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The Influence of Various Restoration Techniques on the Content of Selected Ions in Water of an Urban Lake

Jolanta Katarzyna Grochowska * and Renata Augustyniak-Tunowska

Department of Water Protection Engineering and Environmental Microbiology, Faculty of Geoengineering, University of Warmia and Mazury in Olsztyn, St. Prawocheńskiego 1, 10-720 Olsztyn, Poland; rbrzoza@uwm.edu.pl

* Correspondence: jgroch@uwm.edu.pl

Abstract: The research was carried out on Lake Długie, which, from the mid-1950s was transformed into a receiver for domestic and storm water sewage. Together with the sewage, 51 tons of phosphates, 51 tons of ammonia, 2.6 tons of nitrates, 243 tons of calcium, and 294 tons of chlorides were introduced into the lake. The lake was completely degraded (P > 4 mg/L, N > 30 mg/L, Cl > 70 mg/L). Cutting off the sewage inflow did not improve the environmental conditions in the water body, which indicated that it was necessary to carry out further protection and restoration treatments: artificial aeration with destratification (1987–2000), a phosphorus inactivation method with the use of PAX 18 liquid coagulant (2001, 2002, 2003), cutting off the inflow of storm water (2015), and biomanipulation via the removal of macrophytes (2020). Research has shown that the protective measures carried out in the lake's catchment area, in combination with appropriately selected restoration methods, are an example of good practices that enable the improvement of water quality. The phosphate concentrations in the bottom layers of water do not exceed 0.2 mg P/L, and the ammoniacal nitrogen does not exceed 1.2 mg N/L. The chloride content in the lake water is kept at the level of 20 mg Cl/L, and the calcium in the range from 28 to 40 mg Ca/L.

Keywords: artificial aeration; biomanipulation; lake; phosphorus inactivation; pollution; restoration; selected ions

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1. Introduction

The hydrosphere is the Earth's aquatic shell, and contains approximately 1.4 billion m^3 of water. The vast majority of the water is stored in the seas and oceans, in the form of salt water, and only 3.5% of the resources are fresh water, in the form of glaciers and permanent frost (as much as 69%), and lakes, rivers, swamps, groundwater, and atmospheric water [1,2]. In this context, the world's freshwater resources are limited; hence, their protection is a priority. Water is a vital element for humans, animals, and plants [3–7]. The lakes are natural retention reservoirs, accumulating water when there is excess water, and returning it in periods without rainfall. Lakes regulate the flow of rivers and smooth it over time, which helps to prevent flooding and the excessive depletion of water during periods of drought [8,9]. Lakes regulate the climate, create specific ecosystems with rich flora and fauna, and are tourist and recreational attractions [10,11]. There are about 7000 lakes in Poland and, in total, they cover an area of 2810 km^2 (0.9% of the country's area), and store 19,500 km^3 of water [12]. Most of the lakes in Poland are postglacial reservoirs. Unfortunately, since their inception, a significant proportion has disappeared as a result of both natural succession and excessive anthropogenic pressure. Natural succession is a process of eutrophication that takes place in lakes under the influence of a constant supply of nutrients and organic compounds [13,14]. Its rate depends on the size of the external load, which, in turn, is determined by the natural fertility of the catchment area [15–17]. In turn, excessive human pressure is mainly caused by the development of cities and industrial plants in areas surrounded by water bodies, and the transformation of lakes into municipal, industrial, and rainwater receivers. Moreover, the increase in agricultural land, where fertilizers and plant protection products are applied, also stimulates the growth of nutrient loads flowing into the waters, and accelerates the eutrophication process. The bad condition of the lake water is visible in the form of algae blooms, a lack of oxygen in the bottom water, the presence of hydrogen sulfide, a low water transparency, and a high content of biogenic compounds. Such a situation causes the lake to lose its aesthetic value, and the water cannot be used for economic and recreational purposes [18–20].

In many countries around the world, various protective and restoration techniques (chemical, biological, and technical) are being implemented, due to the great importance of lakes, as well as the need to protect the hydrosphere's water resources, and improve water quality [21–25]. Flotation processes are being used more and more often [26,27], and various solutions for purifying water from heavy metals or toxic substances are also being tested around the world [28–31]. The aim of all techniques is to improve environmental conditions as a result of the permanent immobilization of nutrients in sediments, or the removal of phosphorus and nitrogen excesses, beyond the lake [32–34].

In Poland, during the post-war period, urban areas were intensively expanded, and industrial plants were established. The process of urbanization did not always go hand in hand with equipping cities with water and sewage systems. Water for municipal purposes was collected from wells, surface water reservoirs, and watercourses, and the wastewater generated as a result of its consumption was delivered, in a raw or insufficiently purified form, directly to receivers: rivers and lakes. This situation led to the contamination of many surface waters.

An example of a water body that has been destroyed as a result of inadequate water and sewage management is Lake Długie in Olsztyn (Olsztyn Lake District, north-eastern Poland). From the mid-1950s, for over 20 years, with the help of seven storm-water collectors, rainwater from the residential district located by the lake, and household wastewater, were fed to this reservoir by means of an emergency overflow, in the amount of about 400 m^3 per day.

Studies of the environmental condition of Lake Długie carried out in the 1970s during the discharge of sewage into the lake showed strong pollution. The overoxygenation of the surface water reached 290% oxygen saturation, and the waters below 5 m in depth were deoxygenated. High concentrations of nutrients were also found, with about 12 mg P/L and 30 mg N/L in the near-bottom water [35–37]. According to Mucha [38], the daily gross primary production in the summer period in this lake reached an average of 20 g O_2/m^2/day, and the excessive inflow of pollutants did not stimulate primary production, but limited it. In Długie Lake, a massive development of phytoplankton was also observed, which was manifested by extremely high values of chlorophyll, reaching on average up to 200 µL/L, with a maximum value of about 500 µL/L [39], and a very poor species composition, with a clear dominance of cyanobacteria and green algae [40]. The benthic macrofauna was represented mainly by *Chaoborus flavicans*, an indicator of hypertrophy [41].

The results of the microbiological research carried out by Zmysłowska and Sobierajska [42] showed a very poor sanitary condition in Lake Długie. The total number of bacterioplankton in the water, to the order of 106–108 cells in 1 cm^3, the large number of heterotrophic bacteria, the low coliform count of up to 0.0001, and the possibility of pathogenic bacteria indicated high pollution with sanitary sewage.

