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A Unique Application Methodology for the Use of Phosphorus Inactivation Agents and Its Effect on Phosphorus Speciation in Lakes with Contrasting Mixing Regimes

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Abstract: The efficiencies of the restoration of two lakes of varied morphometries and trophic states—meromictic, hypertrophic Lake Klasztorne Małe, and dimictic, eutrophic Lake Klasztorne Duże—with the use of the phosphorus inactivation method with sequential application of iron and aluminum compounds have been compared. The total dose of the agents applied for Lake Klasztorne Małe was 38 tons of PAX 18 (aluminum polychloride) and 14 tons of PIX 111 (iron chloride), and for Lake Klasztorne Duże, it was 74 tons of PAX 18 and 46 tons of PIX 111. After the application of the compounds, better efficiency of phosphate removal from the surface water layers was obtained in the case of the dimictic, eutrophic Lake Klasztorne Duże. The use of two doses of compounds did not lead to complete precipitation of phosphates from the bottom water layers of either lake. It is noteworthy that in the case of both lakes, inhibition of the internal loading process was observed. The obtained results for the Klasztorne lakes showed that the use of two types of compounds makes it possible to reduce the cost of restoration, and moreover, the dosing of iron salts in the coastal areas of the lakes ensures a higher level of ecological safety.

Keywords: lake; eutrophication; phosphorus compounds; restoration; phosphorus inactivation

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1. Introduction

Human activities in the lake catchment area, which started in the nineteenth century, consisting of intensive development of industry, increasing the area of cities and agricultural lands, and intensive fertilization of fields and discharge of untreated sewage, among others, cause a decrease in the share of biologically active areas in which water retention occurs and thus an increase in the amount of pollutants flowing into the lake basins [1–3]. As a result of the influx of an excessive amount of organic and mineral pollutants, especially nitrogen and phosphorus compounds, the intensive primary production of phytoplankton and phytobenthic organisms is observed in aquatic ecosystems. This process, called eutrophication, occurs very slowly under natural conditions, but intensified anthropopressure in the catchments of water bodies leads to its acceleration and, consequently, faster degradation of lake ecosystems [4–7]. Symptoms of eutrophication and degradation of lakes include, among others, blooms of phytoplankton and cyanobacteria, lowered transparency of the water, reduced biodiversity at all trophic levels, increased amounts of bottom sediments, and increased levels of siltation [8]. The decomposition of organic matter causes the consumption of oxygen in the bottom layers of the lake, which triggers the process of supplying water with nutrients stored in the bottom sediments. In extreme cases, the degraded conditions occur in the entire volume of the lake, which results in the death of the fish and the exclusion of the water body from use [9,10].

Quickly, the progressive degradation of the water became so burdensome that people began looking for ways to limit this process and its unfavorable consequences. Moreover, achieving or maintaining the so-called good status of natural waters is a key aspect of ecological and social problems in the countries of the European community [11,12]. First, the implementation of various protective solutions was started, the goal of which is to completely cut off, or at least radically reduce, the load of pollutants flowing in from the catchment area. In those cases where the degree of degradation is so high that the process of supplying water with nutrients from bottom sediments has started, the protective methods do not bring the expected results. Thus, a properly selected restoration method should be implemented, taking into account the thermal-oxygen conditions, acid–base balance, nitrogen and phosphorus circulation in the water, metabolism of the lake ecosystem, the processes of the formation of bottom sediments in lakes, and their role in the migration of nutrients in the water–bottom sediment interface [13,14]. In Poland and in the world, many different restoration treatments (technical or biological) have been applied to permanently immobilize nutrients in bottom sediments or remove them from the lake entirely [15,16]. Known methods of restoration include selective removal of bottom waters, dilution of lakes, artificial aeration, removal of bottom sediments, isolation of bottom sediments, water-balance control systems in flowing lakes, and biomanipulation [17,18]. One of the most popular, cheap, and effective methods of phosphate removal from the water column is chemical inactivation with iron, aluminum, calcium, and even magnesium salts [19–22]. The best choice of compound to be used in restoration efforts is dependent on water chemistry, in particular the pH of the water and the oxygen conditions in the near-bottom water. For aluminum compounds, the optimal pH is in the range of 6–8 because in the case of acidic water's pH, the form Al^{+3}, which is toxic to organisms, dominates in the solution, and with an alkaline pH, the solubility of amphoteric aluminum hydroxide $Al(OH)_3$ increases [23–25]. The water pH is less significant with inactivation using iron salts. A disadvantage of the inactivation of phosphorus with iron salts is the high sensitivity to a decrease in the redox potential. Under reducing conditions, when the concentration of dissolved oxygen in the overhead zone drops practically to zero, iron becomes an electron acceptor; Fe(III) is reduced to Fe(II), and phosphates are released into the water column. This means that the occurrence of anaerobic conditions in the bottom waters of degraded lakes may decrease the effectiveness of iron compounds [26].

A completely new solution for the restoration of lakes was conducted by scientists from the University of Warmia and Mazury in Olsztyn, consisting in the inactivation of phosphorus by sequential application of iron compounds (iron chloride PIX 111) and aluminum compounds (polyaluminium chloride PAX 18). The use of two types of compounds makes it possible to reduce the cost of restoration, and moreover, the dosing of iron salts in the coastal areas of the lakes ensures a higher level of ecological safety, due to the presence of many plant and animal organisms in this part of the lakes.

The aim of this study is to determine the impact of this method on the concentration of phosphorus compounds in two morphometric and tropically different lakes: Klasztorne Małe (LKM) and Klasztorne Duże (LKD).

2. Material and Methods

2.1. Study Area

Klasztorne Małe and Klasztorne Duże lakes are located in Poland, approximately 30 km west of Gdańsk, within the administrative boundaries of the city of Kartuzy in the Kashubian Lake District (Figure 1). It is a physical and geographic mesoregion belonging to the East Pomeranian Lakeland macroregion [27]. According to the regionalization prepared by the Ministry of Environment, the Kashubian Lake District is entirely located in the Lower Vistula region.

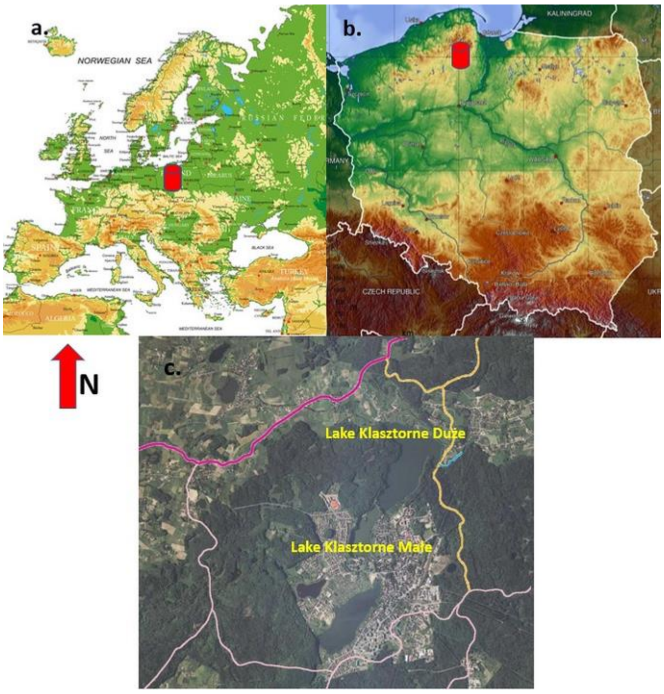
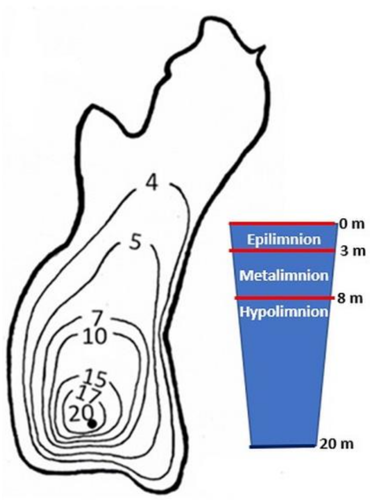


Figure 1. Study area: (**a**) location of research lakes in Europe, (**b**) location of research lakes in Poland and (**c**) lake catchment.

