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# PHOSPHATES IN SEDIMENTS OF HYPERTROPHIC ŁASIŃSKIE LAKE. REMOVE OR IMMOBILIZE?

On the basis of available literature it was stated that the most commonly used methods of restoration of water reservoirs were: aeration, oxygenation with pure oxygen, oxygenation with ozone produced by generator; biomanipulation, i.e. selective fish removal or introduction; sediment dredging being mostly aimed at removing accumulated phosphorus; phosphorus precipitation from a water volume, more seldom its immobilization directly in sediments, e.g. by capping or adding aluminum or iron compounds.

Integrated methods are being used more frequently and techniques like restocking with fish or applying flocculants are being repeated for few (even 7) years.

The results of the investigation carried out in the year 2001 revealed that: 1. The optimal conditions for maximal inactivation of $PO_4$ in the bottom sediments of the Łasińskie Lake were as follows: 8.5 $cm^3$ $dm^{-3}$ dose of $FeCl_3$ and pH reduced to 6.0.2. 2. Introduction of $FeCl_3$ to the sediments in the deepest parts of the lake before dredging which decreased by 30 times the concentration of $PO_4$ in drainage water.

## 1. INTRODUCTION

### 1.1. RESTORATION METHODS

Every restoration programme for a water reservoir requires us to articulate clearly the goals and the chances of achieving them, as well as to define precisely expected ecological effects. Is it a self-sufficient, rejuvenated but almost natural aquatic ecosystem or rather, what the user expects, is it a multifunctional reservoir suitable for everyone and everything, serving as a source of drinking water and attractive both for tourists and anglers, that are aimed to be its final result?

In many countries, especially in Poland, restoration of water reservoirs can become the priority. In the near future, the main aim of restoration will be improvement

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of water quality, so it could serve as a source of drinking water, be used for food production and sanitary purposes.

Certainly, due to increasing anthropopression, a management, cultivation and constant human supervision of water reservoirs will be indispensable. Choosing a particular method one has to take into account a degree of interference in a complex ecological system, duration of work, and foremost durability of expected results.

Implementation of one particular method is exclusively technical, economic and organizational problem, and scientific analysis of the problem is superficial in the most of cases. Even biomanipulation, which due to its meaning is supposed to be a scientific method, often reduces to non-selective fish removal or, on the contrary, to introduction of excessive amount of carnivorous fish. In most of such cases, all results are mediocre, the improvement lasts only for a short time, and the reservoir system quickly regains its previous or even worst conditions, and eventual side effects are unpredictable.

What guarantees the best results is application of many integrated and complementary methods [6].

Table 1

Methods of phosphare precipitation, inactivation and removal applied in lakes [25] – modified. (L – low, H – high, ST – short time, LT – long time)

| Method | Efficiency | Duration | Reference |
|---|---|---|---|
| Oxygenation, $NO_3$ or $O_2$ | L | ST | [21], [6] |
| Precipitation, $Al^{+3}$, | H | ST – LT | |
| $Al_2(SO_4)_3$, | | | [15], [23], [13] |
| PAX | | | [8], [14] |
| Precipitation, Fe(II, III) | L – H | ST | |
| $FeCl_2$ | | | [5] |
| $FeCl_3$ | | | [27] |
| $Fe_2(SO_4)_3$ | | | [16] |
| Fe + gypsum | | | [1] |
| PIX | | | [7] |
| Co-precipitation, Ca | L – H | ST – LT | |
| $Ca(OH)_2$ and $CaCO_3$ | | | [19], [20] |
| gypsum | | | [26] |
| Sediment capping, sealing | Measurement-dependent | ST – LT | |
| physical | | | [17] |
| chemical (diatomite + $Al^{+3}$) | | | [9] |
| Sediment dredging | L – H | ST | [3] |

On the basis of the analysis of numerous publications dealing with the subject (over 400 publications) one can state that the methods being most often applied recently, frequently in various combinations, are:

• aeration, oxygenation with pure oxygen, oxygenation with ozone produced by generator,

• biomanipulation, selective fish removal, also taking advantage of natural ecological disasters like a mass mortality of fishes,

• sediment dredging, mainly aimed at removing accumulated phosphorus and/or toxic compounds,

• precipitation of phosphorus from a water volume, more rarely its immobilization directly in sediments – through capping or adding aluminum or iron compounds.

