



Phosphorus and its Fractionation in Bottom Sediments of Selected Lakes of Wielkopolskie Lakeland in Central and Western Poland

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1. Introduction

Over the last century, many Polish lakes have undergone degradation, usually caused by eutrophication. Eutrophication is a natural process but a very slow one in normal conditions. Anthropogenic pressure drastically accelerated this process, particularly in the lakes located in economically developed, highly urbanized or intensively farmed areas. Eutrophication disturbs homeostasis of these ecosystems by rapidly quickening their senescence and, in extreme cases, causing even their disappearance. Also, deterioration of water quality prevents the lakes from being used for e.g. sports and recreation purposes or as backup source of drinking water (Smith & Schindler 2009).

Stopping these unfavorable processes and restoring good condition of lake water is one of the most important challenges for modern societies. This stems not only from our responsibility for the environment we live in but also from the obligation imposed by the EU Water Framework Directive that binded all member states to achieve good condition of lake water until 2015. In justified situations, this deadline might be extended until 2021 or even 2027. The water quality of 66% of all natural and 55% of all artificial lakes in Poland is below “good ecological status”, as defined in the Water Framework Directive (Łopata et al. 2019). Liquidation of point and non-point sources of contamination is often insufficient for the lakes to return to good condition. This may only be achieved by reclamation treatments (Grochowska et al. 2017, Siwek et al. 2014).

Phosphorus is one of the basic nutrients. In natural conditions it usually limits primary production, and so it is directly responsible for phytoplankton blooms and thus deterioration of light conditions in the pelagic zone and

formation of anoxic zones (Ross et al. 2008). High phosphorus concentrations cause a domination of blue-green algae (Paerl et al. 2011).

Most of the methods for lake restoration consist in limiting phosphorus bioavailability, as this efficiently reduces phytoplankton growth and restores natural conditions of an ecosystem functioning. Phosphorus compounds are relatively poorly soluble and they are usually accumulated in bottom sediments. They contain the largest share of phosphorus in the entire ecosystem. Under favorable conditions, this phosphorus may be re-released into water and incorporated into the biological cycle (Sobczyński 2009a, Søndergaard et al. 2003, Wang et al. 2003). In eutrophic lakes, the bottom sediments are so called internal source of phosphorus and they may supply pelagic zone with considerable amounts of this element, similarly to external sources. This is why limiting or even stopping external phosphorus supply is usually insufficient to improve the condition of a lake (Søndergaard et al. 2003). Therefore, the plans for a lake remediation should account not only for total load of phosphorus accumulated in the surface layer of bottom sediments that exchange components with surrounding water but also for the potential of phosphorus re-release into the pelagic zone depending on its physical and chemical conditions (Kleeberg et al. 2013, Sobczyński 2009b) and the bioavailability (Kostecki 2017a,b). One of the most important solution is a labor and time-consuming fractionation of phosphorus in sediment samples, e.g. according to the method proposed by Psenner (Psenner et al. 1988). This is the only way of identifying the potential risk posed by phosphorus accumulated in the bottom sediments. The aim of the study was to investigate individual fractions of phosphorus differing in their re-release potential in the total pool of phosphorus accumulated in the bottom sediments of selected lakes in Wielkopolskie Lakeland. Four of the eight lakes (Wolsztyńskie, Jelonek, Winary, Góreckie) were subjected of reclamation work, consisting of chemical phosphorus blocking in bottom sediments with iron salts.

2. Materials and methods

The study included bottom sediments of eight eutrophicated lakes in which reclamation treatment was planned or already implemented (Table 1) (Berleć et al. 2013, Bernaciak & Mudrak 2014, Bryl & Wiśniewski 2015, Bryl et al. 2017, Celewicz-Gołdyn & Klimko 2008, Sobczyński & Joniak 2008, 2009a, 2009b). All the investigated lakes are located within Wielkopolska region, in Wielkopolskie Lakeland that is the southernmost late glacial area (Fig. 1). Compared with other lake districts, Wielkopolskie Lakeland comprises much lower number of lakes. It is a macroregion located in central-western Poland, bordered by important rivers of this region: the Lower Warta Valley and Middle Noteć Valley on the north, the Wisła on the east, the Obra on the west, and the Obra and

Middle Warta on the south (Choiński 2006, Jańczak 1996). Annual precipitation is low and amounts to 450-550 mm.

Table 1. Morphometric data of the investigated lakes (Jańczak 1996)

No.	Lake	Water table area [ha]	Height [m a.s.l.]	Volume [m ³ , k]	Mean depth [m]	Max. depth [m]
1.	Wolsztyńskie	124.2	59.8	2522.6	2.0	4.2
2.	Winiary	14.4	104.5	302.4	2.1	4.2
3.	Jelonek	14.4	104.8	172.8	1.2	2.4
4.	Siekiera	12.2	62.0	329.4	2.7	5.6
5.	Pniewskie	59.7	94.1	898.8	1.5	3.3
6.	Umultowskie*	3.0	91.0	59.5	2.0	3.8
7.	Strykowskie	305.3	73.7	13637.4	4.5	7.7
8.	Góreckie	97.4	66.3	6136.2	6.3	15.5

* (Gołdyn et al. 1996)