The direct catchment area of Lake Klasztorne Małe is 0.13 km^2, and that of Klasztorne Duże Lake is 1.03 km^2. Both areas of direct supply are 100% covered with mixed forest.

Lake Klasztorne Małe is described by the following geographical coordinates: 54°20′21″ N, 18°11′35″ E. It is situated at an altitude of 203 m above sea level in the basin of Klasztorna Struga-Mała Słupina-Radunia-Motława-Martwa Wisła-the Baltic Sea (Figure 2). Lake Klasztorne Małe is a flow-through water body (water residence time—0.515 y), with the main direction of water movement being from south to north. In the southern part, it is connected to Lake Karczemne through a drainage ditch. According to Bajkiewicz-Grabowska et al. [1] and Januszkiewicz and Jakubowska [28], Lake Klasztorne Małe was artificially separated from part of a larger Lake Klasztorne.



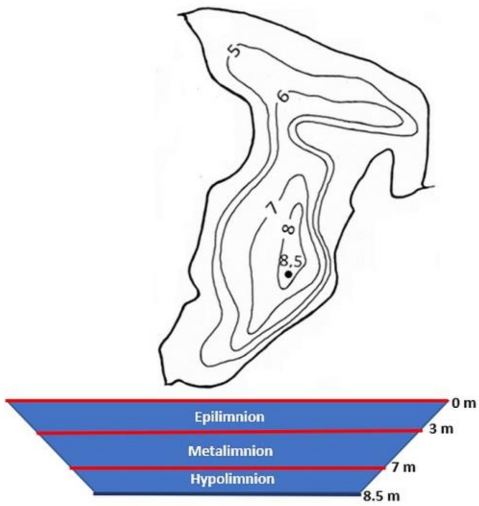
Parameter	Value
Surface [P]	13.7 ha
Maximum depth [D_{max}]	20.0 m
Average depth [$D_{ave}=V/P$]	8.1 m
Relative depth [$D_{rel}=D_{max}/\sqrt{P}$]	0.054
Depth index [$DI=D_{ave}/D_{max}$]	0.40
Volume [V]	1,106,000 m^3
Maximum length [L_{max}]	720 m
Maximum width [W_{max}]	250 m
Elongation [$\lambda=L_{max}/W_{max}$]	2.9
Length of shoreline [$L_{shoreline}$]	1850 m
Shoreline development index [$K=L_{shoreline}/2\sqrt{\pi P}$]	1.4

Figure 2. Morphometric data of Lake Klasztorne Małe (Inland Fisheries Institute in Olsztyn).

Klasztorne Małe is a meromictic lake. Below 10 m deep, there is a hypolimnion, which in recent years has had a monimolimnion layer that is not subject to circulation in spring and autumn. Lake Klasztorne Małe is a hypertrophic reservoir.

From the mid-1950s, the water body was transformed into a raw sewage receiver. It came through 3 collectors with settling tanks. This was domestic sewage from the hospital, slaughterhouse, and veterinary clinic.

Lake Klasztorne Duże is described by the following geographical coordinates: 54°20′52′′ N and 18°12′10′′ E. The lake is located 202.3 m above sea level in the basin of Klasztorna Struga-Mała Słupina-Radunia-Motława-Martwa Wisła-the Baltic Sea (Figure 3). Lake Klasztorne Duże is a flow-through water body (water residence time—1.219 y), with the main direction of water movement flowing from south to northeast.



Parameter	Value
Surface [P]	57.5 ha
Maximum depth [D_{max}]	8.5 m
Average depth [D_{ave}=V/P]	4.8 m
Relative depth [$D_{rel}=D_{max}/\sqrt{P}$]	0.011
Depth index [DI=D_{ave}/D_{max}]	0.59
Volume [V]	2,780,000 m^3
Maximum length [L_{max}]	1320 m
Maximum width [W_{max}]	570 m
Elongation [$\lambda=L_{max}/W_{max}$]	2.3
Length of shoreline [$L_{shoreline}$]	4100 m
Shoreline development index [$K=L_{shoreline}/2\sqrt{\pi P}$]	1.5

Figure 3. Morphometric data of Lake Klasztorne Duże (Inland Fisheries Institute in Olsztyn).

Lake Klasztorne Duże is a stratified, dimictic water body with high water dynamics, which is related to its small depth (8.5 m) with an area of 60 ha. In autumn and spring, this lake is fully circulating. Lake Klasztorne Duże is a eutrophic lake.

One of the symptoms of lake degradation is the unfavorable distribution of oxygen in the water column. Lake Klasztorne Małe is hypertrophic, and additionally, it is a meromictic water body that never circulates to the bottom. These two factors cause the bottom waters of this lake to be deoxygenated throughout the year. At critical moments, anaerobic conditions prevail in waters below 3 m of depth (Table 1). Lake Klasztorne Duże, as a eutrophic reservoir, is characterized by slightly better oxygen conditions. Complete deoxygenation of the bottom waters occurs in the summer (Table 1).

Table 1. Oxygen settings in analyzed lakes.

Depth [m]	LAKE KLASZTORNE MAŁE									
	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
	Oxygen content [mg O_2/L]—spot analyses									
0	15.9	14.6	12.8	14.6	7.9	7.9	10.5	9.7	7.2	9.0
1	15.9	14.6	12.7	14.6	6.7	6.5	10.4	9.7	7.0	9.0
2	10.9	14.6	12.0	5.5	1.2	5.4	9.3	8.7	6.9	8.3
3	1.6	14.4	11.2	0.9	0.3	0.6	8.4	8.7	6.8	8.2
4	0	11.6	10.5	0.2	0	0	7.9	7.3	6.7	8.2

Table 1. *Cont.*

Depth [m]	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
					LAKE KLASZTORNE MAŁE					
5	0	9.9	8.6	0.1	0	0	4.0	3.5	6.7	7.7
6	0	8.7	1.1	0.1	0	0	1.0	1.1	6.6	6.5
7	0	0	0	0	0	0	0.4	0	6.0	5.8
8	0	0	0	0	0	0	0	0	0.4	4.1
9	0	0	0	0	0	0	0	0	0.3	2.4
10	0	0	0	0	0	0	0	0	0	0
11	0	0	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	0	0	0	0
13	0	0	0	0	0	0	0	0	0	0
14	0	0	0	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0	0	0	0
16	0	0	0	0	0	0	0	0	0	0
17	0	0	0	0	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0
19	0	0	0	0	0	0	0	0	0	0
20	0	0	0	0	0	0	0	0	0	0
					LAKE KLASZTORNE DUŻE					
Depth [m]	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
					Oxygen content [mg O_2/L]—spot analyses					
0	14.6	15.8	12.4	12.0	9.4	8.7	10.7	7.9	9.2	11.3
1	13.8	15.8	12.5	12.2	9.4	8.7	9.9	7.5	9.1	11.3
2	13.8	15.9	12.5	9.3	8.7	8.7	9.1	7.2	9.1	11.3
3	13.7	15.9	12.5	6.9	2.3	8.6	8.4	7.4	9.0	10.6
4	13.5	15.8	12.5	4.1	1.0	0.7	7.2	6.8	8.9	10.6
5	13.3	15.8	12.5	1.5	0.5	0.4	6.1	6.8	8.9	10.7
6	13.2	15.8	12.5	0.3	0	0.3	5.8	6.8	8.9	10.7
7	13.1	15.8	12.5	0.1	0	0	1.8	6.7	8.9	10.4
8	13.1	15.8	12.5	0.1	0	0	1.8	6.7	8.9	10.4

2.2. Water Sample Collection and Analysis

The research on Lake Klasztorne Małe and Klasztorne Duże was carried out in 2013 (before the protection and restoration of the lakes), 2020 (after the protection of lakes began), and 2021 (after the protection and restoration of lakes by the phosphorus inactivation method). Samples were taken once a month, using a Ruttner sampler, at the points situated above the deepest part of the lakes (1 m below water surface and 1 m above the bottom) (Figures 2 and 3).