Integrated methods are being used more frequently and techniques like restocking with fish, or applying flocculants are being repeated for few (even 7) years.

Many publications contain a survey of main restoration methods applied in lake ecosystems , e.g. [28], [29]. Table 1 presents partial results of analysis of the methods of phosphorus removal, i.e. precipitation and inactivation of phosphorus in lakes.

### 1.2. RESTORATION OF THE ŁASIŃSKIE LAKE

Attempts at developing an efficient restoration program for a shallow and hypertrophic Łasińskie Lake has been made since a number of years [27], [28] with the main aim of optimizing and testing the existing methods. Other attempts were undertaken in order to study an integrated program adjusted to the lake being highly trophic and degraded. The goal of research carried out in 2001 was to gather information about the methods of $PO_4$ immobilization, which referred to fairly poorly known aspects of the process. The research was applied to:

• the influence of pH on $PO_4$ binding efficiency,

• the influence of $FeCl_3$ added to sediment on the concentration of $PO_4$ in the drainage water after dredging.

An additional research was carried out to detect an influence of ferric chloride on hydrobionts [30].

## 2. MATERIALS AND METHODS

### 2.1. DESCRIPTION OF THE LAKE

The Łasińskie (Castle) Lake, which belongs to Iławskie Lakeland, is situated within the administrative boundaries of the village of Łasin. A watershed encompasses an area of over 8 km$^2$ and serves mainly for agriculture and as an area for communal buildings. Surface of the lake is 155.2 ha. It is shallow and very susceptible to degradation. For many years, sewage has been discharged directly into the lake, which results in its considerable eutrophication and cyanobacterial blooms observed each year. A detailed description of the lake can be found in [27]. Table 2 gives its basic morphometric data.

Table 2

Characteristics of the Łasińskie Lake (western part)

| | |
|---|---|
| Surface, ha | 36.0 |
| Volume, thous. $m^3$ | 936.0 |
| Max length, m | 1150.0 |
| Max width, m | 850.0 |
| Max depth, m | 6.0 |
| Mean depth, m | 2.6 |

### 2.2. MEASUREMENT OF pH INFLUENCE ON THE EFFECTIVENESS OF $PO_4$ IMMOBILIZATION

Samples of sediment were taken from the deepest, west part of the lake at the depth of 5–6 m. Physical and chemical features of sediments from that depth are typical of the profundal zone of deep lakes. Measurements were carried out in 1 $dm^3$ cylinder filled with 0.5 $dm^3$ of tap water, 20 $dm^3$ of sediment and a respective dose of $FeCl_3$ (from 1 to 10 $dm^3$). Water volume was filled up to 1 $dm^3$. Working concentration of iron chloride amounted to 50 g $dm^{-3}$. When it was necessary to supplement water with $PO_4$, the solution of $KH_2PO_4$, containing 1 mg of $PO_4$ in 1 $cm^3$, was added; water pH was adjusted with 1 N HCl or 1 N NaOH.

### 2.3. MEASUREMENT OF AN INFLUENCE OF $FeCl_3$ ON $PO_4$ CONCENTRATION IN THE WATER DRAINED FROM DREDGED SEDIMENTS

Measurement was made *in-situ* at the lakeshore. Two hollows in a ground, each of the capacity of 15 $dm^3$, were lined with technical foil and two layers of net made of artificial material with filter paper between. The grooves used to pipe out drain water into collecting glass were lined with foil as well. One of the hollows was filled with 10 $dm^3$ of sediment of 95% water content, which was taken at the depth of 6.0 m. It was a treated as a control. The second was filled with 10 $dm^3$ of sediment being treated before with $FeCl_3$, while pH was reduced to 6.0. The sediment was conditioned in a 50 $dm^3$ barrel filled with 10 $dm^3$ of sediment and 10 $dm^3$ of a lake water.

