

Role of micrometer sediment particles (SPLITT fractionation) in phosphorus speciation and its recycling in lakes

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Abstract To study the potential of phosphorus (P) release from sediments in the lakes: Chełmżyńskie and Wieczno Płd. was the aim of this study. The task was realized by carrying chemical sequential extractions. The novelty of our approach consists in adopting the SPLITT (split-flow lateral-transport thin) method of particles separation, which was used supplementary to sieving. Sieving provides following sediment fractions: 0.25–0.5, 0.125–0.25, 0.09–0.125 mm, whereas the SPLITT allows separation of particles which smaller than 30 μm , and which constituted >30 % of total sediment mass. The mass distribution of size fractions in sediments from both the lakes was very similar. P content, as the sum of HCl-P, NaOH-P, NH_4Cl -P, was by ca. 20 % lower in the particle size fractions 0.25–0.5, 0.125–25 mm, whereas total P content in SPLITT sediment was much higher in all size fractions (<5, 5–10, 10–30 μm) in the Wieczno Płd. Lake. Although the ecological status is stated to be good in the Wieczno Płd. and moderate in the Chełmżyńskie, the Wieczno Płd. experiences very extensive and frequent algal blooms which form scum on the lake's surface. Based on our findings, we are of the opinion that shallowness of the Lake Wieczno Płd. favors water mixing causing resuspension of fine particles,

which results in enhanced P internal cycling and thus P availability for primary producers. Much higher content of phosphorus in the fractions below 30 μm in the Wieczno Płd. than the Chełmżyńskie Lake supports our statement.

Keywords SPLITT · Fractionation · Speciation of phosphorus · Lake sediments

Introduction

Recent decades have seen a massive increase in lake and coastal eutrophication globally, leading to widespread hypoxia and anoxia, habitat degradation, alteration of food-web structure, loss of biodiversity, and increased frequency, spatial extent, and duration of harmful algal blooms. Eutrophication also decreases the value of rivers, lakes, and estuaries for recreation, fishing, hunting, and esthetic enjoyment (Jeppesen et al. 2005; Schindler 2012; Smith and Schindler 2009; Anderson et al. 2008; Csathó et al. 2007; Heisler et al. 2008; Schindler and Vallentyne 2008; Smal et al. 2005).

Eutrophication is defined as an increase in the rate of supply of organic matter in an ecosystem, which is caused by the enrichment of water bodies by inorganic nutrients (e.g. nitrate, phosphate) (Nixon 1995). It may occur naturally but can also be the result of human activity (cultural eutrophication) and it is particularly evident in rivers, shallow lakes, and coastal areas (Csathó et al. 2007; Duarte 2009; Nixon 2009; Voss et al. 2005; Pastuszek et al. 2003). Cultural eutrophication is the process that speeds up natural eutrophication because of human activity, such as, intensive agriculture with excessive use of fertilizers, deforestation, mining, urbanization, industrialization, irrigation, and damming (Howarth 2008; Humborg et al. 2006;

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Meybeck 2004; Stal et al. 2003; Carpenter et al. 1998; Howarth et al. 1996; Nixon et al. 1996).

Human actions alter the global phosphorus (P) cycle and cause P to accumulate in some of the world's soil (Filippelli 2002; Bennett et al. 2001). Increasing P levels in the soil elevate the potential P runoff to aquatic ecosystems (Sharpley 2006; Hooda et al. 2001; Fluck et al. 1992). Melack (1995) and Howarth et al. (1995) report a 50 % to threefold increase in riverine-P flux to the oceans above the pre-agricultural levels. Using a global budget approach, Bennett et al. (2001) estimated the increase in net P storage in terrestrial and freshwater ecosystems to be at least 75 % greater than preindustrial levels of storage.