In 1973, the inflow of domestic and economic wastewater was limited, and their complete cutoff took place in 1976. Research carried out by Gawrońska [43] reached the conclusion that the effects of the lake degradation are irreversible, and that further improvement of the environmental conditions in the lake is possible only thanks to the implementation of reclamation techniques.

According to Gawrońska et al. [44], after unsuccessful attempts at the dilution/flushing of Lake Długie with water from neighboring Lake Krzywe through Lake Czarne, in 1987, the restoration of this water body began with the use of artificial aeration with thermal destratification. When the improvement of water quality in Lake Długie by means of artificial aeration was no longer possible (due to the low sorption capacity of the bottom sediments, and the lack of iron and manganese in the water), the method of phosphorus inactivation was applied. It consists of precipitating phosphorus from water, and blocking it in bottom sediments. After the coagulant is applied, bottom sediments have a better sorption capacity. Due to the fact that, after the end of artificial aeration, the lake returned to the thermal and oxygen systems from before the restoration (the bottom water was deoxygenated), the PAX 18 aluminum coagulant was used. The technical and chemical activities were supplemented by biomanipulation, consisting of the removal of excess macrophyte vegetation.

The aim of this manuscript is to present a case of an urban lake, in order to demonstrate how easily a lake ecosystem can be destroyed and, above all, how difficult it is to restore a lake to its previous state. Lake restoration, especially when the lake is completely degraded, is extremely difficult, and requires knowledge of the complex processes that take place in a lake ecosystem, the right choice of restoration methods, and a consistent, often long-term study of their effectiveness. The costs are usually very high, often exceeding manifold the expenditure borne in order to prevent the degradation of a lake. There are very few lakes around the world in which the monitoring of the changes in the selected, most important ions, and the environmental conditions caused by various factors (sewage inflow, lake protection by cutting off the sewage inflow, various restoration methods) has been carried over such a long period, almost 50 years, as it has been in the lake we shall discuss.

2. Material and Methods

Lake Długie (17.3 m; 26.8 ha) is situated in the city of Olsztyn (north-eastern Poland). The lake's surface area equals 26.8 ha, the maximum depth is 17.3 m, and the bowl volume amounts to 1,415,000 m^3 (Figure 1). Lake Długie is a dimictic water body, characterized by a limited, slow dynamic of water, in which the mixing of water is hindered by unfavorable morphometric conditions.

Figure 1. Localization of Lake Długie in Poland and Europe (www.google.pl/maps (accessed on 15 July 2023)), and its morphometrical parameters.

In the years 1956–1976, it received untreated domestic sewage and storm water (about 400 m^3 per day). The influx of sewage caused severe pollution in the lake. The inflow of domestic sewage was cut off in 1976, and the inflow of storm wastewater was cut off in 2015. When protective measures, consisting of cutting off the inflow of sewage, did not improve the environmental conditions in the water body, it was necessary to apply appropriate restoration measures.

Taking into account the morphometric and hydrological features of the lake, and the water chemistry, the following restoration methods were used:

1. ARA—artificial aeration with destratification (artificial circulation) [45].
   (1) First stage (in 1987–1990), three ″mini-flok″ type aerators were used, localized in the middle, deepest section of the lake, and a compressor with the capacity of 150 m^3/h
   (2) Second stage (in 1991–2000), 2 ″mini-flok″ aerators (one in the middle section of the lake, and one in the northern part) and two compressors (80 m^3/h).

The reason for changing the aeration system elements (the compressor type, localization of aerators, type of pipes) was the failure of the original system to completely mix the water column [45].

2. PI—phosphorus inactivation due to the low sorptive capacity of bottom sediments. The PI method was carried out using a new-generation aluminum coagulant called PAX 18 (6.79 g Al/m^2 of bottom surface) [46].

First stage—spring 2001 (20 MG of PAX 18)
Second stage—autumn 2002 (20 MG of PAX 18)
Third stage—autumn 2003 (20 MG of PAX 18)
The coagulant was dosed from barrels on boats, and distributed over the entire surface of the lake, through perforated tubes.

3. BM—biomanipulation (2020).

In Lake Długie, it was necessary to use biomanipulation (BM), which involved the removal of plant biomass via the mechanical mowing of aquatic plants to a depth of about 1.5 m above the bottom. For this purpose, boats equipped with an adjustable-depth underwater scythe were used. The removed plants have brittle tissues, and are easily pruned. The vegetation cut with the underwater scythe flowed to the surface, from where it was excavated by vessels to the shores and, after the initial drainage of the lake water as fresh plant mass, it was transferred to containers, and transported, for management.

All restoration methods have been developed and implemented by the Department of Water Protection Engineering and Environmental Microbiology, University of Warmia and Mazury, in Olsztyn.

The results of the research conducted in 1974 (on the inflow of raw municipal sewage), 1976 (limiting the inflow of domestic sewage), 1984 (after cutting off the inflow of domestic sewage), and 1987 (the first stage of ARA) come from the Archives of the Department of Water Protection Engineering and Environmental Microbiology (results of the study by Helena Gawrońska).

The water samples for chemical analysis were taken using a 3.5 l Ruttner sampler (3.5 L, KC Denmark; Geomor Technik, Szczecin, Poland), from the deepest point in the lake (sample from the surface layers, depth 1 m; sample from the bottom layers, depth 16 m) and stored in plastic bottles. The water samples for analysis were taken monthly, during the period from April to November 1998 (second stage of ARA), from April to November 2003 (third, last stage of PI), from April to November 2013 (10 years after the end of the lake restoration), from April to November 2017 (after cutting off the inflow of storm water), and from April to November 2020 (after BM). The scope of the water analysis included: PO_4^{3-} (with the use of ammonium molybdate—$(NH_4)_6Mo_7O_{24} \times 4H_2O$ and $SnCl_2$ as indicator λ = 690 nm—colorimetrically, using the NANOCOLOR spectrophotometer) (GmbH&Co. KG, Düren, Germany), NO_3^-, NH_4^+ (Merck SQ118) (KGaA, Darmstadt, Germany), Ca^{2+}

(titration method with EDTA solution, with $C_{10}H_{14}N_2O_8Na_2$ and $C_{20}H_{12}N_3O_7SNa$ as indicator), and Cl (using the argentometric method, with $AgNO_3$ solution, and K_2CrO_4 as indicator).

