

INTERNAL PHOSPHORUS LOAD IN A MEXICAN RESERVOIR, AND IMPLICATIONS FOR THE REHABILITATION STRATEGIES

Márquez-Pacheco H.¹ and A.M. Hansen²

¹ Universidad Politécnica del Mar y la Sierra (UPMyS), Carretera a Potrerillos del Norote Km 3, La Cruz, Elota, 82700 Sin. México

² Instituto Mexicano de Tecnología del Agua (IMTA), Paseo Cuauhnáhuac 8532, Jiutepec, 62550 Mor. México.
email: [*ahansen@tlaloc.imta.mx](mailto:ahansen@tlaloc.imta.mx)

ABSTRACT

In water bodies, the information on the chemical forms of phosphorus (P) in sediments may be useful for understanding if these act as sinks or sources of P, and how the distribution of P species affects rehabilitation strategies that involve immobilization of P in sediments. Phosphorus fractions extracted from lake sediments can be characterized as weakly adsorbed P, P bound to metal oxides (mainly iron and aluminum), and P bound to calcium. Ferric and manganese oxides have an important role in the mobility of P in sediments because as these oxides are reduced and solubilized under anaerobic redox conditions, P may be released from sediments to aqueous phases. Therefore, sequential extractions of P in sediments allow determining internal P loads in lakes and reservoirs. In this paper, we evaluate the fractions of P in sediment profiles from a eutrophic reservoir in central Mexico. The results indicate an internal P load (IPL) of 23.5 ± 1.4 t/year. Analyzing the behavior of fractions of P in sediment profiles, we found that the dominant fractions are those bound to iron and aluminum oxides, corresponding to approximately 50 % of total P. Since P concentrations of these fractions were twice as high in the top 5-cm of the sediment profiles and decreased with increasing depth, we concluded that these fractions contribute most to the internal P load in the reservoir. We further discuss how these P loads may be influenced by rehabilitation strategies such as application of adsorbents or hypolimnetic oxygenation.

Keywords: Phosphorus Release, Sediment, Redox Conditions, Rehabilitation Strategies

INTRODUCTION

Phosphorus (P) is the nutrient that most often limits primary productivity in water bodies and excess concentrations of this nutrient can lead to eutrophication of lakes and reservoirs [1]. Despite efforts to control P loads through reducing external inputs, it has been observed that eutrophication problems may continue in water bodies due to internal P loads [2-3]. Phosphorus is bound in both organic and inorganic fractions of the sediment, and occurs in the water column as particulate inorganic and organic P, as polyphosphates, and orthophosphates [4]. Phosphorus may accumulate in the sediment from where, under anaerobic conditions, it is released to the water column [5-7]. In this context, several studies have been conducted to better understand the factors affecting the P release from sediments [7-9], finding that redox conditions, pH, dissolved oxygen, nitrates, sulfates, and bacterial activities are the main factors that control the release of P from sediments [9].

Depending on the composition of the sediment, the sedimentation velocity and the environmental conditions, P occurs in sediments in different chemical forms [10]. Therefore, information on the different chemical species of P in sediment is useful

for understanding if these solids act as sinks or sources of P. The different fractions of P are useful to assess the potential of accumulation or release of P in sediment and to determine rehabilitation strategies for eutrophied water bodies. Of special interest are the binding of P to iron, aluminum and calcium, and the adsorption of P by carbonates and clays are [11]. According to Psenner *et al.* [12], fractions of P extracted from sediments can be characterized as (1) weakly adsorbed P, (2) P bound to metal oxides (mainly iron and aluminum), and (3) P bound to calcium.

Iron and aluminum have an important role in retaining inorganic P, and P mobility depends on the redox potential. Iron sulfide formation coupled to sulfate reduction can reduce the abundance of Fe compounds that can complex phosphate and thereby promote its release into sediment porewater [13-14].

Since the sequential extraction of P in sediment makes it possible to determine the P potentially available for release, in this paper we evaluate the fractions of P in sediment profiles from a eutrophic lake in central Mexico, to determine the contributions of each fraction to the internal P load (IPL) and how these influence rehabilitation strategies aimed at immobilizing P in the bottom sediments.

The present study was carried out in a eutrophied lake located in central Mexico that is used for tourism, fishery, and water supply in Toluca and Mexico City. This reservoir has a surface area of approximately 1,680 ha, an average volume of 328 Mm³, average depth of 19.5 m, and a maximum depth of 36 m close to the dam northwest of the reservoir (Figure 1).