When entering the sediment in open waters, phosphorus becomes a part of the numerous chemically and biologically mediated processes and is either permanently deposited in the sediments or released by various mechanisms and returned in dissolved form to the water column via interstitial water (Ruttenberg 2003). Since the phosphorus concentration in sediment is much higher than in lake water, phosphorus release can increase the eutrophication of lakes (Hupfer and Lewandowski 2008; Søndergaard et al. 2003; Laseras 1991). The release of P from sediments of eutrophic lakes is often associated with proliferation of nuisance algal blooms, especially cyanobacteria (Hickey and Gibbs 2009). Phosphorus return to circulation in open water is a result of many interrelated biological (e.g. biological immobilization and mobilization), physicochemical (e.g. sorption/desorption, dissolution), and physical processes (e.g. diffusion, bioturbation, wind induced mixing causing resuspension). These processes are affected by a multitude of factors such as: quantity and quality of the deposited organic matter, different sediment characteristics, redox potential, pH, water temperature, microbial activity, dissolved oxygen content, nitrates, and sulfates (Kowalczywska-Madura et al. 2010; Hupfer and Lewandowski 2008; Kim et al. 2003; Ruttenberg 2003; Filippelli 2002; Søndergaard et al. 1996, 2003; Laseras 1991). As shown in recent studies, the grain size of sediment particles is also of importance (Zhu et al. 2013). These parameters define P speciation in water bodies.

Chemical sequential extractions have been widely used in order to determine various forms in which phosphorus occurs in the sediments (Sobczyński and Joniak 2009a, b; Fytianos and Kotzakioti 2005; Søndergaard et al. 1996, 2003; Kaiserli et al. 2002; Zhou et al. 2001; Rydin 2000). A general aim of sequential extractions is to provide a more precise description of the potentials for phosphorus release from sediment and to predict its future influence on lake water concentrations, thus process of eutrophication. Recent studies indicate that in aquatic systems, not only various forms in which phosphorus occurs in sediment, but also the particle size with adsorbed phosphorus (physical P

speciation) can control bioavailability of P (Selig 2003; Andrieux-Loyer and Aminot 2001).

The aims of our study were (1) supplementary to sieving, to adopt SPLIT method of particles separation in sediment samples collected in the Chełmżyńskie and the Wieczno Południowe (hereafter: Wieczno Płd.) Lakes (central Poland), (2) to carry on the chemical sequential extractions (samples of sediment fractionated according to particle size) in order to receive more extensive information on P speciation, (3) to specify and compare the potentials for phosphorus release from sediments in both lakes; the internal P cycling can be an important source of this nutrient, and thus, can potentially be responsible for strengthening eutrophication.

Materials and methods

Study area

The Wieczno Płd. (Fig. 1), is a moraine, polymictic lake. The lake is located on the North European Plain and on early post-glacial soils which are characterized by high Ca content (>25 mg/L) and high vulnerability for degradation. The lake is very shallow with non stratified water column. The average depth reaches only 2.2 m, and there is only one centrally located deep whose depth does not exceed 4.1 m (Table 1). The water residence time in the Wieczno Płd. Lake is approximately 1.5 year. Water level fluctuations are mostly associated with increased runoff in spring and during the dry periods in summer. The contribution of agricultural land, forest land, and lakes' area to overall catchment area equals to ca. 50, 18, and 27 % (Table 1), respectively. The coastline of the lake is well developed, with trees and scrubs forming a belt along majority of the coastline. Such a belt constitutes a buffer zone effectively limiting surface runoff of water and nutrients. Geomorphology and land cover of the lake's basin speak for rather insignificant diffuse outflow of nutrients. The strongest anthropogenic pressure on the lake is generated by a large tourist complex and use of sandy beach. The monitoring data gathered in 2005 indicated that the ecological state of the lake was good, but with high vulnerability to degradation. Indeed, Schindler's coefficient (limnological parameter, which is a ratio of summed up area of a lake and its catchment area to the lake volume; Kajak 1998) estimated for 2012, was equal to 11.7.

