm (Fig. 1) to sterile 0.5-litre bottles. The containers were filled completely with water, sealed, protected from light and cooled to a temperature of 4°C. After this, they were transported to the laboratory where the tests were carried out. The time from sampling water to the mark up did not exceed 24 hours.

The temperature and pH were measured *in situ* on the day of sampling.

The examination of the concentration of total phosphorus, phosphates, nitrates (III), nitrates (V) and ammonium nitrogen was carried out by the spectrophotometric method using the NOVA 400 spectrophotometer, while total nitrogen in mineralized samples was measured by using the Kjeldahl method in accordance with PN 73 / C-04576.12. Merck sets were used to mark the indicators.

Orthophosphate ions in the solution acidified with sulphuric acid react with molybdenum ions to form the molybdicphosphoric acid.

The resulting acid is reduced with ascorbic acid using phosphomolybdic blue (PMB), which is determined photometrically. The filtered sample was removed from the refrigerator early enough to reach a temperature in the range of 10-35 before analysis was performed °C. 5 ml of the sample was transferred to a beaker, to which 5 drops of P-1A reagent were added, after this solution was mixed. Next, 1 micro-peptide of reagent P-2A was poured. Solution prepared was mixed until reagent dissolved. After 5 minutes, the prepared sample was transferred to a 10 mm cuvette and marked in a spectrophotometer.

Total phosphorus. A solution of water (100 cm^3) and concentrated HCl (15 cm^3) was evaporated to dryness, then the sample with the addition of concentrated H_2SO_4 was mineralized. For discolouration 2 cm^3 of concentrated H_2O_2 was added. After the mineralization process, the sample was transferred to a 100 cm^3 graduated flask and topped up by the distilled water. In the mineralized samples, the total phosphorus was determined by using the colorimetric method (PN-91-C/04537.09).

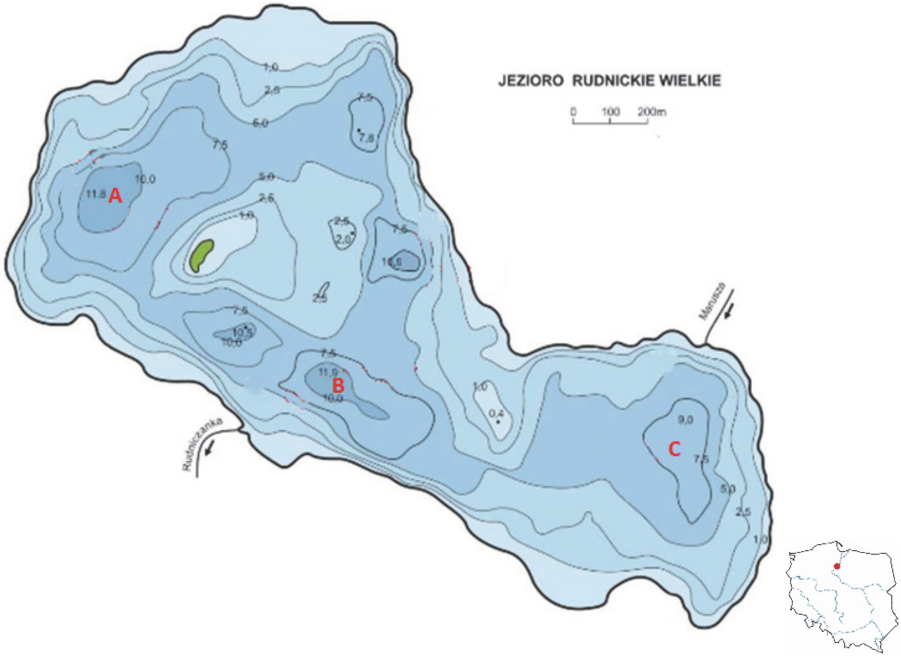

Fig. 1. Water sampling points

Nitrates (III). In a solution acidified with sulphuric acid and phosphoric acid, they react with 2.6-dimethylphenol to form an orange coloured solution of 4-nitro 2.6-dimethylphenol. Preparation of the sample for measurement included the introduction into the flask 4 ml of NO_3-1 reagent, then test water at 20°C was added. The next step was the introduction of 0.5 ml of NO_3-2 reagent and thorough mixing of the sample. After 10 minutes, it was measured using the 10 mm cuvette and the wavelength of 338 nm.