The reservoir is located at approximately 1,800 meters above sea level in an area with temperate and semicalid and subhumid climate with summer rains, temperatures varying between 12 and 22 °C, and annual precipitations, between 1,000 and 1,500 mm. The dam receives water from six tributaries: the Amanalco, Molino and Tizates rivers, and the Santa Mónica, González and El Carrizal streams. The hydrological basin has an extension of 615 km², a human population of close to 80,000 habitants, and the land uses include forestry, agriculture, grassland, livestock, fish culture, and urban areas. In the basin dominate volcanic soils since 74% of the total area

of the basin is covered by volcanic rock [15]. The sediment textures in the reservoir is clayey silt with high contents of organic matter [16] and, according to Villanueva-Beltran [17], the reservoir receives approximately 66 t/year of P, 245 t/year of N and 14.117 t/year of suspended solids from the watershed.

MATERIALS AND METHODS

Sediments were sampled with a gravity core sampler (Wildco Wildlife Supply Co., New York) equipped with a 4.8-cm diameter, 50.8-cm length cellulose acetate butyrate liner. Sediments cores were obtained from three sampling sites at different depths (about 6, 20 and 33 m, Figure 1). The upper 25 cm of the cores were divided in 5-cm sections that were dried at room temperature to constant weight.

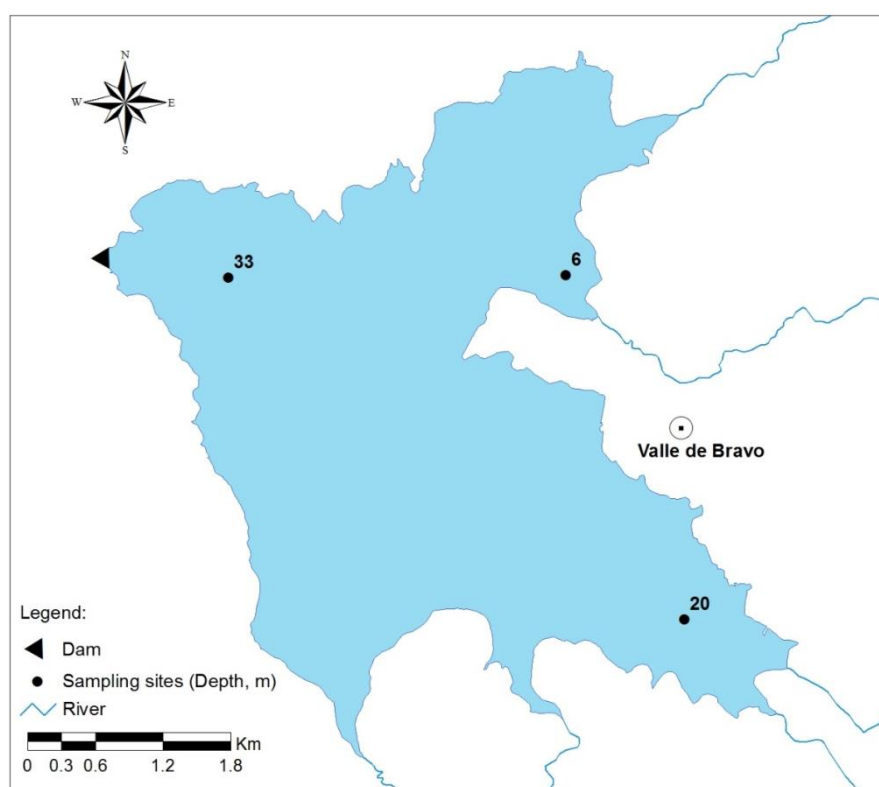


Fig. 1. Location of the sampling stations in the Valle de Bravo reservoir, Mexico

A selective extraction method was used to determine the amounts of P present in different fractions of each section of the sediment cores. For this, different solvents were used in the sequence illustrated in Table 1. The analysis of Soluble Reactive P (SRP) and Total P (TP) were performed using a colorimetric method [18] (Merck Pharo 300 spectrophotometer, Darmstadt, Germany). Non-

Reactive P (NRP) was defined as the difference between the total P and SRP.

The following species were separated: labile P (H₂O-TP), P bound to Fe/Mn (bicarbonate-dithionite fraction, BD-SRP), organic P solubilized by reduction (bicarbonate-dithionite fraction, BD-NRP), P bound to Al/Fe oxides (NaOH-SRP), P bound to organic matter (NaOH-NRP), P bound to

carbonate and apatite (HCl-SRP), Organic P solubilized by acidification (HCl-NRP), and residual P ($K_2S_2O_8$ -TP).