The Chełmżyńskie Lake is located ca. 12 km south-east of the Wieczno Płd. Lake. The city of the Chełmża, with about fifteen thousand inhabitants, is located very close to the northern part of the lake (Fig. 1). It is a ribbon lake; the average depth reaches 6 m, whereas the deepest part has the depth of ca. 27 m (Table 1). The water residence time

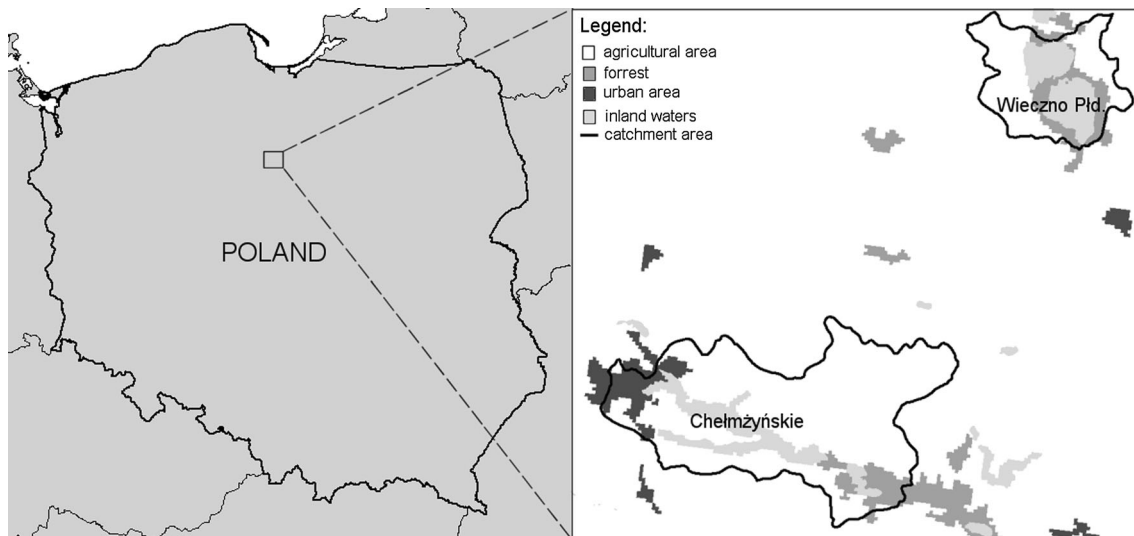


Fig. 1 Site map

Table 1 Comparison of drainage areas of the Chełmżyńskie and Wieczno Płd. Lakes. (source: CLC 2006)

Parameter	Chełmżyńskie	Wieczno Płd.
Total area [ha]	271.1	199.4
Catchment area [ha]	3,404.1	5,367.3
Av. Water volume [m ³]	16 451	4 358
Depth max. [m]	27.1	4.1
Depth av. [m]	6.1	2.2
Land use [%]		
Urban	5.6	–
Industry	0.4	–
Arable	73.6	48.7
Pastures	0.8	1.3
Other agricultural land	2.9	5
Forest	5.3	18.2
Wetlands	0.1	–
Inland waters	11.5	26.8

in the Chełmżyńskie Lake is ca. 3 years. In contrast to the Wieczno Płd. Lake, the water column in the Chełmżyńskie Lake is stratified; in 2012, Schindler’s coefficient was equal to 2.16. The hydrologic system of the drainage area consists of artificial melioration streams and two smaller lakes. The coastline of the lake is sinuous, characterized by the presence of a number of bays and peninsulas. The contribution of agricultural land, forest land, and lakes’ area to overall catchment area equals to ca. 77.5 and 12% (Table 1), respectively.

The EU Water Framework Directive (WFD) includes phytoplankton as one of the four biological elements to be used in the assessment of the ecological status of surface

waters. According to the criteria of water quality in lakes, specified in WFD and then in the National Monitoring Program Guidance, the Wieczno Płd. Lake had a good ecological status of water in 2012. That opinion was based on the small index of Phytoplankton Metric for Polish Lakes (PMPL) (Napiórkowska-Krzebietke et al. 2012), which turned out to be the smallest in the entire Kujawsko-Pomorskie province. A moderate ecological status was estimated for the Chełmżyńskie Lake, mostly because of elevated values of PMPL index and also the diatom index. In both lakes the average annual water transparency was above good level (WIOŚ Report 2012), but as shown in Table 2, the Secchi depth was ca. two times greater in the Chełmżyńskie than in the Wieczno Płd. Lake in 2005–2012. The ecological status of both lakes is of great importance, because they are valuable water bodies for recreation in the region.