Water samples were analyzed for total orthophosphate (P_{min}) using the ascorbic acid method and colorimetric analysis for P-PO_4 (NANO147 COLOR UV/vis spectrophotometer, Macherey Nagel, λ = 690 nm) (GmbH&Co. KG, Düren, Germany). Samples were also analyzed for total phosphorus (TP) and total organic phosphorus (P_{org}.) using Standard Methods [29]. Every analysis was made in triplicate. The coefficient of variation (CV) for the repeated analysis was 2% for the analysis of P_{min} and TP [30].

The results of $P_{min.}$ (P-PO_4), P_{org}., and TP were statistically analyzed (one–way ANOVA, p = 0.05, Tukey's HSD) using a Statistica 13.3 software package (Tibco Software, Palo Alto, CA, USA) [31]. We tested for the presence of significance differences in TP, P_{min}, and P_{org} between the two lakes and between sampling dates.

2.3. Description of Protection and Restoration Techniques

In 2018, protective measures were carried out in the Klasztorne lakes catchment area in order to reduce the flow of stormwater and sewage into the lakes. They consisted of the reconstruction of the stormwater and combined sewage system in the city of Kartuzy and the construction of retention reservoirs for stormwater and pretreatment facilities at the existing stormwater outlets. The main pumping station was also modernized to accommodate excess rainwater.

Due to the contamination of the waters of the Klasztorna Struga supplying Lake Klasztorne Małe, the watercourse was renovated by filling and adjusting the bed. The bottom of the watercourse was planted with hydrophilic plants.

In the spring (23–25 March) and autumn (7–10 November) of 2021, the Klasztorne lakes were dosed with phosphorus inactivation agents. Specifically, treatment was undertaken using a sequential application method, whereby a dose of iron (PIX 111) was followed by a dose of aluminum (PAX 18) compounds. Doses of compounds were calculated based on the results of analyses of the waters and bottom sediments of Klasztorne lakes. The polyaluminium chloride (PAX 18) demand of the profundal bottom for the binding of mineral phosphorus of Lake Klasztorne Małe amounted to 49.7 g m^{-2}. Furthermore, for coastal sediments predisposed to the use of iron chloride (PIX 111), the demand for this element was approximately 73.2 g m^{-2}. The polyaluminium chloride (PAX 18) demand to bind mineral phosphorus of the profundal sludge of Lake Klasztorne Duże amounted to 28.4 g m^{-2}. Moreover, for coastal sediments predisposed to the use of iron chloride (PIX 111), the demand for this element was approximately 45.9 g m^{-2}. Iron chloride (PIX 111) was applied first and only in the coastal areas of both lakes. In Lake Klasztorne Małe, the dosing area was limited by a 2 m isobath and in Lake Klasztorne Duże, by a 5 m isobath. Then, polyaluminium chloride (PAX 18) was applied to the remaining area of the lakes. In 2021, 7054 kg of PIX 111 and 18,839 kg of PAX 18 were introduced into Lake Klasztorne Małe twice, and 23,284 kg of PIX 111 and 37,100 kg of PAX 18 were introduced into Lake Klasztorne Duże twice.

The compounds were spread by the surface method from the deck of the vessels. The chemical dosing system made it possible to regulate the intensity of their administration. During the application, efforts were made to distribute the compounds as evenly as possible over the entire surface of the designated body of water and absolutely avoid uncontrolled discharges of the agent used during standstills or maneuvers of auxiliary vessels. The compounds were applied just below the water surface, using technical solutions preventing aeration of the forming flocs and their flotation.

3. Results

The statistical analysis revealed significant differences between 2013 (before the protection and restoration of Klasztorne lakes), 2020 (after the protection techniques in catchment), and 2021 (after the protection and restoration by the phosphorus inactivation method) in the content of phosphorus compounds in the water column. Statistical analysis also showed significant differences in the content of phosphorus between the meromictic, hypertrophic Lake Klasztorne Małe (LKM) and the dimictic, eutrophic Lake Klasztorne Duże (LKD) (Table 2).

Table 2. Results of one-way ANOVA analyses (with Tukey HSD) for the investigated variables in Lakes Klasztorne Małe and Klasztorne Duże (n = 384).

Variable	F Value	*p* Value	Years which Differ Significantly from 2013 (Before Restoration)
Pmin. surface	9.2473	<0.001	2020, 2021
Pmin. bottom	112.2020	<0.001	2020, 2021
Porg. surface	5.6243	<0.001	2020
Porg. bottom	75.8051	<0.001	2020, 2021
TP surface	3.4114	<0.001	2020, 2021
TB bottom	70.0129	<0.001	2020, 2021

3.1. Mineral Phosphorus

In the surface water layers of LKM, concentrations of phosphate ranged between 0.005 mg P/L and 0.428 mg P/L, but it should be noted that the minimum value was recorded after the application of compounds, and the maximum value was recorded before protective and restoration measures were implemented (Figure 4). In the surface water layer of the dimictic LKD, concentrations of mineral phosphorus ranged between 0.005 and 0.305 mg P/L (Figure 4). As in the case of the meromictic LKM, the maximum values were recorded before the protection and restoration of lake began, and the minimum values were recorded in 2021(after the protection and restoration of lake).

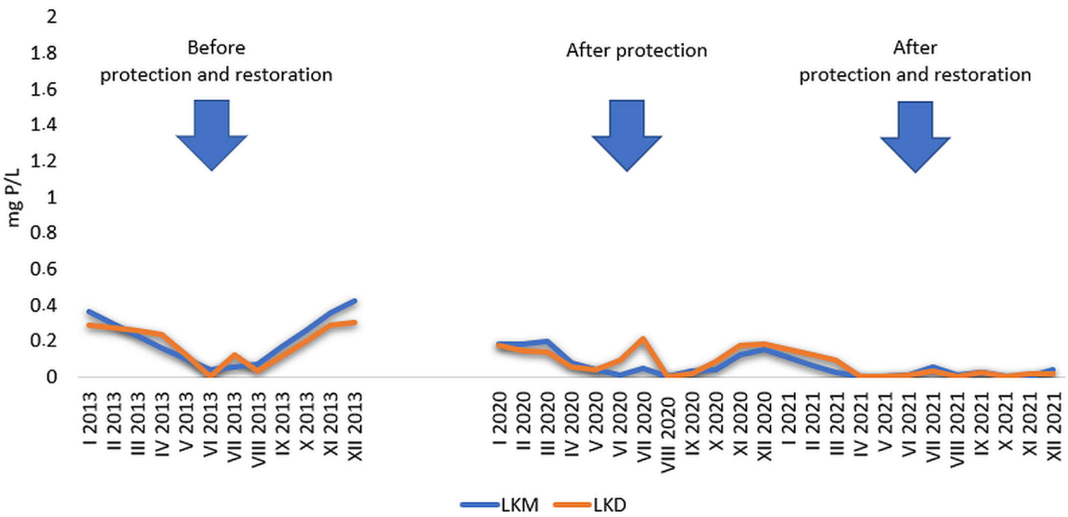


Figure 4. Changes in the content of mineral phosphorus (P_{min}.) in the surface water layer of Klasztorne lakes in selected research years.

Statistical analysis showed highly statistically significant differences in the content of mineral phosphorus in the surface water layers of both LKM and LKD between 2013 (before protection and restoration) and 2020 (after protection), but between 2020 (after protection) and 2021 (after protection and restoration), there were no statistically significant differences between the lakes. The average phosphate concentrations at the surface of the lakes in 2013 (before protection and restoration measures began) were 0.211 mg P L (±0.131) in LKM and 0.187 mg P/L (±0.104) in LKD (Figure 5). After restoration with the use of two types of compounds, a very clear decrease in phosphates was found in both lakes (Figure 5). In LKM, the average value was 0.031 mg P/L (±0.072), and in Lake Klasztorne Duże, it was up to 0.043 mg P/L (±0.051). The reduction of the mineral phosphorus content in the surface water layers of both lakes was about 80% (LKM—77%; LKD—85%).