Table 1. Extraction procedures and corresponding P-fractions [12]

Solvent	Extraction conditions	P species
O ₂ -free water (MilliQ)	Stirring 10 min, 25° C	H₂O-TP (labile P)
Bicarbonate-dithionite	Stirring 30 min, 40° C	BD-SRP (P bound to Fe/Mn) BD-NRP (Organic P solubilized by reduction)
Sodium hydroxide	Stirring 16 h, 25° C	NaOH-SRP (P bound to Al/Fe oxides) NaOH-NRP (P bound to organic matter)
Hydrochloric acid	Stirring 16 h, 25° C	HCl-SRP (P bound to carbonate and apatite) HCl-NRP (Organic P solubilized by acidification)
Potassium persulfate	Autoclaving 30 min	K₂S₂O₈-TP (Residual P)
Total Phosphorus (Sum of concentrations of the species above)		TP-ΣP
TP	=	Total P
SRP	=	Soluble Reactive P
NRP	=	Non-Reactive P

To describe how sediments contribute to the internal P load (IPL), P fractions in the sediment profiles were analyzed and their decreases with depth in the sediment cores, calculated. These were compared with the amount of accumulated P in the lake sediments, determined as 66.6 ± 4.0 t/yr [19]. The contributions of these fractions to IPL were analyzed, considering their reductions in the sediment profiles.

Finally, we discussed the implications of P speciation in sediments on the reduction of IPL by hypolimnetic oxygenation or by application of adsorbents to immobilize P in sediments.

RESULTS AND DISCUSSION

The relative concentrations of the different fractions of P in the sediment profiles (Figure 2) showed that Total Phosphorus (TP-ΣP) in the surface sections (0-5 cm) were higher than in deeper sections (5-25 cm). It was observed that concentrations of P decreased from approximately 950 mg/kg in the upper sections of the sediment cores to around 500 mg/kg in the lower sections.

The dominant fraction of P in the sediment profiles was P bound to Al/Fe oxides (NaOH-SRP), representing approximately half of total P (TP-ΣP) in the sediment cores. The concentrations of the Al/Fe oxides (NaOH-SRP) fraction of P in the upper sections were about twice the concentrations observed in lower sections, and concentrations decreased with increasing depth.

Residual P ($K_2S_2O_8$ -TP) did not vary with depth in the sediment cores. The concentrations of P bound to Fe/Mn (BD-SRP) were two to three times higher in the upper sections of the sediment cores. The concentrations of this fraction, as well as those of organic P solubilized by reduction (BD-NRP), decreased with increasing depth of the sections in the sediment cores.

The decrease of P with increasing depth in the sediment profiles confirms that P bound to Al/Fe oxides (NaOH-SRP), is the fraction which liberates most P to the water column (Figure 3), causing the IPL. This release of P can be explained by the generally observed reduced conditions in sediments [19], causing the release of P bound to ferric oxides in sediment. Furthermore, the decrease in NaOH-SRP with depth can be explained by the decrease of pH, which causes enhanced desorption of P [20].

Given the disappearance of P in the sediment sections and the reported P sedimentation rate of 66.6 ± 4.0 t/year [19] an IPL of 23.5 ± 1.4 t/year was estimated. Phosphorus bound to Al/Fe oxides (NaOH-SRP), P bound to Fe/Mn (BD-SRP), and P bound to organic matter (NaOH-NRP) are all fractions that release P in bioavailable forms to water as orthophosphate [21], being therefore directly available for algae and therefore contributing strongly to primary production [10].

In the typical pattern of cultural eutrophication and pollution of lakes by human activities, external nutrient loads from sewage and runoff from different land uses stimulate phytoplankton growth in warm surface waters [4]. When phytoplankton dies and sinks into colder bottom water, it is degraded by bacteria, consuming oxygen dissolved in the water column. This results in anaerobic conditions in bottom water that promote the release of phosphate and ammonia from decaying organic matter in sediments.