Sampling procedure and basic chemical analyses

The surface 10 cm sediment samples were collected in spring 2012 in two lakes (Chełmżyńskie and Wieczno Płd.). At each site (Fig. 1), fifteen primary samples were collected with the Beeker type sampler during two cruises. Sampling sites cover the most of the surface of both lakes. The distance between neighboring sampling points was around 500 m). The samples were mixed, cleaned from biological residues, such as shells or plants, and homogenized.

Using PN-EN ISO 6878: 2006 method, total phosphorus (TP) content was analyzed in: (1) water samples collected at sampling sites, (2) interstitial water (vacuum filtered from the sediment), (3) dry bulk of sediment

Table 2 Concentrations total nitrogen, total phosphorus, conductivity of water and Secchi depth readings in the Chełmżyńskie and Wieczno Płd. Lakes

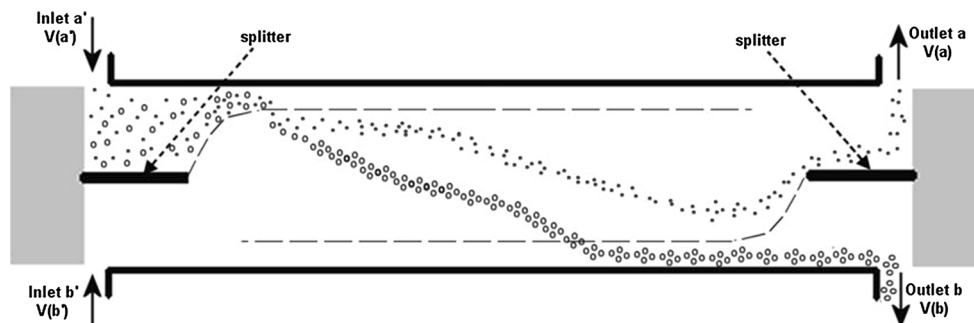
Lake	Year	Secchi depth [m]	Conductivity [$\mu\text{S}/\text{cm}$]	Total nitrogen [mgN/L]	Total phosphorus [mgP/L]
Chełmżyńskie	2012 ^a	2.7	445	1.47	0.083
	2011 ^b	2.1	449	1.78	0.079
	2010 ^b	2.5	445	1.60	0.104
	2009 ^b	2.6	458	1.45	0.100
	2008 ^c	2.4	458	2.09	0.080
Wieczno Płd.	2012 ^a	1.0	478	2.01	0.096
	2005 ^c	1.7	462	1.52	0.039

^a WIOŚ Report (2012)

^b WIOŚ (2013)

^c The formulation ... (2010)

Fig. 2 Cross-section of SPLITT channel and illustration of separation process



samples. pH in the liquid samples was measured using combined glass electrode (pHenomenal, VWR, Germany). Carbon content [total carbon (TC) and inorganic carbon (IC)] was analyzed in sediment samples using carbon analyzer TOC 500 equipped with solid state module (Shimadzu, Japan). Standard titration methods were used to determine calcium, magnesium, and total water hardness.