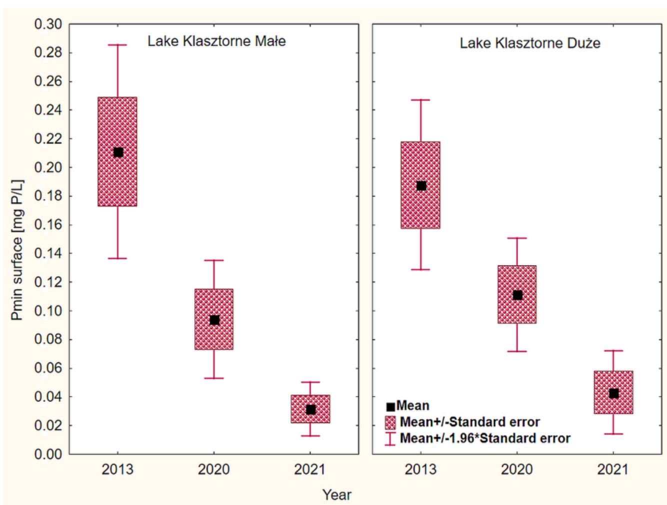
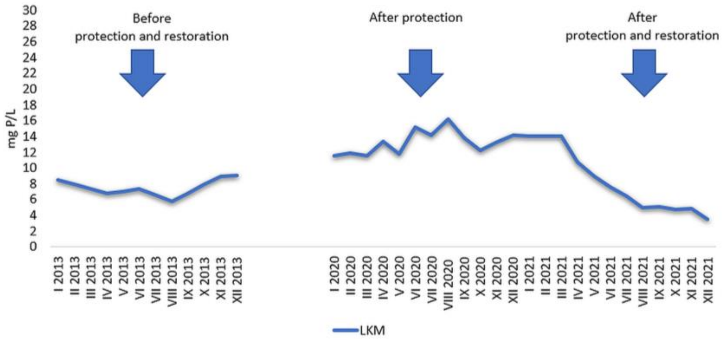


Figure 5. Average annual values of mineral phosphorus (P_{min}.) in the surface water of Klasztorne lakes in selected research years.

The bottom waters were richer in mineral phosphorus. In LKM, phosphate concentrations varied from 3.500 mg P/L (in 2021—year of restoration) to 16.200 mg P/L (during protection measures in 2020) (Figure 6a,b). In the eutrophic LKD, the range of mineral phosphorus concentrations in the analyzed period was not as wide as in the meromictic reservoir and ranged between 0.011 mg P/L (2021—restoration) and 1.004 mg P/L (2013—before the protection and restoration of the lake) (Figure 6a,b).



(**a**)

(**b**)

Figure 6. (**a**) Changes in the content of mineral phosphorus (P_{min}.) in the bottom water layer of Lake Klasztorne Małe in selected research years. (**b**) Changes in the content of mineral phosphorus (P_{min}.) in the bottom water layer of Lake Klasztorne Duże in selected research years.

Statistical analysis of the obtained results showed highly significant differences in the content of mineral phosphorus in the bottom water layer, both between the studied Klasztorne lakes and between the analyzed research years. The average content of mineral phosphorus in the bottom water layers of LKM in 2013 was 7.517 mg P/L (±1.008), as much as 13.201 mg P/L (±1.559) in 2020, and during restoration, 8.273 mg P/L (±4.036) (Figure 7). The application of compounds resulted in a 63% reduction of phosphates compared to 2020. The situation in LKD was completely different. In 2013, the average phosphate content was 0.485 mg P/L (±0.277), and after restoration, it was 0.063 mg P/L (±0.062). This was a reduction of 87%.

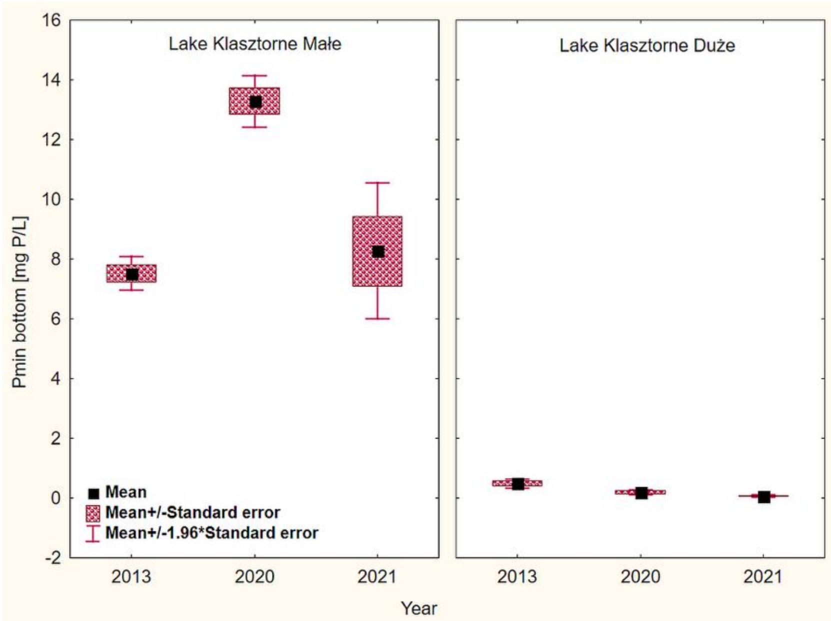


Figure 7. Average annual values of mineral phosphorus (P_{min}.) in the bottom water of Klasztorne lakes in selected research years.

3.2. Organic Phosphorus

In the surface water layers of LKM, concentrations of organic phosphorus ranged from 0.077 mg P/L to 0.791 mg P/L, with both extreme values (minimum and maximum) recorded in the year of restoration—2021 (Figure 8). In the surface water layer of LKD, the concentrations of organic phosphorus ranged between 0.006 and 1.700 mg P/L (Figure 8). The maximum value was recorded in the period before the protection and restoration of the lake and the minimum in the year of restoration—2021.

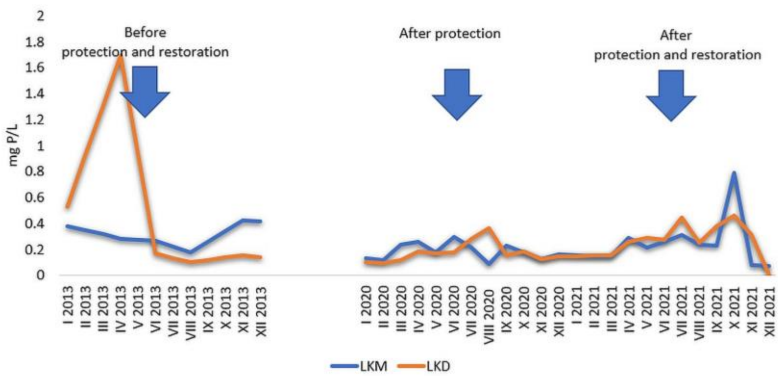


Figure 8. Changes in the content of organic phosphorus (P_{org}.) in the surface water layer of Klasztorne lakes in selected research years.

Statistical analysis showed highly statistically significant differences in the content of organic phosphorus in the surface water layer of both Klasztorne lakes in the analyzed research years. There were no significant differences between the lakes.

In 2013, the average concentration of P_{org}. in the surface water layer of LKM was 0.311 mg P/L (±0.076), and in LKD, it was 0.531 mg P/L (±0.553) (Figure 9). After restoration by phosphorus inactivation, after the second stage, a decrease in organic phosphorus was found in both lakes (Figure 9). In LKM, the average was 0.247 mg P/L (±0.187), and in LKD, it was 0.263 mg P/L (±0.132). The reduction in the content of the organic form of phosphorus in the surface water layer of LKM was 20% and in LKD, about 50%.