Nitrates (V). The nitrite ions in the acid solution reacted with the sulphanilic acid to form a diazonium salt that reacted with N-(1-naphthyl) ethylenediamine dihydrochloride to form a red-purple azo dye. The procedure consisted of introducing 5 ml of the test sample at 20°C, and then adding the NO_2-AN reagent and thorough mixing until the reagent was completely dissolved. After 10 minutes, it was measured using the 10mm cuvette and the wavelength of 338 nm.

Ammonium nitrogen. It occurs partly in the form of ammonium ions and partly as ammonia. There is a pH-dependent equilibrium between the two forms. In the highly alkaline solutions, ammonium nitrogen occurs mainly as ammonia, which reacts with the chlorinating agent to form monochloramine. This reacts with thymol to form a blue-coloured derivative of indophenol, which is determined photometrically. 5 ml of water were successively added to the test tube, 0.6 ml of NH_4-1 reagent was added and mixed. A flat teaspoon of NH_4-2 reagent was then introduced and vigorously shaken until complete dissolution of the reagent. After 5 minutes, 4 drops of NH_4-3 reagent were added and mixed. The process was then paused for another 5 minutes.

3. Results and Discussion

The results of the conducted own research, similarly as in the case of other reclaimed lakes, indicate the low efficiency of the chosen method in relation to the analysed basin.

The level of total phosphorus ranged from 0.074 to 0.495 mg·dm^{-3}. Its highest content was marked in March and April at all sampling points. The average for the entire study period was 0.2 mg·dm^{-3} (Table 2).

Gałczyński's (2008) research showed that the limit value for phosphorus, where extreme fertile of the reservoir can be concluded, is determined at the level above 0.1 mg·dm^{-3}. According to Maehl (2000), adequate transparency of water in shallow lakes guarantees the content of phosphorus from 0.05 to 0.15 mg·dm^{-3}. Its level in relation to the others occurring in the surface waters is lower, although it is one of the most necessary in organism's lifespan. A study of water in the recultivated Głęboczek lake conducted by Szatten (2010) showed that the concentration from 0.07 mg·dm^{-3} (in spring) to 0.08 mg·dm^{-3} (in summer) is satisfactory. At the same time, the amount of total phosphorus in the studied lake reached the maximum value (1.01 mg·dm^{-3}) in late spring – as in our own research, when the content of the analysed element reached its maximum value, classifying lake waters below the good state. In his own study for 2005, Konieczny (2014) states that the water resources of Rudnickie Wielkie lake in phosphorus amounted to an average of 0.188 mg·dm^{-3}.

The higher content of phosphates indicates a significant intensity of release of phosphorus compounds from the bottom sediments into water, which is the effect of processes associated with the degradation of organic forms of phosphorus and thus their rapid availability for primary production (Egemose et al. 2010). The content of organic phosphorus compounds in the research period ranged from 0.15 to 0.25 mg·dm^{-3} (average 0.2 mg·dm^{-3}). According to Goszczyński (2000) the sources of a slight increase in phosphate concentration in the early spring period should be seen in the depletion of oxygen in bottom sediments. The same author's research, conducted in the spring at Głęboczek lake, determined the content of phosphates in the range of 0.042-0.111 mg·dm^{-3}, whose concentrations were lower than those obtained in own research, yet exceeded the norms specified for the lowest class III purity. Similar average concentration (0.089 mg·dm^{-3}) is noted by Konieczny (2014) in the waters of the reclaimed

Rudnickie Wielkie lake. Many years of research on the phosphate content in Głęboczek lake was conducted by Lossow et al (2004). In the spring of 2002 and 2003, orthophosphates were not detected by them, which may indicate that the reclamation procedures have been carried out correctly. The proper selection of the reclamation method, and what is related to its effectiveness, is also supported by the results of research on phosphate content in the lakes of Mąkolno (0.014 mg/dm^3) and Powidzkie (0.0013 $mg \cdot dm^{-3}$), which compared to both lakes reclaimed are only slightly exposed to external influences. Thus, these values were much lower than in the Rudnickie lake (average 0.2 $mg \cdot dm^{-3}$), and especially Powidzkie lake, which is considered as one of the cleanest ones in Wielkopolska (26, 27).