## 3. RESULTS AND DISCUSSION

Table 3 depicts the effects of reduction in phosphate concentration at optimal pH and optimal dosage of ferric chloride. The maximal efficiency of $PO_4$ bonding (with final parameters of pH and conductivity as close as possible to initial ones) for the profundal sediment in the west part of the lake can be gained when the initial pH is about 6.0 and $FeCl_3$ dose amounts to 8.5 $cm^3 dm^{-3}$.

Table 3

Effectiveness of $PO_4$ inactivation using an optimal $FeCl_3$ dose and optimal initial pH

| Initial pH | Optimal $FeCl_3$ dose ($cm^3 dm^{-3}$) | $PO_4$ after 1 h; control – no $FeCl_3$ added ($mg dm^{-3}$) | $PO_4$ after 1 h; optimal $FeCl_3$ dose added ($mg dm^{-3}$) | Amount of inactivated $PO_4$ ($mg dm^{-3}$) | Final pH | Conductivity ($\mu S cm^{-1}$) |
|---|---|---|---|---|---|---|
| 4.1 | 10.5 | 1.44 | 0.29 | 1.15 | 5.5 | 1520 |
| 5.9–6.2 | 8.5 | 1.35 | 0.26 | 1.06 | 6.5 | 1160 |
| 7.1 | 8.0 | 0.72 | 0.14 | 0.58 | 6.9 | 540 |

To avoid the problems of the secondary release of $PO_4$ from sediments in unoxic conditions in restoration project, dredging of sediments from the deepest parts (the surface of about 2 ha) was provided for. The modification proposed was adding an appropriate dose of $FeCl_3$ to sediment before dredging. Reasonability of this improvement was confirmed by phosphate content analysis in the drain water, done *in situ* at the lakeshore (table 4).

Apparently, the concentration of $PO_4$ in the water being drained from sediments treated with $FeCl_3$ is over 30 times lower compared to control sediments.

The choice of the method for the Łasińskie Lake was made based on the results obtained by many researchers for similar, shallow lakes, e.g. [2]. Among the most important conclusions we can found one drawn by many scientists in various publications. They all reported that in the lakes with a high content of phosphorus, its reduction is an indispensable action required before applying any other method. Moreover, implementation of aerators in shallow reservoirs is not very effective: the possible grade of trophy reduction in the lakes whose depth ranges from 2 to 3 m approaches 0–5% [11].

Even biomanipulation projects properly developed not always bring positive results, and their effectiveness approaches 50% [10]. Investigating each reservoir one has to accumulate a sufficient knowledge on its structure and functions. Especially variety of hydrobiont functions in the trophy nets, i.e. the role of the species capable of a special and a general adapting and key stone species, is very important. Biomanipulation requires also the understanding of the evolution of water reservoirs, adaptation cycles and flow nets of ecosystem.

Dredging a sediment from shallow lake is equivalent to elimination of a huge set of chemical and biological factors, which allow the sediment to be formed for many years and are necessary for a proper functioning of the whole lake system. Also in the case of sediment capping, it is difficult to control the durability of this isolation which can deteriorate in extreme hydrological events, e.g. when the water level lowers rapidly, or during strong wind waving responsible for an intense sediment resuspension.

The process of inactivation, especially directly in sediments, seems to be more appropriate. In the case of phosphorus inactivation in water body, some problems may occur. It is necessary to use an increased concentration of flocculant, so when applied to the surface it works effectively at the bottom of a reservoir as well.

A uniform settling of the flocculant at the sediment surface is possible only in hydrologicaly stable reservoirs. In flow-through lakes or during high waving, it is difficult to predict how the layer of flocculants will be formed. An increased concentration of aluminum or iron compounds can have an unpredictable impact on hydrobionts, all the more because aluminium is known to be toxic. Similar objections apply to physical or chemical sealing of sediment surface. Thin, a few millimeter layer can deteriorate easily, for example, as a result of benthos bioturbation, while creating a thicker layer increases the costs of this operation.