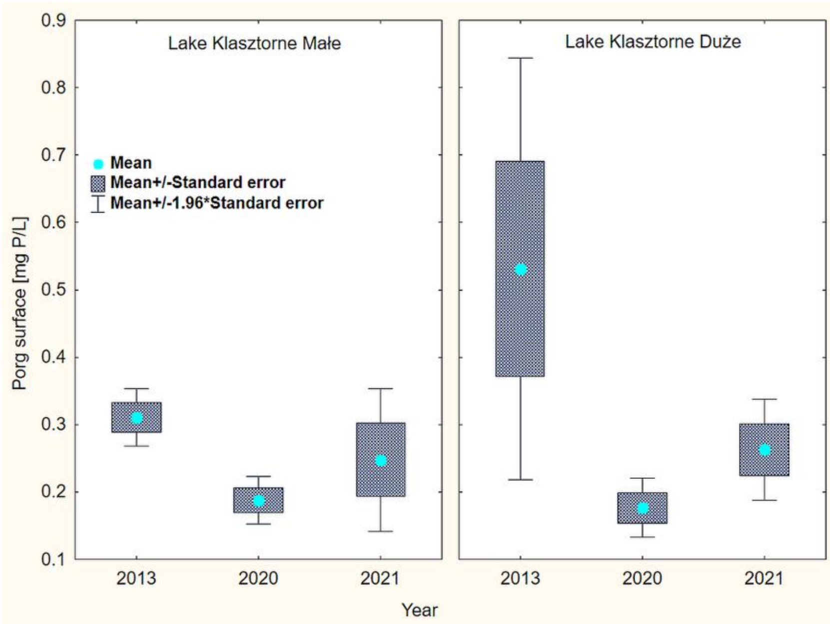


Figure 9. Average annual values of organic phosphorus (P_{org}.) in the surface water of Klasztorne lakes in selected research years.

The bottom water layers of LKM were very rich in organic phosphorus, the concentration of which varied from 0.350 mg P/L to 12.200 mg P/L. Both extreme results were recorded in 2013, before protection and restoration measures were implemented (Figure 10a,b). In the eutrophic LKD, the range of organic phosphorus concentrations was not as wide as in the meromictic water body (LKM) and was between 0.005 mg P/L (2021-after protection and restoration) and 0.926 mg P/L (2013—before the protection and restoration of the lake) (Figure 10a,b).

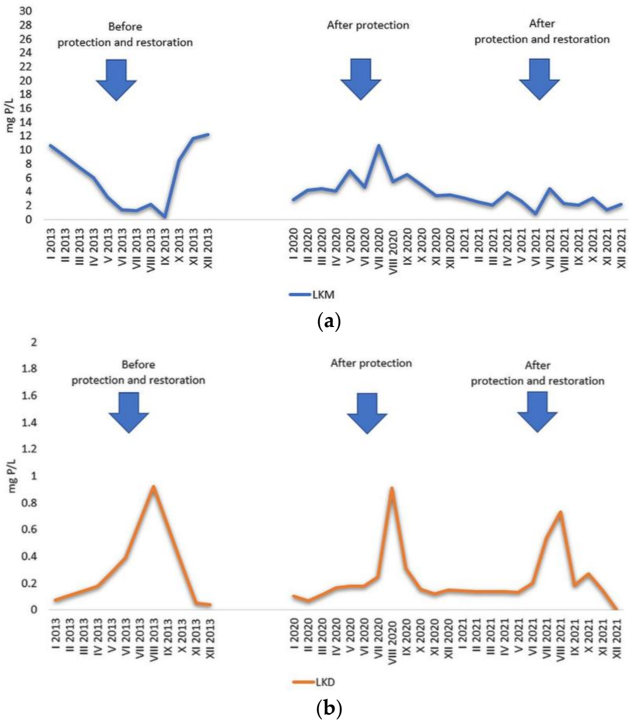


Figure 10. (**a**) Changes in the content of organic phosphorus (P_{org}.) in the bottom water layer of Lake Klasztorne Małe in selected research years. (**b**) Changes in the content of organic phosphorus (P_{org}.) in the bottom water layer of Lake Klasztorne Duże in selected research years.

Statistical analysis showed significant differences in the content of organic phosphorus in the bottom water layers of LKM between the analyzed research years. No such differences were found in the case of LKD. Statistical analysis showed highly statistically significant differences in the P_{org}. content between lakes.

In 2013, the average concentration of P_{org}. in the bottom water of LKM was 6.173 mg P/L (±6.339), and in LKD, it was 0.320 mg P/L (±0.285) (Figure 11). After restoration with the phosphorus inactivation method, a very clear decrease in the content of organic phosphorus in the bottom water was found only in the case of LKM (Figure 11). After restoration, at the bottom of LKM, an average value of 2.527 mg P/L (±1.008) for Porg. was recorded, and in LKD, it was 0.231 mg P/L (±0.203). The reduction of the organic phosphorus content at the bottom water of LKM was at the level of 60% and in LKD, about 20%.

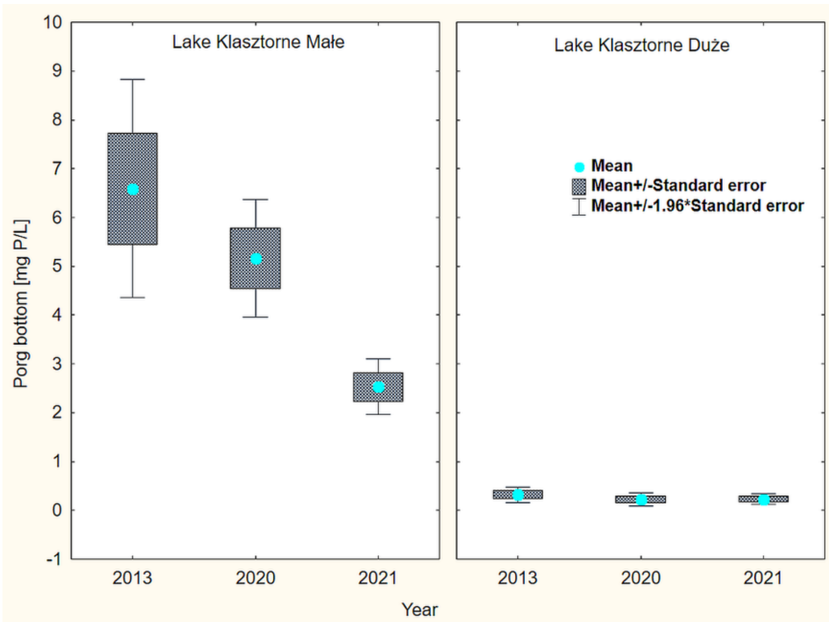


Figure 11. Average annual values of organic phosphorus (P_{org}.) in the bottom water of Klasztorne lakes in selected research years.

3.3. Total Phosphorus

In the surface water layer of the meromictic LKM, the concentration of TP ranged from 0.090 mg P/L (November 2021) to 0.844 mg P/L (December 2013) (Figure 12). In the surface waters of the dimictic LKD, TP concentrations varied between 0.027 mg P/L (December 2021) and 1.568 mg P/L (March 2013) (Figure 12). In both types of lakes, the maximum values occurred before protection and restoration, while the minimum values occurred during the restoration period, using the phosphorus inactivation method.

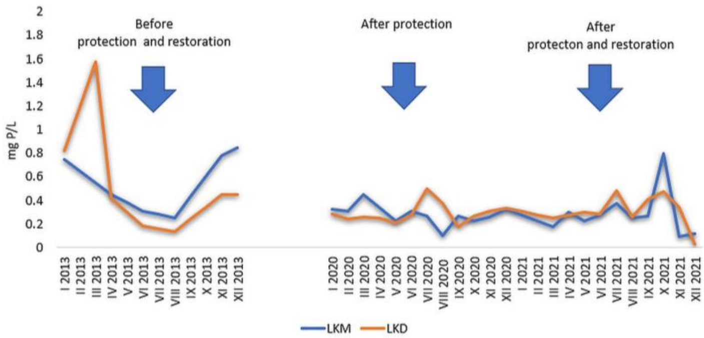


Figure 12. Changes in the content of TP in the surface water layer of Klasztorne lakes in selected research years.

Statistical analysis showed highly statistically significant differences in the content of TP in the surface water layer of both Klasztorne lakes in the analyzed research years but did not show significant differences between the lakes.

In 2013, before the protection and restoration of the lakes, the average concentration of TP was 0.522 mg P/L (±0.204) in LKM and 0.519 mg P/L (±0.450) in LKD (Figure 13). After restoration with the use of two types of compounds, a very clear decrease in the amount of TP was found in both lakes (Figure 13). In LKM, the average value was 0.279 mg P/L (±0.180) and in LKD, up to 0.306 mg P/L (±0.119). The reduction in TP content in surface water layers as a result of the protection and restoration measures was approximately 47% for LKM and 42% for LKD (Figure 13).