Nitrogen, which is a biofilm, undergoes cyclic circulation in nature, during which a series of biochemical processes takes place in waters Gonzales et al. 2005). Its content in the water, along with phosphorus, determines their productivity.

Mineral nitrogen compounds in the surface waters are ammonium nitrogen, nitrates (III) and nitrates (V), while the latter are found in lake waters in small amounts in their transitional form. Of the total nitrogen in lake waters about 50% falls on organic compounds, the content of which varies depending on the intensification of processes in the tank, as well as the content of mineral nitrogen, which depends primarily on the season of the year (Kudelska et al. 1994).

Analysis of the waters of the Rudnickie Wielkie lake showed that the highest concentrations of total nitrogen (16.9 $mg \cdot dm^{-3}$) were recorded in October, and the lowest (8.3 mg/dm^3) in April. Its average, the concentration was 13.56 $mg \cdot dm^{-3}$. Gawrońska et al. 2004) in the research conducted in the waters of Głęboczek lake, a few years after its reclamation, recorded the presence of total nitrogen in the range of 0.075-0.125 $mg \cdot dm^{-3}$. The same authors Gawrońska et al. 2005) also found a high concentration of total nitrogen in Długie lake in Olsztyn, which before reclamation in 1972 in surface layers ranged from 3.5 to 12.5 $mg \cdot dm^{-3}$. Two years later, after the sewage system in the catchment was regulated, the waters were subjected to further analyses, which recorded total nitrogen at the level of: 2.6-21.5 $mg \cdot dm^{-3}$ in 1974, 1.9-12.6 $mg \cdot dm^{-3}$ in 1975 and 2.1-18.2 $mg \cdot dm^{-3}$ in 1976. After subsequent reclamation treatments, nitrogen concentration overall did not exceed 2.0 $mg \cdot dm^{-3}$. The lower maximum level of total nitrogen content was characteristic for the Durowskie lake, in the waters of which Gołdyn et al. (2010) recorded it at the level of 2.18 $mg \cdot dm^{-3}$ to 5.25 $mg \cdot dm^{-3}$. The maximum values were recorded in the summer months, when according to Dojlido (1995) they should be lower.

Table 2. Development of selected physiochemical variables of waters of the Rudnickie Wielkie Lake

Moonth of sam-pling	Place of collection	Temperature °C	pH	P_t $mg \cdot dm^{-3}$	PO_4 $mg \cdot dm^{-3}$	N_T $mg \cdot dm^{-3}$	N-NO_3 $mg \cdot dm^{-3}$	N-NO_2 $mg \cdot dm^{-3}$	N-NH_4 $mg \cdot dm^{-3}$
October	A	4.1	7.15	0.098	0.24	16.9	8.9	0.21	0.09
	B	4.1	7.22	0.115	0.21	16.9	8.8	0.23	0.08
	C	4.0	7.17	0.083	0.19	16.6	8.9	0.22	0.10
November	A	4.6	7.31	0.129	0.18	16.5	9.1	0.21	0.11
	B	4.4	7.19	0.148	0.18	16.6	9.0	0.19	0.09
	C	4.4	7.21	0.137	0.21	16.7	9.2	0.18	0.10
December	A	4.9	7.45	0.151	0.20	14.8	9.2	0.20	0.08
	B	4.8	7.51	0.129	0.17	14.3	9.0	0.17	0.07
	C	4.9	7.58	0.134	0.18	14.5	9.1	0.22	0.11
January	A	6.1	7.63	0.089	0.17	14.4	8.7	0.19	0.12
	B	6.2	7.71	0.132	0.15	14.3	9.2	0.18	0.11
	C	6.2	7.68	0.112	0.15	14.4	9.2	0.18	0.13

Table 2. cont.