The investigated reservoirs are glacial lakes, usually shallow and characterized by large variations in water level. Lake Wolsztyńskie (52°07.6'N 16°06.9'E) is a polymictic, non-stratified, flow-through lake supplied mostly by the Dojca river. It is located in the northern part of Wolsztyn. Winiary (52°32.9'N 17°36.8'E) and Jelonek (52°32.1'N 17°35.5'E) are small, shallow, polymictic lakes with limited possibilities of water exchange. They are located in the central part of the city of Gniezno. Jelonek is supplied by the Struga Gnieźnieńska (Berleć et al. 2013). Winiary, the greatest reservoir in Gniezno, is connected via a canal with Lake Wełnickie and a small reservoir Koszyk. Lake Siekiera (53°01.6'N 17°06.5'E) is located in the western part of Szamocin, near the Struga Młyńska, within the river basin of the Warta and the Noteć. It is very popular for recreational activities, particularly fishing. It discharges into the Młynówka Szamocińska. Pniewskie (52°30.8'N 16°14.6'E) is a moraine lake of low mean depth. It is supplied by waters from Lubosz Wielki Lake, and its waters are discharged into the Mogilnica. The lake contains large amount of organic deposits distributed all over its area. It is located in the western part of the city of Pniewy. Lake Umultowskie (52°28.3'N 16°56.2'E) is a small (ca. 0.3 ha) postglacial, moraine reservoir located in the north of Poznań. Its maximum depth is ca. 4.0 m. It is a flow-through lake with some eutrophic features. It is supplied by and discharges into the Umultowski Stream. Strykowskie (52°15.9'N 16°36.5'E), the largest of the investigated lakes (305 ha), is a relatively shallow, polymictic, ribbon lake

(maximum depth 7.7 m, 4.5 m on average). It is supplied by a few small water-courses and drainage ditches (Sobczyński & Joniak 2009a). The lake is located west of the city of Stęszew. Góreckie (52°15.9'N 16°47.9'E) is an example of a non-flow through, dimictic, ribbon lake. It is characterized by considerable depth and is located in Wielkopolski National Park (Sobczyński & Joniak 2008, 2009b).

Of all the studies lakes, only Wolsztyńskie, Winiary and Jelonek were subjected of reclamation work by means of the innovative Prote-fos method involving chemical inactivation (blocking) of phosphorus directly in bottom sediments with iron salts (PIX preparation). The innovative approach of this method is based on the use of two-module vessel named Proteus, with surface and underwater unit, which is responsible for triggering and controlling all process of chemical reclamation work (Wiśniewski et al. 2010). Prote-fos method is a modified Riplox method (Ripl 1976). Works were performed on the entire surface of the reclaimed lakes. Góreckie Lake was recultivate in 2010 with use of mobile pulverizing aeration technology with precise phosphorus inactivation by iron salts (Rybak et al. 2015, Sobczyński et al. 2012).

Physical and chemical analyses of bottom sediments from Lake Wolsztyńskie were conducted in the years 2012-2014. Bottom sediments samples were collected on 12 dates from four monitoring points. In the years 2012-2013, the lake was reclaimed. Control monitoring was performed in 2014. The fractions of phosphorus of bottom sediments from lakes Winiary and Jelonek was investigated in 2011, after the reclamation works that were conducted in the years 2009-2010. The analysis included data from one monitoring point per lake. Studies in Siekiera were carried out in the years 2014-2015 (three sampling dates) for two monitoring points. The data for Lake Pniewskie were obtained in May 2011 and the sediments were collected from four monitoring points. Samples of bottom sediment from the remaining lakes were collected at once (Góreckie in 2008, before reclamation works, Strykowskie in 2008, Umultowskie in 2015) from several points (Góreckie: 9 points, Strykowskie: 1 point, Umultowskie: 6 points).

The samples of bottom sediments were collected from profundal zone with a tube probe from the surface layer of 10 cm thickness, i.e. the layer that exchanges matter with the surrounding water. The collected sediments were placed in sealed, plastic containers to their full capacity to minimize its contact with atmospheric air. The samples were kept in a refrigerator at 4°C until the analysis. The samples of bottom sediments were collected in various amounts from the studied lakes. If the number of samples was larger, they constituted an element of a detailed research for the purpose of ongoing reclamation works.

After opening the containers, the sediments were thoroughly homogenized. Moist material was used to prepare two analytical samples of 4 g each. First of them was dried at 105°C to the constant mass. After drying hydration was calculated (Bolałek 2010). Organic matter content was determined as ignition losses at 550°C.

Residue after ignition was digested with diluted hydrochloric acid. The extract was used to determine total phosphorus content using a molybdate method with ascorbic acid as a reducing agent (Bolałek 2010, Hermanowicz et al. 1999).