Changes in the content of iron and manganese ions were not presented in the paper, because the presence of these elements in the water was not detected in the analyzed period. Changes in the magnesium content were also not presented, because the concentration of this metal was 3–4 times lower than calcium, and its changes were analogous to the changes in calcium.

Every analysis was performed in triplicate. The coefficient of variation (CV) for the repeated analysis was 2% [47]. The obtained results were statistically analyzed (one-way ANOVA, $p = 0.05$, Tukey's HSD) using the Statistica 13.0 software package [48]. The alternative tested hypothesis presumed the presence of significant differences in the content of selected ions between the control year (1974) and experimental years (1976—limiting the inflow of municipal sewage, 1984—after cutting off the inflow of domestic sewage, 1987—the first stage of ARA, 1998—the second stage of ARA, 2003—the third stage of PI, 2013—the years after the end of lake restoration, 2017—after cutting off storm water, and 2020—after BMI).

3. Results and Discussion

In recent years, the pollution of water with various substances, both natural and related to human activity, has been a global problem [49,50]. Since the 1950s, the intensive development of industries, urbanization, and agriculture has caused organic matter, phosphorus and nitrogen compounds, heavy metals, polychlorinated biphenyls, or polycyclic aromatic hydrocarbons to reach water, and they have had a negative impact on water environments [49,50]. Human activities aimed at slowing down the eutrophication process, and removing its negative effects, also influence the chemistry of lake waters. Long-term research carried out on Lake Długie confirms this. The statistical analysis revealed significant differences in the content of PO_4^{3-}, NH_4^+, Ca^{2+}, and Cl^- between 1974 (during the inflow of domestic sewage) and 1976 (after limiting the inflow of domestic sewage), and in the years 1984 (after cutting off domestic sewage), 1987, 1998 (during ARA), 2003 (the last year of PI), 2013, 2017, and 2020 (10 years after the end of the restoration measures, after cutting off the inflow of storm water, and after BM) (p value < 0.05; F value > 2). In the case of NO_3^-, there were no statistically significant differences in the content of these ions between the analyzed research years (p value 0.524; F value 0.9).

3.1. Phosphates (PO_4^{3-})

Phosphorus is chemical element which occurs in water bodies as orthophosphate, pyrophosphate, polyphosphates, organic phosphate esters and phosphodiesters, or organic phosphonates [51–54]. Phosphorus is a very dynamic, biologically active element. According to Drozd [55], the average content of phosphates in the wastewater supplied to Lake Długie was 6.6 g P m^{-3}. Taking into account the daily volume of sewage discharged into the lake at the level of 350 m^3, 2310 g of phosphorus were introduced per day. During the year, the load of phosphorus introduced into Lake Długie was 843,150 g of phosphorus, i.e., 843 kg. P is an important driver of primary production in surface waters. According to Kajak [56], the introduction of 1 kg of phosphorus into surface waters causes an increase of 1 ton in the fresh weight of algae. Such a high load in the research lake caused its complete degradation. In 1974, during the inflow of sewage, the mean content of PO_4^{3-} (± SD) in the surface water layer was 0.83 ± 0.41 mg P/L and, in the over-bottom, 3.52 ± 0.37 mg P/L (Figure 2). After the loading of pollutants was limited, the mean content of PO_4^{3-} in the surface water layer decreased to 0.72 ± 0.27 mg P/L and, in the over-bottom water layer, to 2.46 ± 0.68 mg P/L (Figure 2). In 1984, the mean quantity of PO_4^{3-} in the surface water layer was 0.08 ± 0.08 mg P/L and, near the bottom, was 2.28 ± 0.27 mg P/L (Figure 2). The PO_4^{3-} concentrations in Lake Długie were similar to those in diluted sewage. The reservoir was not able to process the excess matter within the ecosystem and the organisms inhabiting it. Phosphates could not be precipitated to the bottom sediments, due to the anaerobic conditions in which iron Fe^{+3} is reduced to Fe^{2+}, and the connections between phosphorus and iron break down. Moreover, divalent iron combines with hydrogen sulphide into a stable compound, FeS, which does not decompose, even in the autumn, when the oxygenation conditions improve as a result of water circulation and its contact with atmospheric air. In deoxygenated hypolimnion, only 30% of PO_4^{3-} can form chemical bonds with Fe [57,58]; 30% of $P_{min.}$ can be incorporated into the algae biomass, while the remaining P is dissolved in water. In the analyzed water body, the amount of PO_4^{3-} trapped by the sediment was low, due to the lack of Fe^{3+} in water, and the decomposition of complexes with Fe^{3+}, Mn^{4+}, and Ca^{2+}, due to the anaerobic conditions prevailing in the lower parts of the waters. The P released by the desorption and mineralization of organic matter in the sediment diffused toward the over-bottom water layer and, later, to the trophogenic layer, as a result of the vertical transport [58,59]. These phenomena additionally intensified the primary production process, which was limited by the excess of nutrient solution supplied with the sewage.