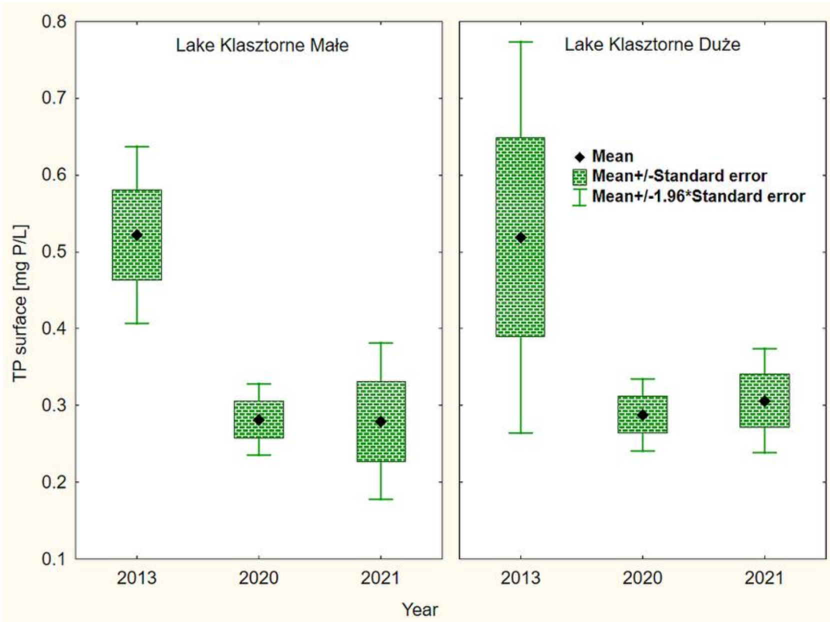


Figure 13. Average annual values of TP in the surface water of Klasztorne lakes in selected research years.

The bottom water of LKM contained very high amounts of TP (Figure 14). TP concentration varied from 5.650 mg P/L (in 2021) to 29.720 mg P/L (in 2013) (Figure 14a,b). In the eutrophic LKD, the range of TP concentrations in the analyzed period was not as wide as in the meromictic LKM and ranged between 0.020 mg P/L (2021) and 1.930 mg P/L (2013—before the protection and restoration of lake) (Figure 14a,b).

The statistical analysis showed highly statistically significant differences in the TP content in the bottom water layers of LKM among the analyzed research years. No such differences were found in the case of LKD. Statistical analysis also showed highly statistically significant differences in the TP content between lakes.

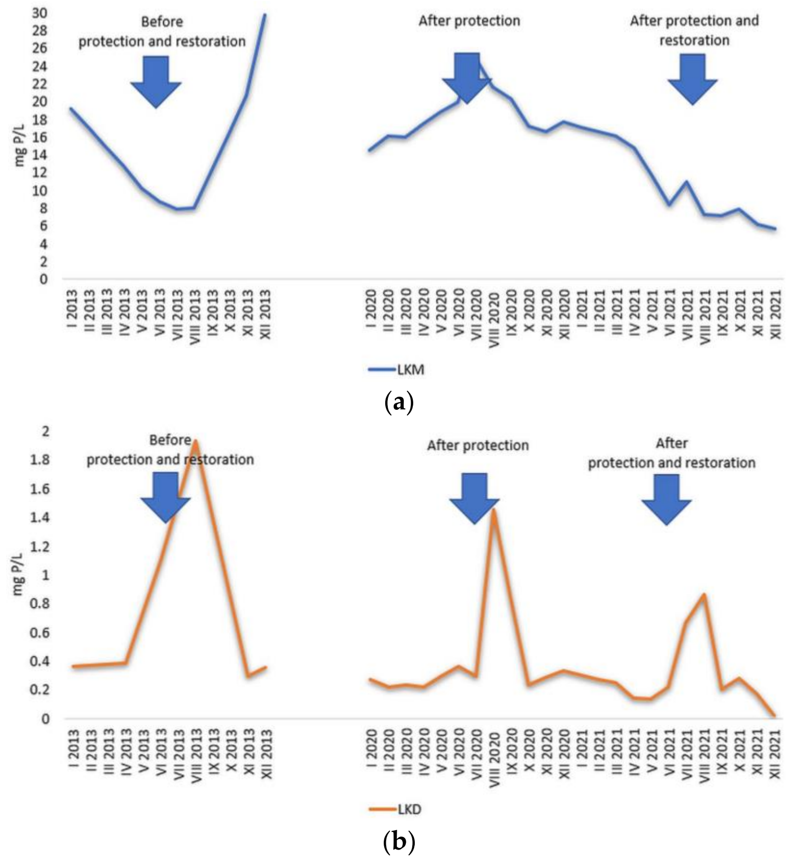


Figure 14. (**a**) Changes in the content of TP in the bottom water layers of Lake Klasztorne Małe in selected research years. (**b**) Changes in the content of TP in the bottom water layers of Lake Klasztorne Duże in selected research years.

In 2013, the average concentration of TP in the bottom water layer of KLD was 14.810 mg P/L (±6.364), and in LKD, it was 0.805 mg P/L (±0.556) (Figure 15). After the application of PAX 18 and PIX 111, a clear decrease in the TP content was found in the bottom water layers of the Klasztorne lakes (Figure 15). After protection and restoration, an average value of 10.800 mg P/L (±4.331) for the TP was recorded at the bottom of LKM and 0.294 mg P/L (±0.238) in LKD. The reduction of TP content at the bottom of LKM was at the level of 28%, and in LKD, it was about 64%.

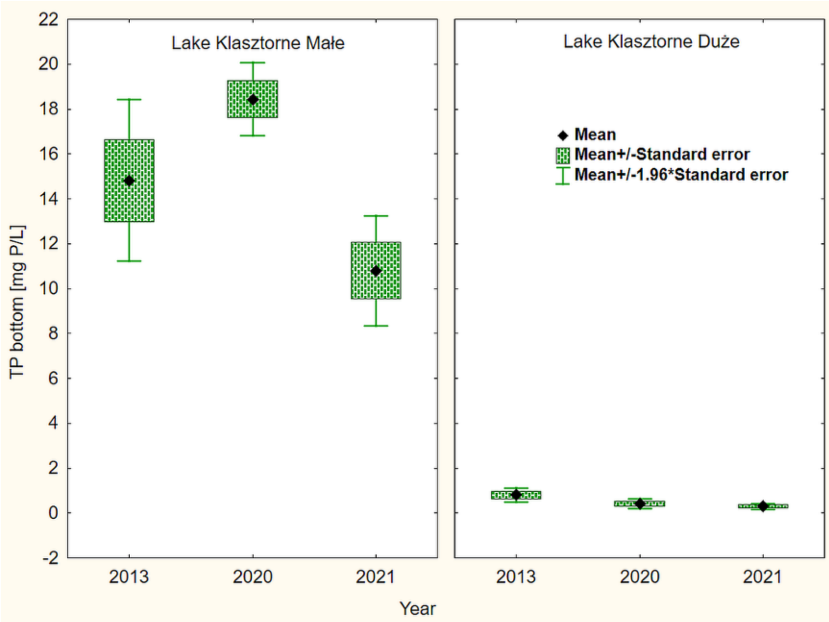


Figure 15. Average annual values of TP in the bottom water of the Klasztorne lakes in selected research years.

4. Discussion

Phosphorus is the most important element responsible for a lake's eutrophication process [32]. This element in water is taken up by primary producers for photosynthesis and is partially withdrawn from the water column as a result of accumulation in aquatic organisms and in bottom sediments, where it is accumulated in the form of organic compounds; seston; and complexes with iron, aluminum, or calcium [33–35]. However, the withdrawal of phosphorus into the sediments is temporary. According to Schindler and Fee [36] and Boers and de Bles [37], phosphorus compounds accumulated in sediments are processed via the participation of microorganisms and returned to circulation, and this phenomenon is called internal loading. The process of phosphorus release from bottom sediments into the water is favored by anaerobic conditions in which phosphorus desorption from iron and manganese complexes takes place, and the sediment's low sorption capacity is affected by the low content of phosphorus-binding elements.