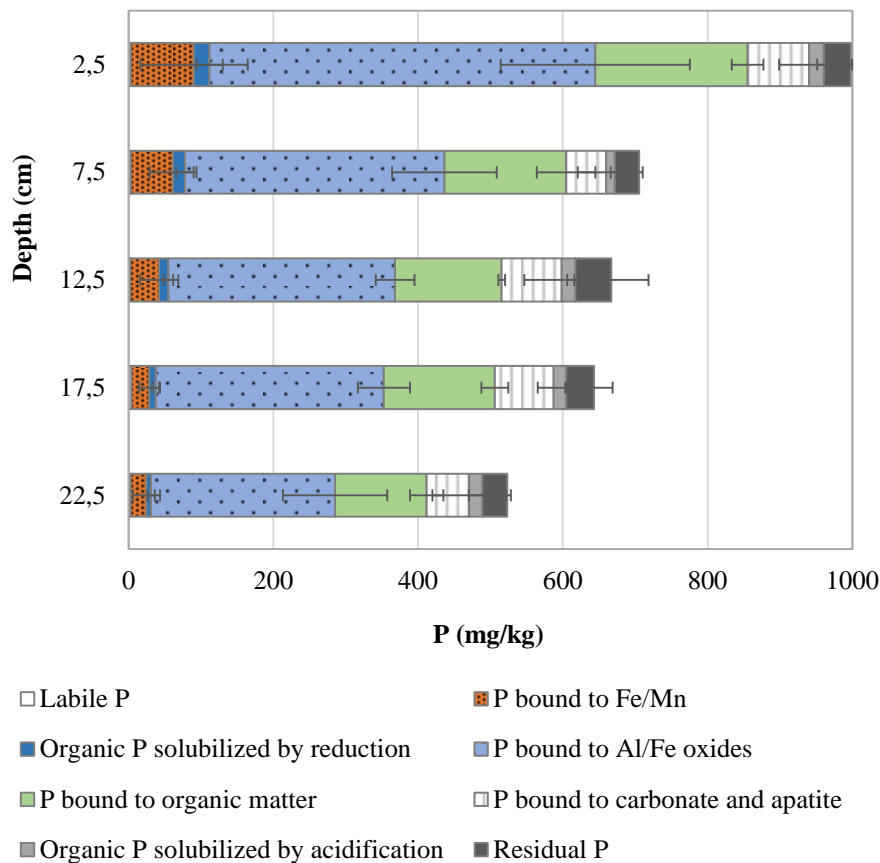


Fig. 2. Speciation of P in sediment profiles from the Valle de Bravo reservoir, Mexico

Cooler temperatures and windy conditions during the fall lead to the mixing of such cold nutrient-rich bottom water into surface water, with negative ecological consequences as phosphate and ammonia are mixed into surface waters where they stimulate phytoplankton growth, which in turn reinforces the anaerobic conditions that promote nutrient release from sediments [20-22].

While it has long been recognized that both external and internal loading of nutrients must be controlled to decrease phytoplankton growth and improve water quality in polluted lakes and reservoirs [1], current regulatory approaches to regulate surface water pollution focus on controlling external loading from watersheds. As a result, managers and funding agencies have lost sight of the need to develop and implement strategies to control internal loading of pollutants in lakes and reservoirs [22].

In the case of the Valle de Bravo reservoir, several methods have been recommended to control IPL from sediments to the water column. Among the more promising methodologies are (1) application of adsorbents and (2) hypolimnetic oxygenation.

Hypolimnetic Oxygenation Systems are designed to supply dissolved oxygen to the hypolimnion of lakes and reservoirs [23], where anoxic conditions

are reversed as dissolved oxygen concentrations are increased in the hypolimnion, thereby reducing or even eliminating IPL by avoiding reductive dissolution of the substrates Fe oxides (NaOH-SRP) and Fe/Mn hydroxides (BD-SRP). Although degradation of organic matter in the sediments will most probably be degraded more efficiently due to the aerobic conditions in the sediment, causing IPL, released P will be immobilized by the metal oxides and hydroxides in the sediment.

The application of adsorbents such as lanthanum (La) modified clays (i.e. La modified bentonite commercialized as Phoslock), aim at dephosphatising the water column and at reducing the IPL. This method not only controls IPL but also P from external sources such sewage and runoff from the watershed. The advantage of this adsorbent is that it does not dissolve under anaerobic conditions and also that it selectively binds P.

Analyzing the speciation of P in sediment profiles from the Valle de Bravo reservoir, Mexico (Figures 2 and 3), the application of Phoslock could potentially reduce the release from the following species labile P (H_2O -TP), P bound to Fe/Mn, (BD-SRP), Organic P solubilized by reduction (BD-NRP), P bound to Al/Fe oxides (NaOH-SRP), P bound to organic matter (NaOH-NRP).