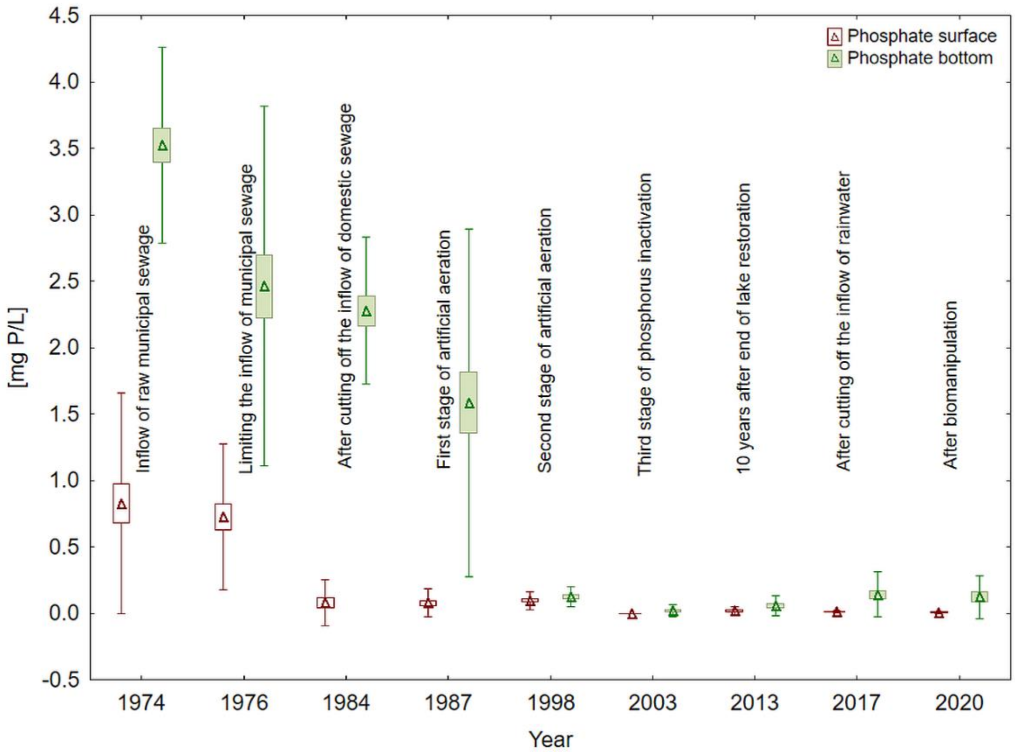

Figure 2. The mean annual values of the phosphate content (±SD) in the water of Lake Długie.

ARA was the first method of restoration used on Lake Długie. The main purpose of this method is to improve the oxygen conditions in the bottom layers of the water body, thanks to which the redox potential in the water–sediment interface increases [59]. The process of nutrient release from the bottom sediments is inhibited, and redox-dependent metals (Mn, Fe) accumulate, as well as harmful and poisonous substances, such as ammonia and hydrogen sulphide [60–62]. The increased oxygen content may also increase the mineralization of organic matter in the sediment, thereby reducing the long-term oxygen demand [63,64].

During the first stage of ARA, the mean values of PO_4^{3-} were 0.07 ± 0.05 mg P/L in the upper water layer, and 1.58 ± 0.65 mg P/L near the bottom. During the second stage of ARA, the average values of PO_4^{3-} in the surface water layer were 0.09 ± 0.03 mg P/L and, in the near-bottom, 0.124 ± 0.04 mg P/L. The research on Lake Długie during the ARA procedure did not show significant changes in the phosphates content in the surface water layer, but a very large reduction in the PO_4^{3-} amount was observed in the over-bottom water. During the second aeration stage, the phosphate concentration was about 10-fold lower than before the restoration. Probably, the reduction in the phosphate amount in the near-bottom water was caused by its distribution in the whole water volume. In addition, owing to the improved oxygenation of the over-bottom water, the release of mineral phosphorus from sediments was inhibited and, consequently, the phosphate content decreased in the over-bottom water, as well as in the whole lake. Similar results were obtained by Solim and Wanganeo [65] and Søndergaard et al. [66]. Despite the good oxygenation of the bottom waters, a complete reduction in phosphates from the midwater was not achieved, which was related to the low sorption capacity of the lake-bottom sediments, which made it impossible for phosphorus to precipitate as iron (III) compounds. According to Søndergaard et al. [66], the essential conditions for this process are good water oxygenation and an Fe:P ratio above 3.

Due to the low content of Fe and Mn in the sediment, and the absence of these elements in the water column of Lake Długie, further restoration via ARA was impossible. The next method used on the analyzed water body was PI, which is based on the precipitation of phosphorus from water, and its inactivation in the bottom sediment, the sorptive properties of which are improved via the application of a coagulant. Due to the properties of Al in anoxic conditions; with the aluminum forming strong bonds with phosphorus, even a low redox potential; it was decided that the aluminum coagulant PAX 18 (polyaluminum chloride, which contains ca 9% Al) would be applied. The P inactivation method caused a further reduction in the phosphates amounts to 0.00 ± 0.00 mg P/L at the surface, and 0.02 ± 0.02 mg P/L in the over-bottom water (Figure 2). The coagulant PAX 18 spread over the surface of the lake water dissociated with the release of free Al^{3+} ions, and then underwent hydration to form hexahydrate $Al(H_2O)_6{}^{3+}$ complexes. At the same time, the hydrolysis process took place, leading to the formation of aluminum hydroxide, which, in the initial phase, appears as a "milky" colloidal suspension, and then turns into flocs. These particles show strong sorption properties in relation to phosphates (adsorption). The additional mechanisms of P removal from the water column are the precipitation of seston containing undissolved mineral and organic phosphorus, and the chemical precipitation of phosphates (e.g., $AlPO_4 \downarrow$). Phosphates precipitated from the waters to bottom sediments were blocked in the latter, in combination with aluminum. Thanks to the use of the PI method in Lake Długie, there was a radical blockage of mineral P released from the sediment, as an effect of the improvement in the sorption properties of the bottom sediment.

In 2013, the mean $PO_4{}^{3-}$ content increased to 0.02 ± 0.02 mg P/L at the surface, and to 0.06 ± 0.04 mg P/L near the bottom (Figure 2). In 2017, the mean values of $PO_4{}^{3-}$ remained on the level 0.01 ± 0.00 mg P/L at the surface, and 0.14 ± 0.08 mg P/L near the bottom (Figure 2). After BM, the average content of phosphates at the surface water layer was 0.01 ± 0.00 mg P/L, and 0.12 ± 0.08 mg P/L near the bottom (Figure 2).

The complicated and long-term restoration of Lake Długie turned this degraded lake into a water body with a low trophic level. This is confirmed by the low concentration of phosphates observed in 2013 and 2017, and in 2020 after the removal of vascular vegetation.