The long-term use of the Klasztorne lakes as receivers of domestic sewage and stormwater was evident in the high concentration of phosphorus in the water columns of both lakes (over 29 mg P/L in LKM and almost 2 mg P/L in LKD). The high concentrations of TP in the bottom water layers of the analyzed lakes, which persisted before restoration, were related to the constant deoxygenation of the bottom water and, thus, the limited possibilities of phosphate removal from the water into the bottom sediments. According to Nürnberg [38], in lakes with a deoxygenated hypolimnion, only 30% of phosphates form complexes with iron.

The main goal of lake restoration by the phosphorus inactivation method is to reduce the concentration of phosphates in the water to a level that limits primary production and, moreover, to permanently immobilize phosphorus in bottom sediments [15,16]. Preparations based on iron and aluminum salts, mainly chlorides and sulphates, in the form of acidic solutions dosed into water are used to inactivate phosphorus. Upon contact with lake water, in which the pH is generally much higher, these salts undergo hydrolysis, forming metal hydroxide precipitates, which flocculate and settle suspended particulate material on the lake bed, thus stripping nutrients from the water column. The microlayers created in this way, rich in phosphorus-binding metals, constitute an additional barrier to the phosphates released from the bottom sediments. The choice of compounds used for restoration is determined by the pH of the water and oxygen conditions. A combination of iron (PIX 111) and aluminum (PAX 18) compounds was used to inactivate phosphorus in the Klasztorne lakes. The iron coagulant was applied in coastal areas of the lakes, where the bottom layers of water were not deoxygenated. In the case of Lake Klasztorne Małe, the iron chloride dosing was limited by the 2 m isobath (bottom area 4.2 ha), and in Lake Klasztorne Duże, the isobath of 5 m (bottom area 22.5 ha). In the rest of the area of the lakes, an aluminum coagulant was used, which is not sensitive to the decrease in redox potential. Both compounds were applied in early spring, right after the ice cover had come down, and in late autumn. In both terms, the pH of the water was in the range of 6 to 8, so it was ecologically safe for the use of aluminum compounds. The results obtained on the Klasztorne lakes justify the sequential application of two types of compounds.

After the application of compounds, better efficiency of phosphate removal from the surface water layers was obtained in the case of the dimictic, eutrophic Lake Klasztorne Duże. In this lake, a larger amount of PIX 111 iron compounds was used, which was spread over an area of 22.5 ha (area limited by the 5 m isobath), which is about 40% of the total lake area. Studies by Amunda and Amoo [39] on the effectiveness of various types of compounds in removing phosphates from aqueous solutions showed that PIX 111 obtained the best results. The assumed decrease in phosphorus was achieved at low doses, i.e., with a molar ratio of Fe: PO_4^{3-} of 0.8: 1. In the Klasztorne lakes, a substantially higher Fe: P ratio (up to 25:1) was used, due to the high phosphorus content, both in the water column and in bottom sediments.

The use of two doses of compounds did not lead to complete precipitation of phosphates from the bottom water layers of either lake. The concentration of P_{min}. remaining in the monimolimnion layer of Klasztorne Małe Lake was still very high, which indicates the need to apply further doses of PAX 18, which had been dosed where the waters above the bottom remained deoxygenated. It is noteworthy that in the case of both lakes, the inhibition of the internal loading process was observed, as evidenced by the persistent low concentrations of P_{min} in the near-bottom waters of both lakes after application of iron and aluminum compounds. This was achieved with low doses of PAX relative to those used in other lakes. For Lake Klasztorne Małe, the introduced single dose of PAX 18 compounds was 24.8 g of Al per m^2 of bottom area, and for Lake Klasztorne Duże, it was 14.2 g of Al per m^2 of bottom area. For comparison, in other lakes, 44 g of Al. per m^2 of bottom area was required to achieve complete phosphorus immobilization [40], while there are known cases where even 139 g of Al per m^2 of bottom area had to be introduced [41].

The phosphorus inactivation method does not directly affect the content of organic phosphorus. The reduction of the organic form was the result of reduced primary production due to a reduced pool of phosphates in the surface water layer (on average by about 80%). Moreover, the metal hydroxides formed as a result of the hydrolysis of the compounds' precipitates to form large-surface flocs which coagulate the organic suspension from the water and sink with it to the bottom. The same dependencies were noted by Grochowska et al. [42] in Lake Długie in Olsztyn, which was restored, inter alia, by phosphorus inactivation.

The phosphorus inactivation method with the sequential application of PIX 111 and PAX 18 compounds reduced the total amount of phosphorus in both types of lakes. About a 40% reduction of TP was achieved in the surface water layer in both Klasztorne lakes, about 30% in bottom water layers of LKM, and 60% in LKD. The use of subsequent doses of compounds will certainly result in further precipitation of phosphorus from the waters and its immobilization in bottom sediments.

The most important ions, which, apart from phosphorus forms, were analyzed during the application of coagulants were Fe, Al, and Cl. In the case of Fe and Cl, a temporary, slight increase in concentration was noted, which was maintained only during dosing of the compounds. There was no increase in the amount of Al in the water. During the application of PAX 18, the maximum concentration of Al in the water was 0.005 mg Al/L, while the allowable standard is 0.350 mg Al/L. No negative effects of dosing coagulants on aquatic plants and animals have been found. Hydrobiological observations will be published.

5. Conclusions

The obtained results confirm the effectiveness of the sequential application of a combination of iron (PIX 111) and aluminum (PAX 18) compounds in the reduction of mineral phosphorus which is available to hydrobionts. The surface application of both types of compounds stimulated not only the reduction of phosphates from the lake water, but also their effective immobilization in the bottom sediments. The obtained results for the Klasztorne lakes showed that the use of two types of compounds makes it possible to reduce the cost of restoration, and moreover, the dosing of iron salts in the coastal areas of the lakes ensures a higher level of ecological safety.

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References

1. Huser, B.J.; Futter, M.; Lee, J.T.; Perniel, M. In-lake measures for phosphorus control: The most feasible and cost-effective solution for long-term management of water quality in urban lakes. *Water Res.* **2016**, *97*, 142–152. [CrossRef]
2. Rosińska, J.; Kozak, A.; Dondajewska, R.; Kowalczewska-Madura, K. Water quality response to sustainable restoration measures-Case study of urban Swarzędzkie Lake. *Ecol. Indic.* **2018**, *84*, 437–449. [CrossRef]
3. Kowalczewska-Madura, K.; Dondajewska, R.; Gołdyn, R.; Podsiadłowski, S. The influence of restoration measures on phosphorus internal loading from the sediments of a hypereutrophic lake. *Environ. Sci. Pollut. Res.* **2017**, *24*, 14417–14429. [CrossRef] [PubMed]
4. Spears, B.R.; Mackay, E.B.; Yasseri, S.; Gunn, I.D.M.; Waters, K.E.; Andrews, C.; Cole, S.; De Ville, M.; Kelly, A.; Meis, S.; et al. A meta-analysis of water quality and aquatic macrophyte responses in 18 lakes treated with lanthanum modified bentonite (Phosclock®). *Water Res.* **2016**, *97*, 111–121. [CrossRef] [PubMed]
5. Rybicki, P.; Osuch, A.; Osuch, E.; Przygodziński, P.; Przybylak, A.; Kozłowski, R. Technology of mechanical removal of cyanobacterial blooms from the surface of water bodies. *Ecol. Eng.* **2018**, *19*, 69–76. (In Polish) [CrossRef]
6. Tõnno, I.; Katrin, O.; Nõges, T. Nitrogen dynamics in the steeply stratified, temperate Lake Verevi, Estonia. *Hydrobiologia* **2005**, *547*, 63–71. [CrossRef]
7. Müller, S.; Mitrovic, S.M.; Baldwin, D.S. Oxygen anddissolved organic carbon control release of N, P and Fe from the sediments of a shallow, polymictic lake. *J. Soils Sediments* **2015**, *16*, 1109–1120. [CrossRef]
8. Cottingham, K.L.; Ewing, H.A.; Greer, M.L.; Carey, C.C.; Weathers, K.C. Cyanobacteria as biological drivers of lake nitrogen and phosphorus cycling. *Ecosphere* **2015**, *6*, 1–19. [CrossRef]
9. Zhang, E.; Liu, E.; Jones, R.; Langdon, P.; Yang, X.; Shen, J. A 150-year record of recent chang-es in human activity and eutrophication of Lake Wushan from the middle reach of the Yangze River, China. *J. Limnol.* **2010**, *69*, 235–241. [CrossRef]
10. García-Alix, A.; Jimenez-Espejo, F.J.; Lozano, J.A.; Jimenez-Moreno, G.; Martinez-Ruiz, F.; Garcia, S.L.; Aranda, J.G.; Garcia, A.E.; Ruiz-Puertas, G.; Scott, A.R. Anthropogenic impact and lead pollution throughout the Holocene in Southern Iberia. *Sci. Total Environ.* **2013**, *449*, 451–460. [CrossRef]
11. Grochowska, J.; Tandyrak, R.; Parszuto, K.; Brzozowska, R. A proposal of protection techniques in the catchment of a lake in the context of improving its recreational value. *Limnol. Rev.* **2016**, *16*, 33–39. [CrossRef]
12. Parszuto, K.; Tandyrak, R.; Łopata, M.; Mikulewicz, S.; Grochowska, J.; Dunalska, J. Development of Drwęckie lake in Ostróda for tourist and recreational purposes, and its impact on the burden to the natural environment in the shoreline zone. *Pol. J. Nat. Sci.* **2017**, *32*, 105–120.
13. Gawrońska, H.; Lossow, K.; Grochowska, J. Restoration of Lake Długie. *Edycja* **2005**, 52. (In Polish)
14. Grochowska, J.; Augustyniak, R.; Łopata, M. How durable is the improvement of environ-mental conditions in a lake after the termination of restoration treatments. *Ecol. Eng.* **2017**, *104*, 23–29. [CrossRef]
15. Cooke, G.D.; Welch, E.B.; Peterson, S.A.; Newroth, P.R. *Restoration and Management of Lakes and Reservoirs*; Taylor & Francis, A CRC Press: Boca Raton, FL, USA, 2005; pp. 1–591.
16. Klapper, H. Technologies for lake restoration. *J. Limnol.* **2003**, *62*, 73–90. [CrossRef]
17. Lin, J.; Zhan, Y.; Zhu, Z. Evolution of sediment capping with active barrier systems (ABS) using calcite/zeolite mixtures to simultaneously manage phosphorus and ammonium release. *Sci. Total Environ.* **2011**, *409*, 638–646. [CrossRef]