Fractionation

Classical sieving technique was used to receive three sediment fractions: 0.25–0.5; 0.125–0.25; 0.09–0.125 mm. The amount of fourth fraction, with diameter of 0.03–0.09 mm, constituted less than 0.1 % of total mass of sediment, therefore this size frame was not taken into the consideration. Particles smaller than 30 μm constituted more than 30 % of the total mass and these were fractionated with gravitational split-flow thin channel fractionation technique (SPLITT) using SF1000STD (Postnova Analytics, Landsberg, Germany). The SPLITT technique was developed by Giddings in the early 80's (Giddings, 1985) and has become a semi-preparative sub-technique supplementary to the field-flow fractionation (FFF) family. Separation in SPLITT is based on the same principles as in other FFF methods (Kowalkowski et al. 2006), however, the construction of channel differs. The fractionation channel consists of two inlets and two outlets (Fig. 2). Separation is based on combined action of the laminar flow

of a liquid through the channel and transverse gravitational field applied perpendicularly to this flow.

SPLITT has an ability to separate relatively large quantities of sample (milligrams or even grams of dry particles) in reasonable amount of time. Fractionation can be performed in full-feed depletion mode (FFDSF) (Contado et al. 1997; Kowalkowski 2010). In this mode only one upper inlet a' with suspended sample is used (Fig. 2). In such an operational mode the dilution of sample is avoided. A separation mechanism remains nearly the same as in conventional mode with two inlets (Contado et al. 1997). A strategy to remove particles equal or bigger to specific cutoff diameter (d_c) is usually applied. Cutoff diameter is related to velocity of transport region described by a simple equation:

$$d_c^2 = \frac{18\eta_o}{bLG|\Delta\rho|} V(t) \quad (1)$$

where, $V(t)$ is velocity of transport region, b and L are dimensions of SPLITT channel, G is gravitational constant, $\Delta\rho$ is the difference of density between the particle and the carrier liquid, η is carrier liquid viscosity. $V(t)$ is equal to the difference between velocity in the upper inlet $V(a')$ and lower outlet $V(b)$ multiplied by factor 0.5. In theory, there are infinite numbers of pairs of $V(b)$ and $V(a')$ for given $V(t)$. In practice, however, an appropriate ratio of $V(a')$ to $V(a)$ has to be optimized to obtain an appropriate resolution and throughput of sample in the same time. In case of the lakes studied, optimized flow rates differed as the density

Table 3 Selected values of $V(a')$ and $V(t)$ for fractionation of micrometer particles from sediments collected in the Chełmżyńskie and Wieczno Płd. Lakes

Cut-off [μm]	Chełmżyńskie		Wieczno Płd.	
	$V(a')$ [ml min^{-1}]	$V(t)$ [ml min^{-1}]	$V(a')$ [ml min^{-1}]	$V(t)$ [ml min^{-1}]
10	55.7	41.82	16.6	22.08
5	15.6	10.45	4.41	5.52

Table 4 Particle size distribution of SPLITT fractions

	<5 μm	5–10 μm	10–30 μm
Chełmżyńskie			
d(0.1)	2.2	3.9	7.9
d(0.5)	5.2	8.2	26.7
d(0.9)	7.3	12.1	83.9
Wieczno Płd.			
d(0.1)	1.0	2.8	10.7
d(0.5)	4.0	9.1	34.3
d(0.9)	9.5	14.1	97.2

of both the sediments was not uniform (Table 3), mostly because of difference in sediments' particle density.

With these values, three additional fractions were collected: 10–30 μm , 5–10 μm , and smaller than 5 μm . Particle size distribution of those fractions was checked by light scattering analyzer (Mastersizer 3000, Malvern). The results of these measurement are given in Table 4, where d(0.1), d(0.5), and d(0.9) stand for particle diameter in 10, 50 and 90 % of cumulative volume of particle size distribution chart.

Sequential extraction description

The amount of material collected with sieves (fractions: 0.25–0.5 mm; 0.125–0.25 mm; 0.09–0.125 mm) was large enough to perform the additional measures of chemical P speciation. In order to characterize various P species in lake sediments, a sequential extraction scheme by Psenner et al. (1984), with some modifications by Hupfer et al. (1995), was used in our study. The fractions, which covered also sub-micrometer ones (Table 4), were as follows:

1. $\text{NH}_4\text{Cl-P}$ -labile (desorbed, hydrolyzed) loosely bound or adsorbed phosphorus extractable with water solution of NH_4Cl gives an estimate of readily available P for phytoplankton
2. Fe-P -bound with iron hydroxide surfaces and iron oxides, extractable with water solution of sodium hydrocarbonate and sodium thiosulfate; P bound to Fe-hydroxides and Mn compounds is redox sensitive and it is considered as a potentially mobile pool of P
3. NaOH-P -bound with aluminium and organic matter and extractable with water solution of NaOH; this

Table 5 General characteristics of unfractionated sediments and as well as lake water in the Chełmżyńskie and Wieczno Płd. Lakes

	Chełmżyńskie	Wieczno Płd.
Sediment		
pH	7.17 \pm 0.34	7.92 \pm 0.43
TC [%]	14.77 \pm 2.15	6.79 \pm 0.48
IC [%]	2.15 \pm 0.65	1.38 \pm 0.32
TP [$\mu\text{gP/dm}^3$] in interstitial water	186.6 \pm 2.1	194.3 \pm 3.3
Water		
pH	7.87	7.92
Total hardness [mg/dm^3]	266.4	280.4
Calcium hardness [mg/dm^3]	171	190.7
Magnesium hardness [mg/dm^3]	95.4	89.7
TP [$\mu\text{gP/dm}^3$]	95.32	94.49

- fraction can be released for the growth of phytoplankton when anoxic conditions prevail at the sediment/water interface
4. The HCl-P -bound with calcium and extractable with water solution of HCl; this fraction is sensitive to low pH and it is assumed to mainly consist of apatite P (natural and detritus) including P bound to carbonates and traces of hydrolysable organic P
 5. Res.-P-residual, permanently bound with matrix after complete mineralization.

Phosphorus concentrations were measured in the first four fractions, whereas P content in the fifth, Res.-P fraction was neglected, as the latter was very small and constituted less than 0.001 % (w/w). The relative standard deviations were smaller than 3 %; therefore, they are not included in figures presented. All the analyses were done in three repetitions.

Results

General characteristics of the sediments prior to the fractionation i.e. pH, contribution of total carbon (TC) and inorganic carbon (IC), total phosphorus concentrations (TP) in interstitial water, as well as general characteristic of water i.e. pH, total hardness, calcium and magnesium hardness, and TP content in lakes' water are presented in

Fig. 3 Mass distribution of size fractions in sediment samples from the Chełmżyńskie and Wieczno Płd. Lakes

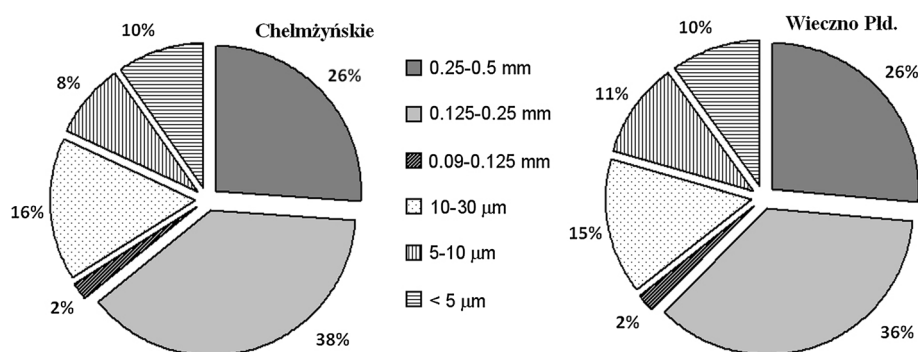


Table 5. Numbers written in bold indicate that the parameters significantly differ between both the lakes (*t* test, $P = 0.05$).