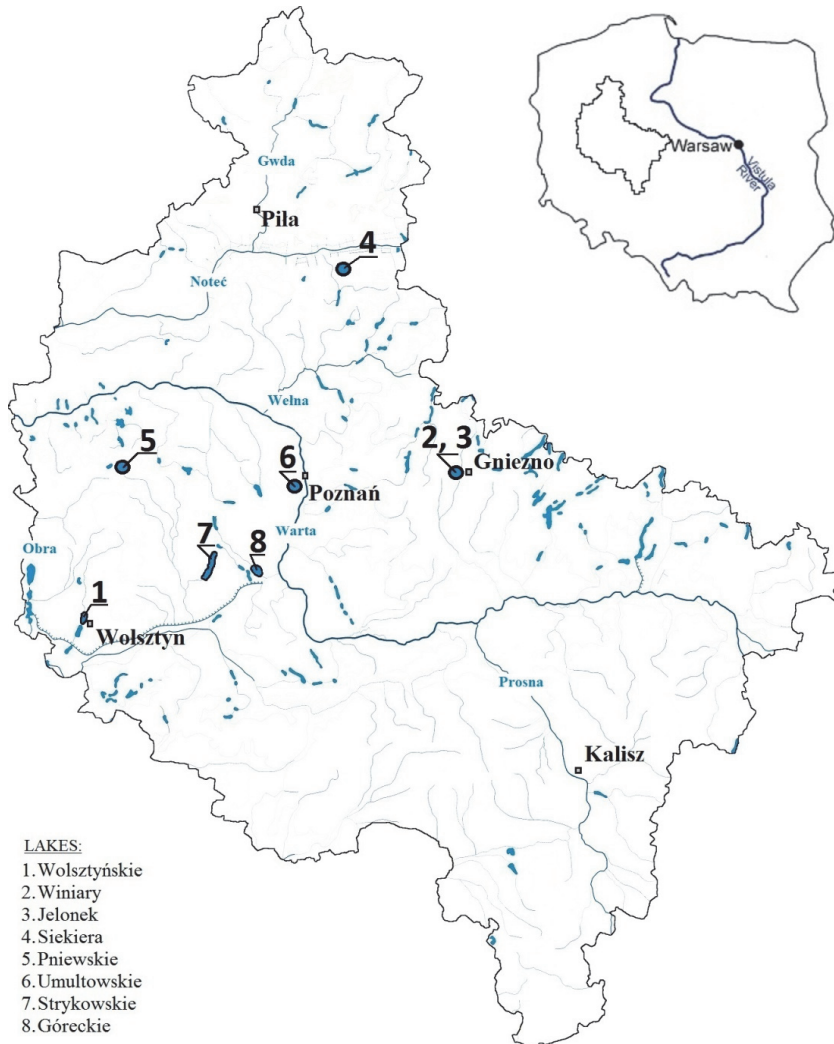


Fig. 1. Location of the investigated lakes on the map of Wielkopolska Province

Second sample of wet sediments was placed in 50 ml polyethylene screw-top tubes for phosphorus fractionation by means of sequential extraction as described by Psenner (Psenner et al. 1988). Five phosphorus fractions differing in their potential to be released into water were distinguished: fraction I ($\text{NH}_4\text{Cl-P}$)

– mobile, exchangeable phosphorus – extracted for 2 h with aqueous solution of NH_4Cl ; fraction II (BD-P) – iron-bound phosphorus – extracted for 2 h with the solutions of 0.11 M $\text{Na}_2\text{S}_2\text{O}_4$ and 0.11 M NaHCO_3 mixed in 1:1 ratio; fraction III (NaOH-P) – phosphorus bound to organic matter and aluminium – extracted for 18 h with 1 M NaOH; fraction IV (HCl-P) – calcium-bound phosphorus – extracted for 18 h with 0.5 M HCl; fraction V (res-P) – residual phosphorus – the remains of the first four fractions were calcinated at 500°C , cooled and then digested with diluted hydrochloric acid.

Extraction was performed at room temperature on a rotary shaker. The samples were centrifuged after each stage and the extract was removed. The remaining sediment was treated with another extraction solvent. Phosphorus contained in the extracts was determined using molybdate method. The extracts that were colorful, were evaporated to dryness, calcinated at 550°C and again digested in diluted HCl.

For determination of calcium, iron and aluminium the samples were digested or wet mineralized with aqua regia (Sobczyński et al. 1996) and then the metal content was recorded with atomic absorption spectrometry (AAS). The results were statistically analyzed in the program Statistica 6 PL.

3. Results

Phosphorus in bottom sediments is bound mainly to organic matter and such metals as iron, aluminium and calcium, which is why their higher content is desired from the ecological perspective (Lampert & Sommer 2001). Total content of phosphorus in the bottom sediments of the investigated lakes was similar (Table 3) and analogous to that determined in bottom sediments of other eutrophic lakes of Wielkopolskie Lakeland: 0,86 – 1,82 g P kg^{-1} d.w. (Sobczyński et al. 1996) and 0,13 – 3,43 g P kg^{-1} d.w. (Karwacka et al. 2015) and also other lakes of Poland (Bojakowska 2016). Phosphorus content was the highest in Siekiera and the lowest in Lake Umultowskie (Table 3). The content of iron, aluminium, calcium and organic matter were much more variable (Table 2).

The presence of these macroelements in the lakes depends on the formation and use of the catchment, hydrogeological conditions and anthropopressure. Their migration occurs as a result of complex physico-chemical processes due to water and wind erosion. The highest mean content of Al in bottom sediments of the studied lakes was observed in Winiary Lake (20,6 g Al kg^{-1} d.w.) and the lowest in Umultowskie (2,03 g Al kg^{-1} d.w.) and Wolsztyńskie (2,44 g Al kg^{-1} d.w.) lakes. The highest mean content of Ca was in Wolsztyńskie Lake (243 g Ca kg^{-1} d.w.), but the lowest in Strykowskie Lake (19.8 g Ca kg^{-1} d.w.). The lowest mean content of Fe was detected in Umultowskie Lake (1,86 g Fe kg^{-1} d.w.) and the highest in

Wolsztyńskie (10,3 g Fe kg⁻¹ d.w.), Winiary (32,9 g Fe kg⁻¹ d.w.), and Jelonek (17,0 g Fe kg⁻¹ d.w.) lakes (Table 2).