3.2. Ammonia and Nitrates ($NH_4{}^+$; $NO_3{}^-$)

Nitrogen is the second element, after phosphorus, that plays an important role in the eutrophication process of lakes. This element occurs most often in the form of ammonium and nitrate ions, and much less often as nitrites, which are an unstable form [67]. The ammonium ions in water mainly come from the biochemical breakdown of organic plant and animal compounds. Their source can also be industrial or municipal wastewater, as well as the reduction of nitrates and nitrites by hydrogen sulfide, pyrite, or other reducing compounds. The ammoniacal nitrogen content fluctuates significantly throughout the year. According to Addy et al. [68], ammonia concentrations are low in summer, when ammonia is consumed by plants, and is nitrified at the same time. However, in winter, at low temperatures, when biological life disappears and nitrification is inhibited, ammonia concentrations are high. Nitrates get into waters with municipal and industrial sewage, from mine drainage, and as a result of runoff from fields fertilized using artificial nitrogen fertilizers [69,70].

Untreated domestic sewage was introduced into Lake Długie over 20 years. According to Drozd [55], the average concentration of ammonia in the wastewater was 20 mg N/L, and nitrates were 1 mg N/L. During the 20 years, 51 tons of nitrogen were released into the lake as ammonia, and 2.6 tons of nitrogen as nitrates. The many years of discharge of raw and rainwater domestic sewage into Lake Długie resulted in the lake having extremely high nitrogen concentrations, similar to the values found in diluted sewage. In 1974, the concentrations of ammonia in the surface water layer ranged from 0.11 to 2.37 ± 1.26 mg N/L, and those of nitrates, from 0.06 to 0.15 ± 0.028 mg N/L. At the bottom, the ammonia concentrations ranged from 13.72 to 19.37 ± 1.83 mg N/L, and those of nitrate from 0.00 to 0.13 ± 0.039 mg N/L.

After the protection of the lake, there was no decrease in the amount of N compounds, especially NH_4^+. The environmental conditions in Lake Długie have not improved. The mean NH_4^+ content at the bottom of the water body was 20.7 ± 3.19 mg N/L (Figures 3 and 4).

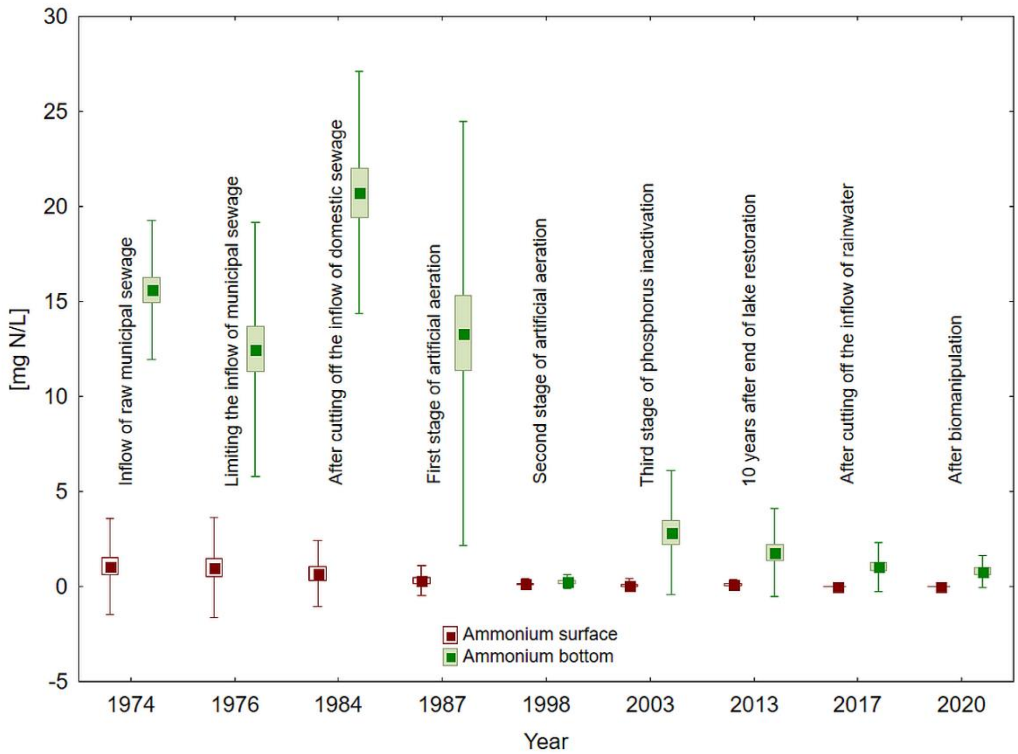

Figure 3. Mean annual values of ammonium content (±SD) in the water of Lake Długie.

Microorganisms play the most important role in the transformation of N compounds. The activity of microorganisms depends on the temperature, pH, and oxygen content. Ammonification takes place at a wide range of pHs and temperatures, and in aerobic and anaerobic conditions. Moreover, the intensity of ammonification depends on the number of individual groups of bacteria [71,72]. In the period before restoration, the bottom water of the analyzed lake was deoxygenated for most of the year, and $NH4^+$ was present in very high concentrations, and was the dominant form of N compounds (Figure 3). The improvement in the oxygenation in the bottom parts of the lake via ARA caused a rapid decrease in the content of ammonium, as a result of its oxidation to NO_3^- (Figures 3 and 4). The nitrification processes were favored by a higher temperature, which was achieved via the artificial mixing of water, and heating through contact with the atmosphere. Nitrates in the surface layer of the water are used by phytoplankton in the photosynthesis process [73] and, in the bottom waters, they can be reduced to gaseous nitrogen (denitrification). Denitrification is the most important process leading to the decrease in N content in water, and takes place with the participation of heterotrophic bacteria, at a temperature between 5 and 35 °C [74]. The temperature of the bottom water in the studied lake, both before and during ARA, favored denitrification. The pH of the water also affects the intensity of this phenomenon (with the optimum between 7.0 and 8.2 pH). However, the most important factor determining the direction of N transformations is having the appropriate oxygen conditions [75–77]. In Lake Długie, during ARA, denitrification could only take place in the bottom sediments, which were favored due to a high content of organic matter, and a lower pH. ARA caused a tenfold decrease in the total amount of nitrogen in the water of the ecosystem. In 1998, in the near-bottom water layer, the mean content of $NH4^+$ was 0.25 ± 0.18 mg N/L, and the average concentration of nitrates increased to 1.25 ± 0.23 mg N/L (Figures 3 and 4). In the study lake, after the end of the restoration via ARA, a return to the natural oxygen settings was noted. The bottom water was deoxygenated, and the bottom sediment again became a source of $NH4^+$, which could not be oxidized to NO_3^-. It is worth noting that, in 2003, the average concentration of ammonia in the bottom waters did not exceed 2.5 mg N/L. This situation shows the improved environmental conditions in the bottom sediment of the lake. During artificial circulation, a large proportion of the organic matter was mineralized, due to the higher temperature of the water (naturally 5 °C, and during aeration—20 °C) and good oxygenation. In the analyzed water body, a new layer of sediment was created, with a changed chemical composition.