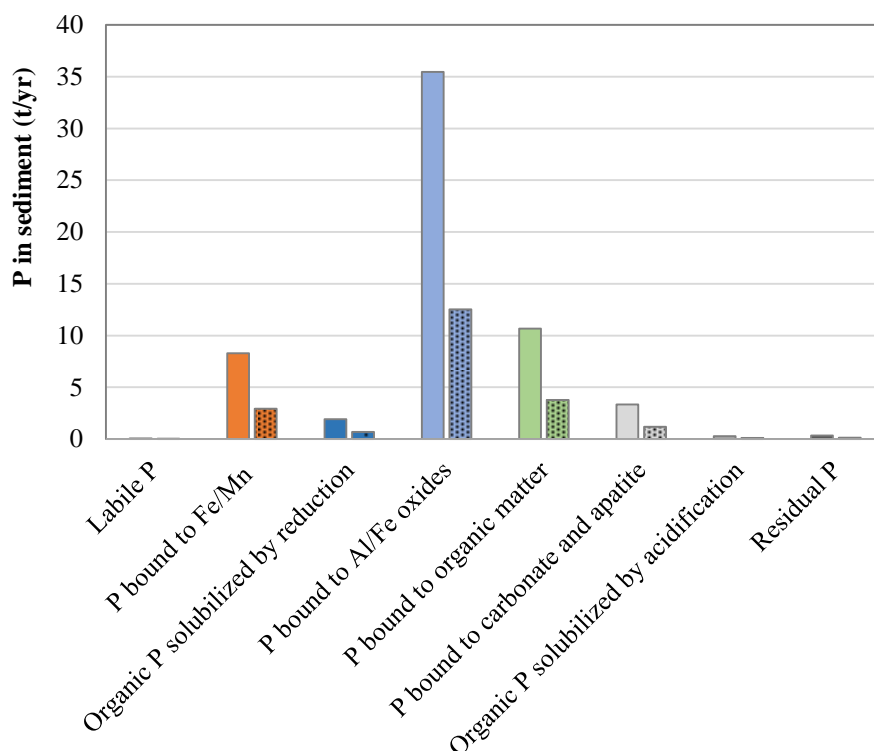


Fig. 3. Accumulation and release of P species in the sediment profiles of the Valle de Bravo reservoir, Mexico

CONCLUSIONS

The sequential extraction method contributes to a better understanding of IPL, indicating labile and bioavailable fractions. IPL in the Valle de Bravo reservoir, is in the order of 23.5 ± 1.4 t/year, with the fractions of P bound to Al/Fe oxides (NaOH-SRP) and P bound to organic matter (NaOH-NRP) contributing most to IPL.

Knowledge on the speciation of P in sediments allows for better planning of rehabilitation strategies of water and sediments in eutrophied water bodies.

ACKNOWLEDGEMENTS

The authors wish to thank the Organismo de Cuenca Aguas del Valle de México from the Mexican National Water Commission (CONAGUA) for financial support (contract no. OAVM-DT-MEX-11-479-RF-CC), the technical support from P. van Goethem and N. Traill from Phoslock Europe, S. Yasserli from Institut Dr. Nowak, Germany, and A. Falcón-Rojas and C. Corzo-Juárez from the Mexican Institute of Water Technology.

REFERENCES

- [1] Cooke GD, Welch EB, Peterson SA and Nichols SA. "Restoration and management of lakes and reservoirs", Taylor and Francis Group, 3rd. Ed. Nueva York, 2005.
- [2] Steinman A and Ogdahl M. "Ecological Effects after an Alum Treatment in Spring Lake, Michigan". J. Environ. Qual., Vol 37, 2008, pp. 22–29.
- [3] Schauser I, Lewandowski J and Hupfer M. "Decision support for the selection of an appropriate in-lake measure to influence the phosphorus retention in sediments", Water Research, Vol 37, 2003, pp. 801–812.
- [4] Søndergaard M, "Nutrient dynamics in lakes – with emphasis on phosphorus, sediment and lake restoration", Doctor's dissertation (DSc), 2007, p 74.
- [5] Heggie DT, Logan GA, Smith CS, Fredericks DJ, Palmer D, "Biogeochemical processes at the sediment–water interface, Bombah Broadwater, Myall Lakes, Hydrobiologia, Vol 608, 2008, pp. 49–67.
- [6] Chowdhury M, Bakri DA, "Diffusive nutrient flux at the sediment-water interface in Suma Park Reservoir, Australia", Hydrological Sciences-Journal-des Sciences Hydrologiques, Vol 51, No 1, 2006, pp. 144-156.
- [7] Haggard BE, Moore PA, De Laune PB, "Phosphorus Flux from Bottom Sediments in Lake Eucha, Oklahoma", J. Environ. Qual., Vol 34, 2005, pp. 724–728.
- [8] Solim SU, Wanganeo A, "Factors influencing release of phosphorus from sediments in a high productive polymictic lake system", Water