The organic matter content of the studied bottom sediments ranged from 13% d.w. (Lake Wolsztyńskie) to 70,4% d.w. (Lake Umultowskie). The largest amount of organic matter was found in the sediments from Umultowskie Lake, on average: 63,8% d.w. and Pniewskie Lake, on average: 40,7%. The lowest amount in the sediments of the lakes Winiary and Jelonek, on average: 17,8-20,4% d.w. (Table 2).

Almost in all analyzed cases (except Jelonek Lake) the fraction bound with organic matter and aluminium (NaOH-P) had the largest participation in bottom sediments, on average: 35,1-45,3% TP. The largest participation of mobile fractions (NH₄Cl-P and BD-P) was observed on the lakes: Wolsztyńskie (total 25%), Siekiera (total 27,7%) Strykowski (total 18%) (Table 3).

Average annual phosphorus content decreased from year to year: from 1.077 g P kg⁻¹ d.w. to 1,000 g P kg⁻¹ d.w. In the case of stable, permanently bound forms, i.e. phosphorus bound to calcium and phosphorus in residual form, the average annual phosphorus values were at the level of 0.11-0.12 (res-P) and 0.22 (HCl-P) g P kg⁻¹ d.w. The share of the fraction related to organic matter and aluminium (NaOH-P) was the largest but also decreased each year: from 0.54 to 0.39 g P kg⁻¹ d.w. In 2014, a slight increase in the share of fraction NH₄Cl-P was observed (Fig. 2).

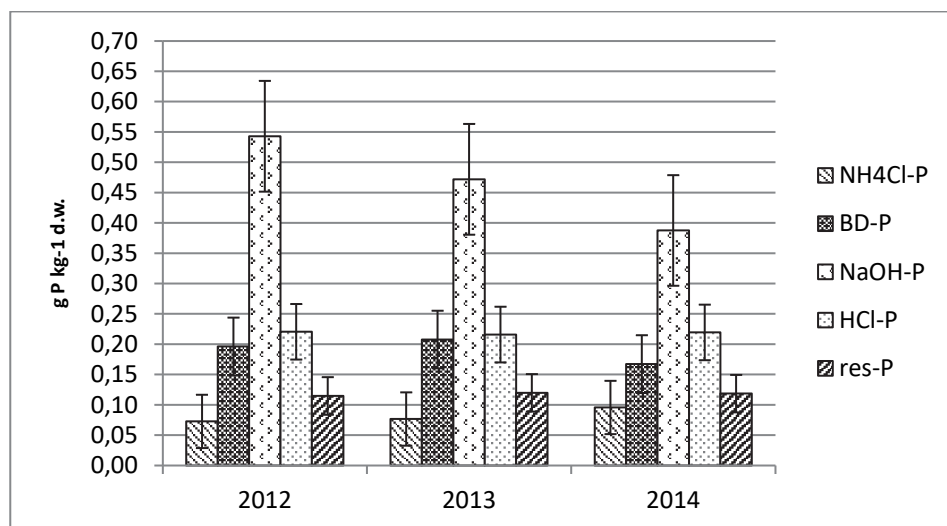


Fig. 2. Average annual phosphorus content in each fraction on the example of Wolsztyńskie Lake

Analysis of vertical changes of phosphorus fractions concentrations in the bottom sediments of Wolsztyńskie Lake (Fig. 3) showed that only in the case of the samples taken at monitoring point no. 3 (the deepest place in the lake) the sum of the bioavailable phosphate fractions (NH₄Cl-P and BD-P) sometimes exceeded 30% of the overall content. However, the mean for all other monitoring points was usually around 25% (Tab. 3). Despite the fact that biologically less accessible fractions (HCl-P, res-P) constituted a much larger share in the total phosphorus pool, intense phytoplankton blooms are observed on this lake. This situation proves that there is big the problem of the external supply of nutrients to the lake from the catchment.