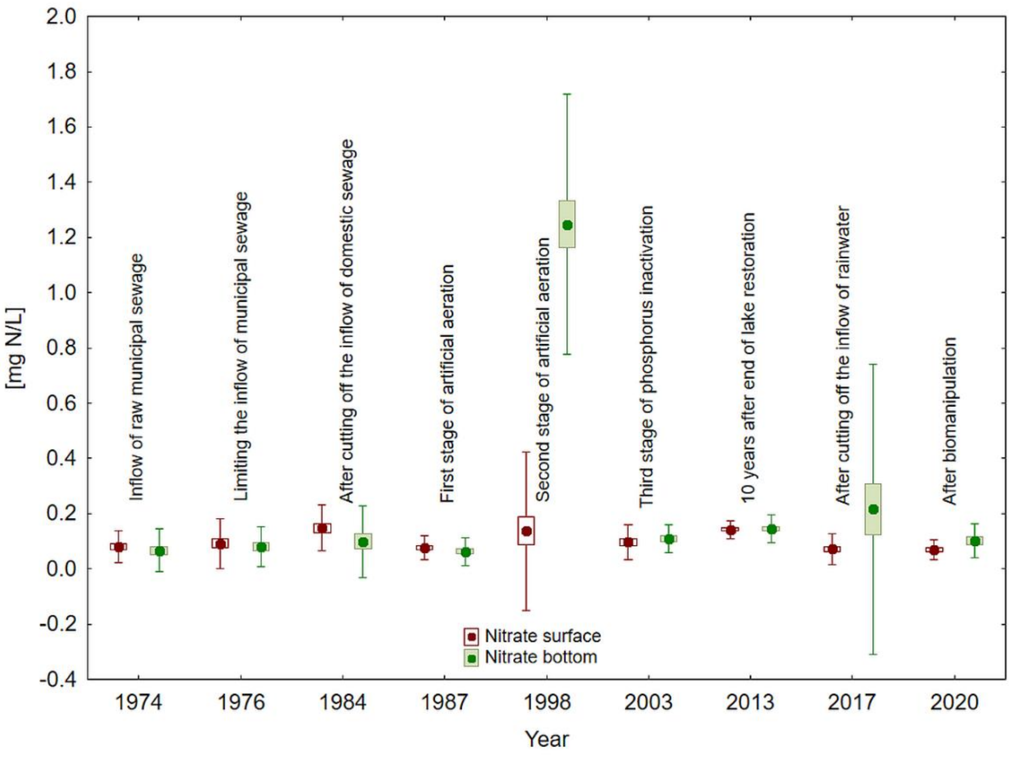

Figure 4. Mean annual values of nitrate content (±SD) in the water of Lake Długie.

The phosphorus inactivation method does not substantially influence the content of N compounds. However, due to the P removed from the water, this method caused the limiting of primary production, and a decrease in the content of organic nitrogen and, finally, a further decrease in the ammonium content in the near-bottom water.

In 2020 (seventeen years since the end of the lake restoration via the PI method, and after BM), the mean content of ammonium in the near-bottom water did not exceed 0.85 mg N/L, and the NO_3^- content in the whole water column was around 0.10 mg N/L (Figures 3 and 4).

3.3. Calcium (Ca^{2+})

Calcium is an element commonly found in rocks and soil (anortite $CaAl_2Si_2O_8$, calcite $CaCO_3$, dolomite $CaMg(CO_2)_2$, anhydrite $CaSO_4$, gypsum $CaSO_4 \cdot 2H_2O$, fluorite CaF_2, fluoroapatite $Ca_5(PO_4)_3F$, hydroxyapatite $Ca_5(PO_4)_3OH$). The source of calcium found in surface waters is leaching from rocks and soil, but also the inflow of municipal and industrial wastewater [78]. The calcium concentrations recorded in the water of Lake Długie were quite high.

Untreated municipal sewage was introduced into Lake Długie over 20 years. According to Drozd [55], the average concentration of calcium in the wastewater was 95 mg Ca/L. Over 20 years, 243 tons of Ca^{2+} were released into the lake. During the period of wastewater discharge to Lake Długie, the concentration of Ca^{2+} in the surface water layers fluctuated around 40 mg Ca/L, while, in the bottom layers, the average amount was 55 mg Ca/L (Figure 5). After the implementation of protective measures, which consisted of cutting off the inflow of municipal wastewater in the water of Lake Długie, a strong vertical stratification was observed in the content of calcium, with increasing values toward the bottom (29.2 mg Ca/L at the surface; 51.4 mg Ca/L at the bottom, on average) (Figure 5).