- Science & Technology, Vol 60, No 4, 2009, pp. 1013-1023.
- [9] Kim LH, Choi E, Stenstrom MK, “Sediment characteristics, phosphorus types and phosphorus release rates between river and lake sediments”, *Chemosphere*, Vol 50, 2003, pp. 53–61.
- [10] Yalçın S, Demirak A, Keskin F, “Phosphorus fractions and its potential release in the sediments of Koycegiz Lake”, *Turkey, Lakes Reserv. Ponds*, Vol 6, 2012, pp. 139–153.
- [11] Jensen H, Kristensen P, Jeppesen E, Skytthe A, “Iron:phosphorus ratio in surface sediment as an indicator of phosphate release from aerobic sediments in shallow lakes”, *Hydrobiologia*, Vol 235/236, No 1, 1992, pp. 731–743.
- [12] Psenner R, Puesko R, Sager M, “Die Fractionierung Organischer und Anorganischer Phosphorverbindungen von Sedimenten - Versuch einer Definition Okologisch Wichtiger Fractionen”, *Archiv für Hydrobiologie*, Vol 10, 1984, pp. 115–155.
- [13] Perrone U, Facchinelli A, Sacchi E, “Phosphorus Dynamics in a Small Eutrophic Italian Lake”, *Water Air and Soil Pollution*, Vol 189, 2008, pp. 335–351.
- [14] Miao S, De Laune RD, Jugsujinda A, “Influence of sediment redox conditions on release/solubility of metals and nutrients in a Louisiana Mississippi River deltaic plain freshwater lake”, *Science of the Total Environment*, Vol 371, No 1-3, 2006, pp. 334–343.
- [15] INEGI (Instituto Nacional de Estadística, Geografía e Informática) “Prontuario de información geográfica municipal de los Estados Unidos Mexicanos, Valle de Bravo, México, Clave geoestadística 15110”, 2010, Available at: <http://www3.inegi.org.mx/sistemas/mexicocifr> as/datos-geograficos/15/15110.pdf. Consulted May 2016)
- [16] Márquez-Pacheco H, Hansen AM, Falcón-Rojas A, “Phosphorous control in a eutrophied reservoir”, *Environ Sci Pollut R.*, Vol 20, No 12, 2013, pp. 8446-8456.
- [17] Villanueva-Beltrán JT, “Evaluación de la carga externa de fósforo y nitrógeno en la Presa Valle de Bravo y propuesta de solución”, MSc thesis, Posgrado de Ingeniería (Ambiental), Mexican National Autonomous University, 2011, México, UNAM, 134 p.
- [18] APHA (American Public Health Association), “Standard Methods for examination of water and wastewater”, 21st Edition, 2005, Washington, DC, USA.
- [19] Hansen AM, Márquez-Pacheco H, “Internal phosphorus load in a Mexican reservoir: Forecast and validation”, *Environmental Toxicology and Chemistry*, Vol 34, No 11, 2015, pp. 2583-2589.
- [20] Gonsiorczyk T, Casper P, Koschel R, “Phosphorus binding forms in the sediment of an oligotrophic and an eutrophic hard water lake of the Baltic district (Germany)” *Water Science Technology*, Vol 37, 1998, pp. 51–58.
- [21] Zhou Q, Gibson CE, Zhu Y, “Evaluation of phosphorus bioavailability in sediments of three contrasting lakes in china and UK”, *Chemosphere*, 2001, Vol 42, pp. 221–225.
- [22] Søndergaard M, Bjerring R, Jeppesen E, “Persistent internal phosphorus loading during summer in shallow eutrophic lakes”, *Hydrobiologia*, 2013, Vol 710, No 1, 95–107.
- [23] Beutel MW, Horne AJ “A review of the effects of hypolimnetic oxygenation on lake and reservoir water quality”, *Lake Reserv Manage* 199, Vol 15, pp. 285–297.