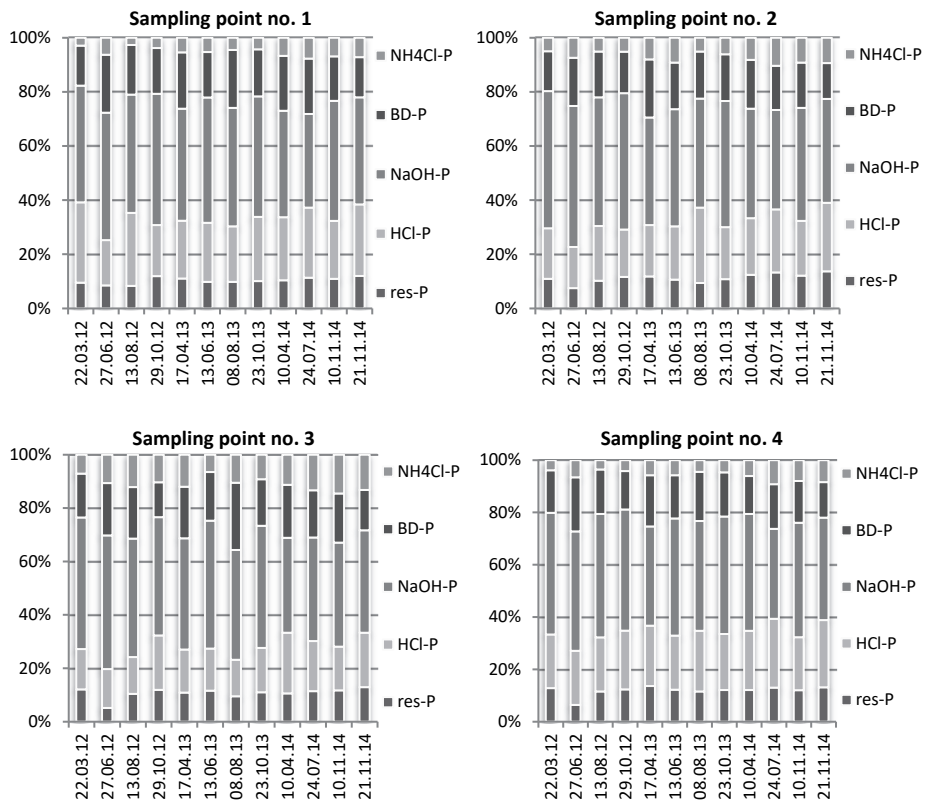


Fig. 3. Vertical changes of phosphorus fractions concentrations in bottom sediments of Wolsztyńskie Lake

Table 2. The content of iron, aluminium, calcium and organic matter in the dry weight of bottom sediments samples of the studied lakes

Lake (name)		Ignition losses (organic matter)	Iron	Aluminium	Calcium
		% d.w.	g Fe kg ⁻¹ d.w.	g Al kg ⁻¹ d.w.	g Ca kg ⁻¹ d.w.
Wolsztyńskie (n=48)	a	21.1	10.3 ±0.52	2.44 ±0.12	243 ±12.2
	b	21.4	9.68 ±0.48	2.41 ±0.12	229 ±11.5
	c	13.0-28.5	5.19±0.26-18.0±0.90	0.98±0.05-4.35±0.22	188±9.40-417±20.9
Winiary * (n=5)	a	17.8	32.9 ±1.65	20.6 ±1.03	127 ±6.35
	b		31.7 ±1.59	7.58 ±0.38	134 ±6.70
	c		30.9±1.55-35.8±1.79	6.94±0.35-72.0±3.60	95.0±4.75-149±7.45
Jelonek * (n=5)	a	20.4	17.0 ±0.85	8.91 ±0.45	145 ±7.25
	b		16.5 ±0.83	6.71 ±0.34	138 ±6.90
	c		11.8±0.59-22.5±1.13	5.28±0.26-18.5±0.93	136±6.8-169±8.45
Siekiera (n=6)	a	34.2	7.43 ±0.37	3.25 ±0.16	145 ±7.25
	b	35.9	7.28 ±0.36	3.12 ±0.16	141 ±7.05
	c	27.0-38.6	1.05±0.05-12.6±0.63	1.91±0.10-4.86±0.24	78.9±3.95-206±10.3
Pniewskie (n=4)	a	40.7	6.61 ±0.33	no data	91.8 ±4.59
	b	41.4	6.74 ±0.34	no data	92.2 ±4.61
	c	34.5-45.5	4.95±0.25-8.03±0.40	no data	87.1±4.35-95.8±4.79
Umultowskie (n=6)	a	63.8	1.86 ±0.09	2.03 ±0.10	97.7 ±4.90
	b	62.8	1.88 ±0.06	2.06 ±0.10	108 ±5.40
	c	58.4-70.4	0.78±0.04-3.41±0.17	1.53±0.08-2.50±0.13	5.98±0.30-204±10.2
Strykowskie* (n=1)	a	25.0	5.92 ±0.30	3.05 ±0.15	19.8 ±0.99
	b				
	c				
Góreckie (n=9)	a	27.0	7.27 ±0.36	4.59 ±0.23	101 ±5.05
	b	27.1	6.53 ±0.33	4.37 ±0.22	112 ±5.60
	c	26.2-28.1	3.56±0.18-11.5±0.58	3.02±0.15-6.88±0.34	71.0±3.55-128±6.40

a – mean, b – median, c – range,

* – Ignition losses was performed only for one sample of the bottom sediments

Table 3. Phosphorus content in samples of bottom sediments of studied lakes and its distribution between each individual fractions