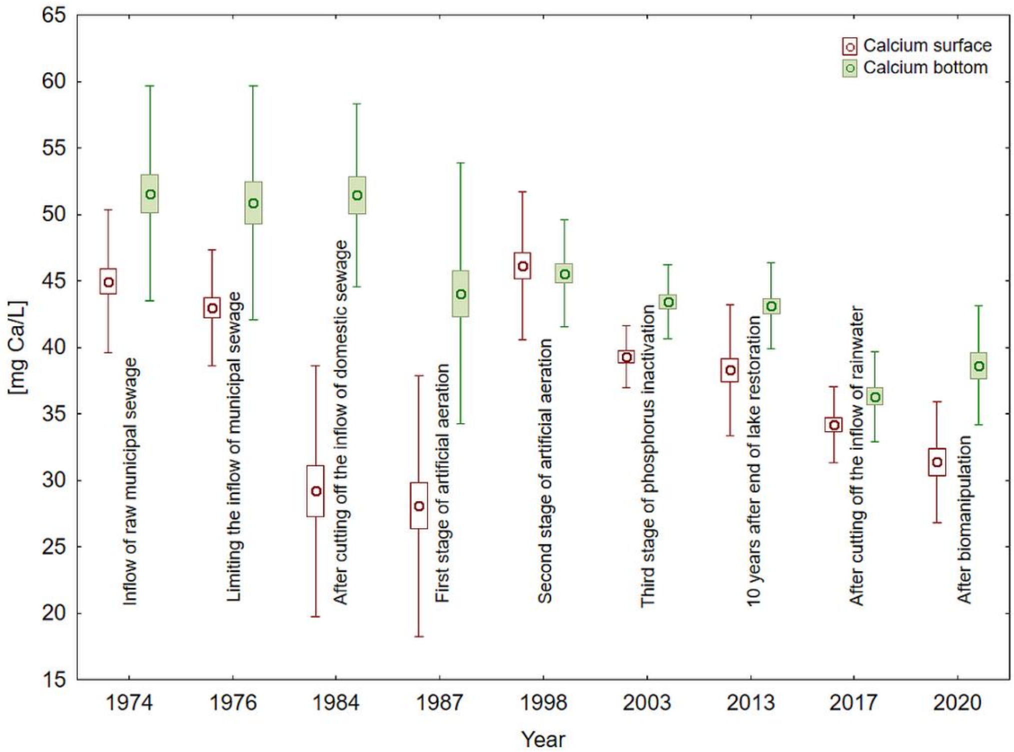

Figure 5. Mean annual values of calcium content (±SD) in the water of Lake Długie.

This situation can be explained by the fact that, despite the protection treatments, in 1984, algal blooms were observed due to the still-high content of P and N. Primary production leads to the depletion of free CO_2, and the shifting of the chemical equilibrium between the forms of $CaCO_3$ [79]. As a result, $CaCO_3$ is precipitated to the near-bottom water zone (hypolimnion), which is rich in CO_2, and it is dissolved, causing an increase in the Ca^{2+} content in the hypolimnion. The more intensive the primary production, the clearer the difference in the alkalinity and Ca content between the surface and the bottom. A similar situation was recorded by Grochowska [80] for the degraded Lake Klasztorne Małe.

The beginning of the ARA caused a decrease in the N and P amount, resulting in a reduction in the production processes in the water body. It was reflected in a decrease in the Ca^{2+} concentration in the lake water, and in the destruction of the vertical stratification of Ca^{2+} concentration, too (Figure 5).

The lower Ca content in the water was due to the increased sedimentation and calcite deposition in the bottom sediment. Calcite is stored in sediments only when the pH of the water is alkaline and there are no high concentrations of CO_2 [81]. Artificial aeration caused the water temperature in the entire volume of the lake, even the bottom, to be high. It was conducive to the mineralization process of the organic matter, the product of which was CO_2. This gas was distributed in the entire volume of water, which did not cause a drop in the pH at the bottom and, at the same time, favored the deposition of calcite in the sediments.

The phosphorus inactivation method caused a decrease in the P and N content, to the range of values characteristic of lakes with a low trophy level [82], and a further reduction in primary production. In the upper water layers, the pH was higher than 8.3, and the depletion of free CO_2 was observed. In the over-bottom water layers, CO_2 was observed continuously, but its concentration did not exceed 50 mg CO_2/L, despite the anoxic conditions. During 2001–2003, and in 2013, 2017, and 2020, it was recorded that—as was the case prior to the lake aeration period—a vertical stratification of calcium content was observed, with slight increasing values toward the bottom (Figure 5).

It is worth noting that differences in Ca^{2+} between the surface water and over-bottom water were much lower than those recorded before the restoration. This situation seems to confirm the durability of changes caused by the application of all the restoration methods.

3.4. Chlorides (Cl^-)

Chlorides are ions that are considered when determining the degree of contamination of water by minerals. The currently observed excessive chloride concentrations in surface waters in urban areas may be caused by the inflow of sewage, but are primarily caused by rainfall and meltwater runoff from streets and pavements and, to a lesser extent, by atmospheric precipitation and components triggered by the natural weathering processes occurring in the soil, and soils in the catchment area [83]. Over the course of the 20 years of untreated municipal wastewater discharge, 294 tons of chlorides were introduced into Lake Długie. In the 1970s, the chloride concentrations in the waters of the studied lake remained in the range from 40 to 50 $\pm$ 3.3 mg Cl/L in the surface layers, and from 41 to 122 $\pm$ 14.5 mg Cl/L in the waters near the bottom (Figure 6). After the sewage inflow was cut off, the chloride content in the surface water layers was similar, while, in the bottom layers, it slightly decreased. The source of chlorides at that time was the runoff from paved surfaces and the rainwater drainage system. In the temperate climate zone, enormous amounts of chemical deicing agents are used on pavements and roads in winter, to eliminate slippery surfaces. The use of salt to melt snow first occurred in the 1930s [84]. There are a very wide range of deicing agents; for example magnesium chloride, calcium chloride, calcium magnesium acetate, potassium acetate, urea, and glycols. However, the most popular way to combat icy road surfaces is the use of solid or moistened NaCl, sometimes mixed with substances that increase the surface roughness—sand or gravel. The reasons for the popularity of NaCl as a de-icing agent are its low price, ease of use, and high efficiency down to -9 °C. It is estimated that over 100 kg of salt is applied to 1 km of road, and the amount of chloride introduced may vary from 45 to 98 t/km^2/year [83,84]. The use of deicing salt causes the presence of chlorides and sodium in the snowmelt runoff, contamination of the soil and groundwater adjacent to the road, and an increase in the salinity of the surface waters to which the snowmelt flows.