Flocculant application directly to the bottom sediments seems to be the best solution. The advantage is an even distribution of focculant in the top layer of a sediment, whose thickness depends on vertical distribution of accumulated phosphorus. It is also possible to control precisely the concentration of applied flocculant and to avoid the problems resulting from the hydrobionts influence on a water volume. The oldest and very effective method of inactivating phosphates in sediments with simultaneous organic matter mineralisation is the Riplox method [21]. It is applied rarely because of technical complexity and the necessity of using a special equipment.

Another issue to be mentioned is the durability of the results obtained and the possibility of releasing phosphorus bonded with $FeCl_3$ under unoxic conditions and at low redox potential [4], [31]. The role of Fe-sediments in bonding $PO_4$ is still studied [16], [18]. According to [18] the majority of $PO_4$–P in sediments is bonded with iron and iron-containing minerals, and only those restoration methods that lead to a greater number and durability of Fe–P bonds can improve sediment capacity with respect to phosphates.

It was also clearly stated that only an increase in the iron-sediment concentration can lead to a significant reduction in phosphates released from sediments [25]. On the other hand, to make the bonds of $PO_4$ firm in unoxic conditions, all of Fe–P bonds should be replaced with Al–P ones [23]. In cases, where the content of iron in sediments is naturally high, it is necessary to apply such doses of $Al_2(SO_4)_3$ that the concentration of 90 mg of Al per 1 g d.m. of sediments will be reached. Due to such high doses of aluminium an additional research in side effects is inevitable. Maybe, the most recent research e.g. [24], in decision supporting systems used to increase phosphorus retention in sediments, will solve these problems.

Table 4

Influence of $FeCl_3$ added to sediment (before dredging) on $PO_4$ concentration in drain water

| Feature | Combination | |
|---|---|---|
| | Control sediments without $FeCl_3$ | Sediments with $FeCl_3$ added |
| $PO_4$, mg dm$^{-3}$ | 15.7 | 0.42 |
| pH | 7.1 | 6.0 |
| μS, cm$^{-1}$ | 900 | > 1500 |

Treating the sediment with $FeCl_3$ before its dredging seems to be purposeful as well, which is corroborated by other researchers, e.g. of [22] and [12]. As it was stated, in the drain water produced from sediments in sewage treatment plant, 95% of the whole amount of phosphorus was fed as $PO_4$ at low oxygen concentration. Aeration of sediments reduced this amount to 20–30%.

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## FOSFORANY W HYPERTROFICZNYCH OSADACH JEZIOR. USUWAĆ CZY IMMOBILIZOWAĆ?

Omówiono wybrane, aktualnie stosowane metody rekultywacji zbiorników wodnych. Na podstawie analizy ponad 400 publikacji stwierdzono, że najczęściej stosowanymi metodami, zwykle w różnych kombinacjach, były:

- napowietrzanie, natlenianie czystym tlenem, natlenianie z użyciem generatora ozonu,
- biomanipulacja – selektywne odławawianie bądź introdukowanie ryb,
- bagrowanie osadów, przede wszystkim w celu usunięcia nagromadzonego fosforu,
- wytrącanie fosforu z toni wodnej, rzadziej jego immobilizacja bezpośrednio w osadach – przez izolowanie (*capping*) bądź dodawanie związków glinu lub żelaza.

Coraz częściej stosuje się metody zintegrowane, a techniki takie jak zarybianie lub użycie flokulantów są ponawiane przez kilka (nawet 7) lat.

Przedstawiono także wyniki badań prowadzonych w Jeziorze Łasińskim w 2001 roku. Stwierdzono, że: a) optymalnymi warunkami dla maksymalnej inaktywacji fosforanów w osadach dennych Jeziora Łasińskiego jest dawka $FeCl_3$ równa 8,5 $cm^3$ $dm^{-3}$ przy pH obniżonym do 6, b) podanie $FeCl_3$ do osadów najgłębszych partii jeziora przed ich bagrowaniem zmniejsza ponad 30-krotnie koncentrację fosforanów w wodzie odciekowej.