Lake (name)		Total P content	NH ₄ Cl-P	BD-P	NaOH-P	HCl-P	res-P
		g P kg ⁻¹ d.w.					
Wolsztyńskie (n=48)	a	1.08 ±0.04	7.4	17.6	43.3	20.7	11.0
	b	1.04 ±0.04	6.8	17.3	43.8	20.6	11.5
	c	0.66±0.03- 1.56±0.06	2.7-14.5	13.1-25.2	34.4-52.1	13.7-29.7	5.1-13.7
Winiary * (n=5)	a	1.01 ±0.04	0.3	7.0	45.9	30.1	16.7
	b						
	c						
Jelonek * (n=5)	a	0.98 ±0,04	4.8	8.6	25.4	44.8	16.4
	b						
	c						
Siekiera (n=6)	a	1.36 ±0.05	15.1	12.6	35.1	20.8	16.4
	b	1.32 ±0.05	15.7	12.5	34.7	19.0	15.6
	c	0.99±0.04- 1.76±0.07	6.9-19.7	6.7-17.8	32.7-38.6	17.0-32.1	12.5-20.8
Pniewskie (n=4)	a	1.03 ±0.04	7.4	9.9	39.0	31.3	12.4
	b	0.98 ±0.04	7.8	9.9	40.2	29.5	12.5
	c	0.89±0.04- 1.27±0.05	5.9-8.2	8.6-11.2	30.9-44.7	25.1-40.9	11.4-13.4
Umultowskie (n=6)	a	0.74 ±0.03	10.2	6.2	44.1	26.3	13.2
	b	0.73 ±0.03	9.7	6.3	45.0	24.5	12.9
	c	0.61±0.02- 0.86±0.03	6.6-14.7	4.8-7.4	38.7-47.3	20.0-35.8	12.4-14.5
Strykowskie (n=1)	a	1.23 ±0.05	9.5	8.5	38.2	29.8	14.0
	b						
	c						
Góreckie (n=9)	a	1.14 ±0.05	7.2	11.1	45.3	23.3	13.1
	b	1.15 ±0.05	7.1	11.1	46.8	22.8	13.6
	c	1.01±0.04- 1.27±0.05	4.1-12.1	6.4-18.0	38.4-50.6	17.6-29.4	11.9-14.5

a – mean, b – median, c – range,

* – total P content and P-fractions were performed only for one sample of the bottom sediments

4. Discussion

Only three reservoirs (Wolsztyńskie, Jelonek and Winiary) were subjected to reclamation treatment with Prote-fos method that involves binding phosphates in bottom sediments by means of iron ions. This procedure resulted in ecologically favorable increase in iron concentration in the surface layer of the sediments. The reclamation effects were particularly noticeable for Lake Wolsztyńskie, where the share of iron-bound phosphorus (BD-P) was high as compared with the other lakes and amounted to 17.6% TP. Despite high iron content in Winiary and Jelonek lakes, the share of BD-P was not substantial, even in comparison with the lakes in which phosphorus inactivation was not implemented. This may be explained by low content of $\text{NH}_4\text{Cl-P}$, i.e. the mobile phosphorus bound to and inactivated by iron ions in the sediments. Supplying the sediments with iron ions caused sequestration of the mobile phosphorus and its conversion into a less available fraction (Katsev & Dittrich 2013, Kleeberg et al. 2013). Iron surplus introduced during reclamation should protect the pelagic zone against phosphorus released from the other fractions, particularly NaOH-P in which it is bound to organic matter and aluminium and may be released into water in the course of organic matter mineralization. The surface layer of the sediments, artificially enriched with iron, should then bound and immobilize the released phosphorus ions. This process is enhanced by aerobic conditions, as iron(III) forms a poorly soluble salt with phosphate ion (Grochowska & Gawrońska 2004, Sobczyński 2009b). This was confirmed in the lakes in which anoxic conditions (reducing conditions) occur in the deepest parts, where phosphorus release from bottom sediments to the pelagic zone was greater than in shallow zones where oxygen reaches the bottom and oxidizing conditions prevail (Kowalczevska-Madura et al. 2010a,b, Łukawska-Matuszewska & Burska 2011). All this caused that although the relationship between the content of iron in the bottom sediment and the percentage share of the BD-P in the total pool was observed, this relationship was not too strong, it was significantly weaker than the one described in the literature (Siwek 2010). The total share of the first two fractions, i.e. exchangeable phosphorus and iron-bound phosphorus that are most readily released into the pelagic zones was almost 28% TP for Lake Siekiera and 25% TP for Lake Wolsztyńskie. In other lakes, this share was much lower, even by several percent, which was also enough for phytoplankton bloom to occur in these lakes (Bartoszek 2007).

The sediments from Lake Umultowskie were typical organic sediments, as their mean share of organic matter was nearly 64% d.w. High content of organic matter was also detected in the sediments from Pniewskie and Siekiera lakes. The other lakes contained lower amounts of organic matter (Table 2). This was not clearly reflected in percentage share of NaOH-P , i.e. phosphorus bound to organic matter and aluminium. It should be mentioned that aluminium content in the sediments from both Umultowskie and Siekiera lakes was relatively low and this may explain why the share of NaOH-P was not significantly different

from its content in the other lakes. The bottom sediments from both these lakes were rich in phosphorus from $\text{NH}_4\text{Cl-P}$ that is mobile phosphorus. This was probably due to the fact that organic sediments contain considerably greater amounts of interstitial water than mineral sediments and phosphorus from $\text{NH}_4\text{Cl-P}$ is the most abundant in this water (Czerwieniec 2003, Gnauck et al. 2002, Kentzner 2001, Wiśniewski 1995). Aluminium content in Lake Pniewskie was not determined for technical reasons. High amounts of NaOH-P were reported for Wolsztyńskie, Jelonek and Góreckie lakes, which was not justified by high contents of organic matter or aluminium (except for Lake Winiary where the sediments contained significant amount of aluminium). Therefore, no strong relationship was observed between the content of organic matter and aluminium in the bottom sediments and the share of NaOH-P bound with organic matter and aluminium in total phosphorus content as well as the absolute content of this phosphorus fraction. Phosphorus bound to organic matter is transformed into mineral form during organic matter mineralization. Studies on bottom sediment cores featuring layers differing in their accumulation time (age) demonstrated that phosphates released during organic matter mineralization were to a high degree bound to calcium present in the sediments, thus increasing the share of HCl-P (Sobczyński & Joniak 2009a).