Moonth of sam-pling	Place of collection	Temperature °C	pH	P_t $mg \cdot dm^{-3}$	PO_4 $mg \cdot dm^{-3}$	N_T $mg \cdot dm^{-3}$	$N\text{-}NO_3$ $mg \cdot dm^{-3}$	$N\text{-}NO_2$ $mg \cdot dm^{-3}$	$N\text{-}NH_4$ $mg \cdot dm^{-3}$
February	A	7.8	7.71	0.096	0.23	12.1	8.9	0.19	0.12
	B	8.1	7.68	0.088	0.18	12.5	8.9	0.21	0.12
	C	8.0	7.65	0.074	0.21	12.6	8.7	0.22	0.17
March	A	11.1	7.81	0.324	0.22	12.1	9.4	0.20	0,16
	B	11.3	7.88	0.377	0.19	12.1	9.5	0.21	0,18
	C	10.9	7.87	0.401	0.25	11.0	9.1	0.23	0.15
April	A	13.3	7.52	0.456	0.22	8.3	8.7	0.19	0.14
	B	13.1	7.69	0.433	0.23	8.5	9.1	0.18	0.16
	C	12.9	7.71	0.495	0.22	8.7	8.4	0.21	0.16
average		7.39	7.54	0.200	0.20	13.56	9.0	0.20	0.12
min-max		4-13.3	7.15-7.88	0.074-0.495	0.15-0.25	8.3-16.9	8.4-9.5	0.17-0.23	0.07-0.18
Sd		3.34	0.24	0.140	0.03	2.8	0.26	0.02	0.03

Sd – standard deviation

The content of nitrates (III) and other impurities accumulated in surface waters is subject to considerable fluctuations throughout the year. In the nitrogen cycle in surface waters, the nitrate nitrogen has a transitional form, which in addition to affecting the productivity of aquatic ecosystems also dissolves very well in water. The concentration of various forms of nitrogen depends on the degree of washing them out from the soil, and the size of their losses is related to the soil bonitation class, vegetation cover and purpose. On light soils, up to 98% of nitrogen and 7.7% of phosphorus can be washed out (Szpakowska et al. 2003).

In the waters of the Rudnickie Wielkie lake the content of nitrates (III) ranged from 8.4 to 9.5 mg·dm^{-3}, with the average for the whole period of 9.00 mg·dm^{-3}. A much smaller number of them, in the period from March to May (0.12-0.71 mg·dm^{-3}) were noted by Lossow et al. (2002) in the waters of the the reclaimed lake Głęboczek, similar to Rudnickie Wielkie lake Konieczny (2014) determined the value of this indicator at the level of 0.15 mg·dm^{-3}. The results obtained in comparison with the effects of reclamation of other lakes put a great question mark on the selection of the method of reclamation of the Rudnickie Wielkie lake, and it's efficiency. The presence of nitrates (III) in lake waters is considered as a factor accelerating their eutrophication. Views on the concentration of nitrates (III) causing eutrophication of waters are divergent and range from hundredth to tenths of parts mg/dm^3 (Zioła et al. 2003).

The transitional products of nitrogen compounds in surface waters are characterized by low durability nitrates (V), which are quickly reduced to ammonia, and under aerobic condition oxidize to nitrates (III) (Kułakowski & Biernacka 2007). Their presence indicates a fresh inflow of anthropogenic pollution. During the tests, this parameter remained at a similar level in the range of 0.17 to 0.23 mg·dm^{-3}. Much better results and, therefore, a higher efficiency of the reclamation were obtained in the Głeboczek lake, where the concentration was maintained in the range from 0.016 to 0.013 mg·dm^{-3} (Lossow et al. 2004) and in the Rudnickie Wielkie lake in (average 0.012 mg·dm^{-3}) (Konieczny 2014). These results classify the Głęboczek lake in the 3rd class of purity, whereas in the Rudnickie Wielkie lake waters cannot be classified using this parameter.

The unsatisfactory effects of reclamation are also demonstrated by the comparison of the results obtained with the waters of the lakes of Powidzkie and Mąkolskie, where the average content of nitrates (V) was 0.00045 mg·dm^{-3} and 0.0081 mg·dm^{-3}, respectively (WIOŚ Poznań 2009; WIOŚ Poznań 2008).