18. Łopata, M.; Augustyniak, R.; Grochowska, J.; Parszuto, K.; Tandyrak, R. Selected aspects of lake restoration in Poland. In *Polish River Basins and Lakes–Part II: Biological Status and Water Management*; Springer: Berlin/Heidelberg, Germany, 2020; pp. 327–352.
19. Dondajewska, R.; Gołdyn, R.; Kozak, A.; Podsiadłowski, S.; Gruza, A. Reduction of phosphorus release from bottom sediments and changes in phytoplankton composition under the influence of new chemical preparations in in-situ conditions. In *Materials of Conference Protection and Restoration of Lakes*; Pub. Polish Association of Sanitary Engineers and Technicians, Branch in Toruń: Toruń, Poland, 2010; pp. 31–43. (In Polish)
20. Gałczyńska, M.; Buśko, M. Chemical substances and preparations used to inactivate phosphorus in lake ecosystems. *Chem. Ind.* **2018**, *97*, 140–143.
21. Gołdyn, R.; Podsiadłowski, S.; Dondajewska, R.; Kozak, A. The sustainable restoration of lakes-towards the challenges of the water framework directive. *Ecohydrol. Hydrobiol.* **2014**, *14*, 68–74. [CrossRef]
22. Kowalczewska-Madura, K.; Dondajewska, R.; Gołdyn, R. Influence of iron treatment on phosphorus internal loading from bottom sediments of the restored lake. *Limnol. Rev.* **2008**, *8*, 177–182.
23. Zamparas, M.; Zacharias, I. Restoration of eutrophic freshwater by managing internal nutrient loads. A review. *Sci. Total Environ.* **2014**, *496*, 551–562. [CrossRef] [PubMed]
24. Immers, A.K.; van der Sande, M.T.; van der Zande, R.M.; Geurts, J.J.M.M.; van Donk, E.; Bakker, E.S. Iron addition as a shallow lake restoration measure: Impacts on charophyte growth. *Hydrobiologia* **2013**, *710*, 241–251. [CrossRef]
25. Gumińska, J. Effect of changes in Al. speciation on the efficiency of water treatment with pre-hydrolyzed coagulants. *Environ. Prot.* **2011**, *33*, 17–21. (In Polish)
26. Alhamarna, M.Z.; Tandyrak, R. Lake restoration approach. *Limnol. Rev.* **2021**, *21*, 105–118. [CrossRef]
27. Kondracki, J.A. *Regional Geography of Poland*; PWN: Warsaw, Poland, 2011. (In Polish)
28. Januszkiewcz, T.; Jakubowska, L. Lake Klasztorne in Kartuzy—Case study. *Pol. Arch. Hydrobiol.* **1963**, *11*, 275–325. (In Polish)
29. American Public Health Association. *Standard Methods for the Examination of Water and Wastewater, 1998*, 20th ed.; American Public Health Association: Washington, DC, USA, 1998.
30. Kaca, E. Measurements of water flow volume and mass of substance contained in it, and its uncertainty on the example of fish ponds. *Water-Environ.-Rural. Areas* **2003**, *13*, 31–57. (In Polish)
31. Tibco Software Inc. STATISTICA. *version 13.3*; Tibco Software Inc.: Palo Alto, CA, USA, 2021.
32. Kajak, Z. Hydrobiology-Limnology. In *Inland Water Ecosystems*; PWN: Warsaw, Poland, 2001. (In Polish)
33. Wu, X.; Me, T.; Du, Y.; Jiang, Q.; Shen, S.; Liu, W. Phosphorus cycling in freshwater lake sediments: Influence of seasonal water level fluctuations. *Sci. Total Environ.* **2021**, *792*, 148383. [CrossRef]
34. Randall, M.C.; Carling, G.T.; Dastrup, D.B.; Miller, T.; Nelson, S.T.; Hansen, N.C.; Bickmore, B.R.; Aanderud, Z.T. sediment potentially controls in lake phosphorus cycling and harmful cyanobacteria in shallow, eutrophic Utah lake. *PLoS ONE* **2019**, *14*, e0212238. [CrossRef]
35. Søndergaard, M.; Bjerring, R.; Jeppesen, E. Persistent internal phosphorus loading during summer in shallow eutrophic lakes. *Hydrobiologia* **2013**, *710*, 95–107. [CrossRef]
36. Schindler, D.W.; Fee, E.J. Experimental lakes area: Whole—Lake experiments and eutrophication. *J. Fish. Board Can.* **1974**, *31*, 937–953. [CrossRef]
37. Boers, P.; de Bles, F. Ion concentrations in interstitial water as indicators for phosphorus release processes and reactions. *Water Res.* **1991**, *25*, 591–598. [CrossRef]
38. Nürnberg, G.K. Phosphorus from internal sources in the Laurentian Great Lakes, and the concept of threshold external load. *J. Great Lakes Res.* **1991**, *17*, 132–140. [CrossRef]
39. Amuda, O.Z.; Amoo, I. A Coagulation/flocculation process and sludge conditioning in beverage industrial wastewater treatment. *J. Hazard. Mater.* **2007**, *141*, 778–783. [CrossRef] [PubMed]
40. Smeltzer, E. Successful alum/aluminate treatment of Lake Morey, Vermont. *Lake Reserv. Manag.* **1990**, *6*, 9–19. [CrossRef]
41. Huser, B.J.; Egemose, S.; Harper, H.; Hupfer, M.; Jensen, H.; Pilgrim, K.M.; Reitzel, K.; Rydin, E.; Futter, M. Longevity and effectiveness of aluminum addition to reduce sediment phosphorus release and restore lake water quality. *Water Res.* **2016**, *97*, 122–132. [CrossRef] [PubMed]
42. Grochowska, J.; Brzozowska, R.; Łopata, M. Durability of changes in phosphorus compounds in water of an urban lake after application of two reclamation methods. *Water Sci. Technol.* **2013**, *68*, 234–239. [CrossRef] [PubMed]