There was also no relationship between calcium content in the sediments and the share of HCl-P (Ca-bound phosphorus) in the total pool of phosphorus as well as the absolute content of this fraction. This was probably due to substantial surplus of calcium in relation to phosphorus that could be bound with it, which was why further increase in calcium content would not increase the share of HCl-P in total phosphorus pool.

Lack of clear, described in the literature (Siwek 2010), relationship between the sediment content of iron, calcium and aluminium and distribution of sediment phosphorus between BD-P , NaOH-P and HCl-P , i.e. the fractions in which phosphorus is bound to these metals is probably due to the fact that there are various mechanisms of metal precipitation in a lake ecosystem apart from binding to phosphorus (Sobczyński et al. 2004, Zerbe et al. 1995).

Residual-P that contains phosphorus practically non bioavailable in normal environmental conditions was relatively small. This is not favorable from ecological perspective, as phosphorus bound in this fraction is considered to be completely withdrawn from the biological cycle.

In seven out of eight investigated lakes, the most abundant fraction of phosphorus was NaOH-P bound with aluminium and organic matter. The only exception was Jelonek lake, where the bottom sediment contained mostly phosphorus from HCl-P bound with calcium. The share of HCl-P was also high in the other lakes, and together with NaOH-P they accounted for 55.9% TP of phosphorus in Siekiera and 76.0% TP in Winiary. The sum of these two fractions in the bottom sediments from the investigated lakes was considerably higher than the

sum of $\text{NH}_4\text{Cl-P}$ and BD-P comprising easily bioavailable phosphorus. A significant but smaller proportion of phosphorus was contained in the residual fraction V that did not participate in the biological cycle of the lake ecosystems. Its share ranged from 11% TP in Lake Wolsztyńskie to 16.7% TP in Winiary. Nevertheless, all the eight lakes are classified as eutrophic or nearly eutrophic and they experience phytoplankton blooms.

In reclaimed lakes, in the composition of bottom sediments, some differences can be observed in relation to non-reclaimed lakes, resulting for example from of the reclamation methods used. The treated lakes are usually characterized by a lower share of mobile fractions, as in the case of the Gniezno lakes, which show the effect of using bentonite clay enriched with lanthanum (a large percentage of bio-available fractions). In the case of Wolsztyn Lake, the situation is different. Of all the studied lakes, despite the remediation carried out in 2005-2006 by means of introducing aluminum salt into the water column (Gawrońska et al. 2007), the bottom sediments of the Wolsztyńskie Lake were characterized by the lowest concentration of aluminum and a large amount of iron, as a result of feeding iron salts directly to the bottom sediments in 2012-2013. As a consequence, phosphorus has been blocked in mobile forms, which gets into the water column in specific anaerobic conditions. The share of these fractions was higher compared to other lakes. The average annual phosphorus content for stable, permanently bound forms, i.e. phosphorus associated with calcium (HCl-P) and phosphorus in the residual form (res-P) practically does not change. Only the content of mobile forms, that are sensitive to changes in various physico-chemical conditions prevailing in water, are change. In the case of Góreckie Lake, the reclamation was carried out at a later date than the collection of sediments.

5. Conclusions

Phosphorus present in bottom sediments of eight investigated lakes located within Wielkopolskie Lakeland was mostly bound within not readily bioavailable fractions, i.e. those involving organic matter, aluminium and calcium, in total mean 55,9 – 76,0%. The share of residual fraction comprising virtually non bioavailable phosphorus was low and ranged from 5,1 to 20,8% of the phosphorus content in a given sample. Total share of these three fractions was higher than that of two mobile fractions readily released into the pelagic zone but despite this seemingly favorable ratio the lakes were eutrophic and required reclamation treatments. Reclamation work involving the iron salt dosage to bottom sediments of lakes (Wolsztyńskie, Jelonek, Winiary) causes a reduction of the mobile fraction $\text{NH}_4\text{Cl-P}$ in the total pool.

Reclamation of eutrophic lakes should account for the bottom sediments as an internal source of phosphorus. To identify the risk of phosphorus release into water it is not enough to simply determine its total sediment content but it is

also necessary to figure out its distribution among the fractions differing in their potential of phosphorus release and incorporating it into the biological cycle. Even though these fractions are defined as phosphorus combinations with such metals as iron, aluminium or calcium or with organic matter, the knowledge on the content of these components in the sediments is not enough to confirm what amount of total phosphorus is bound to them and how the conditions prevailing in the pelagic zone may affect phosphorus release.

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Abstract

The role of phosphorus contained in bottom sediments of water reservoirs is crucial in the whole eutrophication process. It is an element responsible for the proper functioning of aquatic ecosystems, and its excess leads to deterioration of water quality. The release of phosphorus from bottom sediments directly into the water depends on many factors. This process is particularly intensified at the moment of anaerobic conditions occurring in the bottom layer, or the phenomenon of resuspension of sediments due to external factors, such as intense waving. The persistence of phosphorus deposition in sediments also depends on the nature of chemical connections and changing oxidation-reduction conditions, temperature and pH.