The presence of ammonium nitrogen in surface waters, which additionally mixed with the oxygen stimulates development of nitrifying bacteria, may indicate water pollution with the domestic and industrial sewage. In the study, this form of nitrogen was present in the amount from 0.07 to 0.18 mg·dm^{-3} – an average of 0.12 mg·dm^{-3}. The analysis of waters of the same lake, carried out by

Mientki (2000), showed a higher content of nitrogen (from 1.1 mg·dm^{-3} to 12.3 mg·dm^{-3}). According to this author, the reasons for this state should be found in the sudden delivery of sewage from a nearby sugar factory. n equally high average level (0.713 mg·dm^{-3}) was noted by Konieczny (2014) in the Rudnickie Wielkie lake. It might be worrying that pollution occurred in the second stage of reclamation, in other words theoretically after organizing properly water and sewage management in the catchment. Before the inflow of impurities, the amount of ammonium nitrogen ranged from 2.1 to 4.2 mg·dm^{-3}. Slightly higher results than those obtained in the own research were noted by Gołdyn and Messyasz (2008) who, when examining the Durawskie lake water which was prepared for reclamation, confirmed the presence of this form of nitrogen compounds at the level of 0.23 mg·dm^{-3} in October 2005 by 0.57 mg·dm^{-3} in November to 1.2 mg·dm^{-3} in January 2006. In their opinion, this increase can be explained by the supply of surface water floating towards the surface with hypolimnion waters (mixes) characterized by a high content of ammonium nitrogen and the presence of an ice cover that prevents waving and simultaneous oxygenation of water. The ammonium nitrogen content has been gradually decreasing since March.

4. Summary

Many years of research of the waters of the Rudnickie Wielkie lake indicate that it is constantly under strong anthropopressure. The oxygen deficit in the bottom zone, which was documented by many authors indicates an extremely high degree of degradation. This phenomenon is visible despite the declared limitation of the inflow of sewage and other pollutants to the reservoir. Therefore, it is assumed that the restriction itself, or at best he cutoff of nutrients is insufficient to obtain a specific water state, which encourages the continuation and simultaneous modernization of reclamation methods. The temperature and pH of water analysed in the course of the study were characteristic for the examined seasons and did not have a significant impact on the content of the determined chemical indicators. The level of biogenic elements and their compounds, determined a few years after reclamation, is higher than the results obtained in 2001 (immediately after reclamation), which may indicate improper sewage and agricultural management in the lake's catchment.

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Abstract

The research carried out was aimed at determining the effectiveness of reclamation of the Rudnickie Wielkie lake. Samples were taken 7-fold in 3 places during the period from October to April. In the tested water was determined by the colorimetric method PO_4^{-3}ions, total P and N, nitrate(V), nitrite(III) and NH_4-N. Additionally, the pH and temperature.

The temperature and pH of water analyzed in the course of the study were at the level characteristic for the seasons under study and did not have a significant impact on the content of the determined chemical indicators. The level of biogenic elements and their compounds, determined a few years after reclamation, is higher than the results obtained in 2001 (immediately after reclamation), which may indicate improper sewage and agricultural management in the lake's basin.

Keywords:
reclamation, lake, physicochemical indicators

Ocena wybranych wskaźników fizyko-chemicznych wód jeziora Rudnickiego Wielkiego po rekultywacji

Streszczenia

Przeprowadzone badania miały na celu określenie skuteczności rekultywacji jeziora Rudnickiego Wielkiego. Próbki pobierano 7-krotnie w 3 miejscach w okresie od października do kwietnia. W badanej wodzie oznaczono metodą kolorymetryczną PO_4^{-3}ions, całkowitą P i N, azotan (V), azotyn (III) i NH_4 -N. Dodatkowo pH i temperatura. Temperatura i pH wody analizowanej w trakcie badania były na poziomie charakterystycznym dla badanych sezonów i nie miały istotnego wpływu na zawartość określonych wskaźników chemicznych. Poziom pierwiastków biogennych i ich związków, określony kilka lat po rekultywacji, jest wyższy niż wyniki uzyskane w 2001 r. (Bezpośrednio po rekultywacji), co może wskazywać na niewłaściwe gospodarowanie ściekami i rolnictwem w dorzeczu jeziora.

Słowa kluczowe:
rekultywacja, jezioro, wskaźniki fizykochemiczne