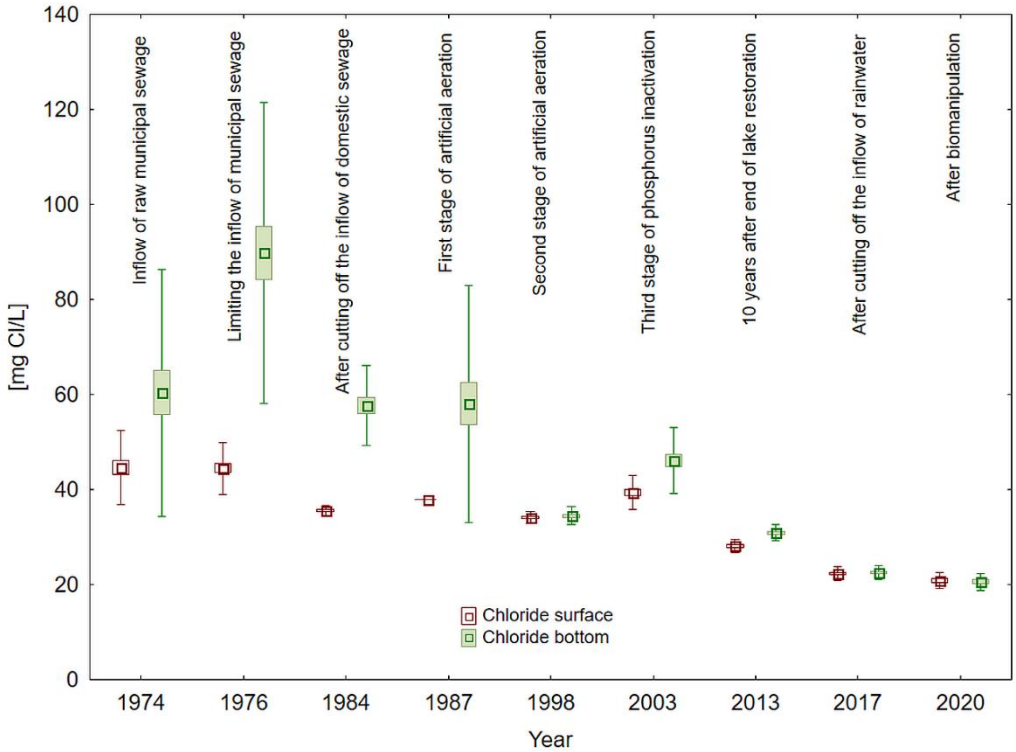

Figure 6. Mean annual values of chloride content (±SD) in the water of Lake Długie.

According to Church and Friesz [85], about 55% of the salt used is transported by the runoff surface, while the remaining 45% infiltrates through soil into groundwater. Muller and Gachter [86] report that, in Lake Constance, the chloride concentration has more than doubled in the last 40 years. It has been estimated to be 101,000 t of chlorides per year. During the restoration of Lake Długie by means of ARA, the chloride content was equal in the entire water volume, and amounted to approximately 35 ± 0.75 mg Cl/L. During the dosing of the coagulant polyaluminum PAX 18, a periodic increase in the Cl^- concentration, even up to 50 ± 3.1 mg Cl/L, was observed. After the flocs of amphoteric aluminum hydroxide settled down, the chloride content in the water also decreased. The most visible decrease in chloride content in the waters of Lake Długie was recorded after the storm water inflow was cut off. However, persistent chloride concentrations are still typical of urban lakes. The chloride concentration in inland surface waters is about 9 mg Cl/L [87]. The presence in surface waters of dissolved salts applied to de-ice roads has a huge impact on organisms living in the aquatic environment [88]. These salts, by affecting the ion exchange, cause the acidification of surface waters, and increase the mobility of other metals, including an increase in the availability of heavy metals. Long-term chloride retention in the seabed water reduces the amount of dissolved oxygen and nutrients, which can lead to a decline in the biodiversity of benthos, aquatic insects, and periphyton, as well as in microorganisms that decompose plant debris. A persistent exposure to chloride concentrations above 25 mg Cl/L may have a negative effect on freshwater fish [88].

4. Conclusions

The location of Lake Długie in the city meant that the reservoir was transformed into a raw domestic sewage and stormwater receiver. Over twenty years, sewage discharge into the lake introduced huge amounts of pollutants. This completely degraded the lake. It should be mentioned that nutrients were also introduced in organic forms. Further anthropogenic activities improved the water quality in Lake Długie. After the cutting off of the inflow of sewage, the recorded content of phosphates, ammonium nitrogen, and calcium was lower. ARA of the lake via the destratification method inhibited the process of internal loading, releasing mineral P from the bottom sediments, which resulted in a

10-fold decrease in the amount of P in the entire water body. Due to the improvement in the water oxygenation, the nitrification process was possible, which was reflected in the increase in the concentration of nitrate nitrogen, and the decrease in the amount of ammonia. Subsequently, the denitrification of nitrates taking place in bottom sediments, the product of which is molecular nitrogen escaping into the atmosphere, resulted in a multiple decrease in nitrogen compounds. The number of chlorides and amount of calcium also decreased during aeration.

Artificial aeration is, therefore, a very good method of restoration, which improves the values of many chemical indicators in water.

Another method of restoration, PI, resulted in a further decrease in PO_4^{3-} from the water column. The coagulant also caused the immobilization of PO_4^{3-} in the bottom sediment. The withdrawal of mineral P from the waters of the lake limited the production processes in the lake, which was reflected in the reduction in the difference in the calcium content between the surface and the bottom of the lake. On the other hand, the number of chlorides constituting a component of the coagulant polyaluminum chloride has increased.

PI is a method that primarily affects phosphorus compounds. Depending on the type of coagulant, lake water may be indirectly enriched by the chemical elements included in the preparation.

In 2015, the inflow of rainwater to the reservoir was cut off, which resulted in a significant decrease in chlorides.

BM activities, consisting of mowing macrophytes, resulted in the removal of a significant phosphorus and nitrogen load from the lake, accumulated in plant tissues.

Thanks to biomanipulation, a significant load of both nitrogen and phosphorus can be removed from the lake. The excavated vegetation can be used as fertilizer.

The example of Lake Długie shows that ill-considered human activities carried out within the catchment area of lakes may cause a dramatic deterioration in the quality of surface waters. In such a situation, it takes much longer, and a whole complex of various activities to restore the water body to a low trophic state.

The example of Lake Długie clearly shows that lakes cannot be transformed into sewage receivers. Lakes show cumulative properties, and everything that is introduced to them from the outside stays in the bottom sediments, causing the shallowing and slow disappearance of the ecosystem. It is often worthwhile to allocate funds to prevent pollution, as the long-term process of restoring the quality of water in a lake is much more costly. The results indicate that a combination of restoration methods in the right sequence provides a very good and long-term improvement in water quality.

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