Bottom sediments from eight selected lakes of Wielkopolskie Lakeland were investigated for their total phosphorus content and the possibility of its re-release into water. The subject of the study were the following lakes: Wolsztyńskie, Winiary, Jelonek, Siekiera, Pniewskie, Umultowskie, Góreckie, Strykowskie. The investigated water reservoirs are glacial lakes, usually shallow and characterized by large variations in water level.

The samples of bottom sediments were collected from profundal zone with a tube probe from the surface layer of 10 cm thickness, i.e. the layer that exchanges matter with the surrounding water. The collected sediments were placed in sealed, plastic containers to their full capacity. Before proceeding to carry out detailed laboratory analyzes, samples were prepared accordingly. First, the bottom sediments were thoroughly homogenized. Then, they were dried and subjected to further testing. The obtained results were statistically analyzed in the program Statistica 6 PL.

Phosphorus was fractionated by means of a sequential extraction described by Psenner. The sediments were also analyzed for the content of phosphorus binding components such as organic matter, iron, aluminium and calcium. Phosphorus was found to be bound mostly to organic matter, aluminium and calcium – the fractions from which it was difficult to release into water. The share of exchangeable and most mobile and bioavailable iron-bound fraction of phosphorus was the lowest but it was still high enough to cause phytoplankton blooms. No clear relationships between the content of individual phosphorus-binding components and the share of phosphorus fractions related to them in total phosphorus pool were identified. Total content of phosphorus in the sediments of the investigated lakes was analogue and similar to that determined in bottom sediments of other eutrophic lakes of Wielkopolskie Lakeland. The content of aluminium, calcium, iron and organic matter were much more variable.

Keywords:

lake, bottom sediments, phosphorus, fractionation of phosphorus, organic matter, iron, aluminium, calcium

Fosfor i jego frakcje w osadach dennych wybranych jezior Pojezierza Wielkopolskiego w środkowej i zachodniej Polsce

Streszczenie

Rola fosforu zawartego w osadach dennych zbiorników wodnych jest kluczowa w całym procesie ich eutrofizacji. Jest pierwiastkiem odpowiedzialnym za prawidłowe funkcjonowanie ekosystemów wodnych, a jego nadmiar prowadzi do pogorszenia się jakości wody. Uwalnianie się fosforu z osadów dennych bezpośrednio do toni wodnej zależy od wielu faktorów. Szczególnie proces ten intensyfikuje się w momencie pojawienia się w warstwie naddennej warunków beztlenowych, czy też zjawiska resuspensji osadów na skutek oddziaływania czynników zewnętrznych, np. intensywnego falowania. Trwałość deopozycji fosforu w osadach zależy również od charakteru połączeń chemicznych oraz zmiennych warunków oksydacyjno-redukcyjnych, temperatury, a także pH.

Badano osady denne z ośmiu wybranych jezior Pojezierza Wielkopolsko-Kujawskiego pod kątem całkowitej zawartości fosforu i potencjalnej możliwości jego ponownego uwalniania do toni. Przedmiotem badań były następujące jeziora: Wolsztyńskie, Winiary, Jelonek, Siekiera, Pniewskie, Umultowskie, Strykowskie, Góreckie. Badane zbiorniki wodne to jeziora polodowcowe, zwykle płytkie, charakteryzujące się dużymi wahaniami poziomu wody.

Próbki osadów dennych pobierano za pomocą sondy rurowej z powierzchniowej warstwy osadu o miąższości 10 cm, czyli warstwy, która uczestniczy w wymianie materii z tonią. Pobrany osad umieszczano w szczelnych, plastikowych pojemnikach napełniając je do pełna. Przed przystąpieniem do przeprowadzania szczegółowych analiz laboratoryjnych próbki zostały odpowiednio przygotowane. W pierwszej kolejności osady denne dokładnie zhomogenizowano. Następnie wysuszono oraz przeprowadzono kolejne analizy. Uzyskane wyniki badań poddano analizie statystycznej w programie Statistica 6 PL.

Frakcjonowanie fosforu realizowano na drodze ekstrakcji sekwencyjnej wg schematu zaproponowanego przez Psennera. Dodatkowo w osadach oznaczano materię organiczną oraz żelazo, glin i wapń, czyli składniki osadu wiążące fosfor. Stwierdzono, że w ogólnej puli fosforu poszczególnych osadów największy udział miały frakcje związane z materią organiczną i glinem oraz z wapniem, czyli stosunkowo trudniej uwalniane do toni. Udział frakcji wymiennej i związanej z żelazem, czyli frakcji najbardziej mobilnych, biodostępnych, był mniejszy co jednak było wystarczające, aby w wodach tych jezior występowały zakwity fitoplanktonu. Nie zaobserwowano natomiast wyraźnych zależności pomiędzy zawartością w osadach poszczególnych składników wiążących fosforany, a udziałem frakcji fosforu z nimi związanych w ogólnej jego puli. Łączna zawartość fosforu w osadach badanych jezior była analogiczna i podobna do tej stwierdzonej w osadach dennych innych eutroficznych jezior Pojezierza Wielkopolskiego. Zawartość glinu, wapnia, żelaza i materii organicznej była znacznie bardziej zmienna.

Słowa kluczowe:

jezioro, osady denne, fosfor, frakcjonowanie fosforu, materia organiczna, żelazo, glin, wapń