Both, the sediment and the water samples were slightly alkaline. Total carbon (TC) content was considerably higher in the sediment of the Chełmżyńskie Lake. The amount of inorganic carbon (IC) in the Chełmżyńskie Lake constituted ca. 15 % of TC, whereas in the Wieczno Płd. Lake that contribution reached ca. 20 %, but at much smaller overall TC content. Total phosphorus in the interstitial water was significantly higher in the Wieczno Płd. Lake. As to water parameters, significant difference concerns total and calcium hardness (Table 5). The percentage contribution of mass in all six fractions obtained during grain size fractionation is presented in Fig. 3. The pattern is very similar for both lakes, with the exception of slightly higher contribution of 0.125–0.25 mm fraction and slightly lower contribution of 10–30 μm fraction in the Wieczno Płd. Lake. Majority of the material has the diameter above 90 μm (65.3 and 63.2 % for the Chełmżyńskie and the Wieczno Płd., respectively). Smaller, more mobile particles constituted about 45 % of the collected material, with slightly higher contribution (by 2 %) in the Wieczno Płd. Lake.

Phosphorus speciation analysis using Psenner's sequential extraction scheme were initially performed in unfractionated sediment samples (Fig. 4). TP content in the sediment sample from the Chełmżyńskie Lake was higher than from the Wieczno Płd. Lake by about 20 % and it was estimated at 0.84 mgP/g. Distribution pattern of P speciation forms was very similar in both the lakes. Above 25 % of phosphorus was loosely bounded with sediment material (NH₄Cl-P fraction). Majority of phosphorus was bounded with calcium–HCl-P and constituted ca. 50 % of TP. Phosphorus accumulated in this form can be released only under severe acidifying conditions. The rest of P (ca. 35 %) was bounded with iron and aluminum. The largest difference between the P forms in the lakes studied was observed in the case of Fe–P, whose content was twice as high in the Chełmżyńskie Lake (14 %) in comparison with that in the

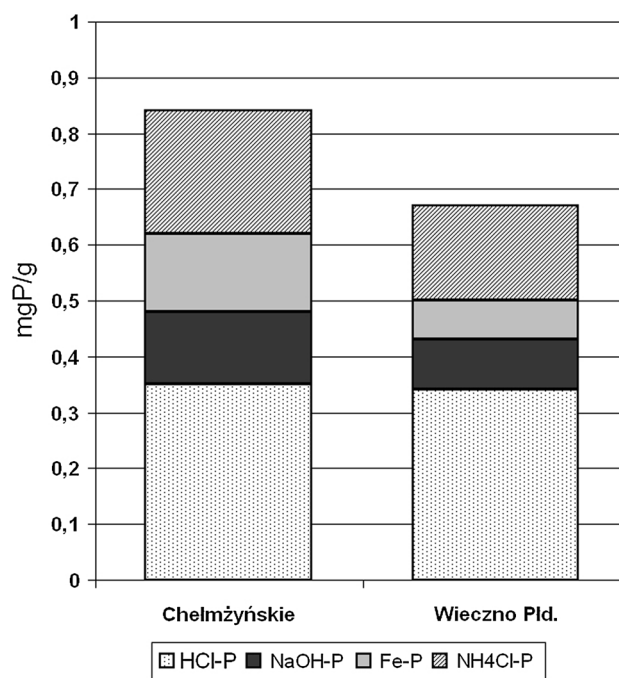


Fig. 4 Phosphorus content in fractions in sediment samples which were not particle size separated—the Chełmżyńskie and Wieczno Płd. Lakes

Wieczno Płd. Lake (7 %). Such a picture of P speciation should lead to similar eutrophication intensity in both the lakes. In reality, the Wieczno Płd. Lake shows symptoms of enhanced eutrophication, with more frequent and extensive algal blooms, the latter confirmed by lower Secchi depth readings as compared with the Chełmżyńskie Lake (WIOŚ Report 2012; Table 2). Investigation of phosphorus content in fractions isolated by sieving and SPLITT fractionation gives the explanation of this fact.

The Psenner extraction conducted in fractions obtained by sieving gave different distribution pattern of phosphorus speciation than in un-fractionated samples (Figs. 4, 5, 6). Analysis revealed that in both fractions (0.25–0.5 and 0.125–0.25 mm) about 45 and 46 % of phosphorus was bounded with aluminium or organic matter (NaOH-P) and

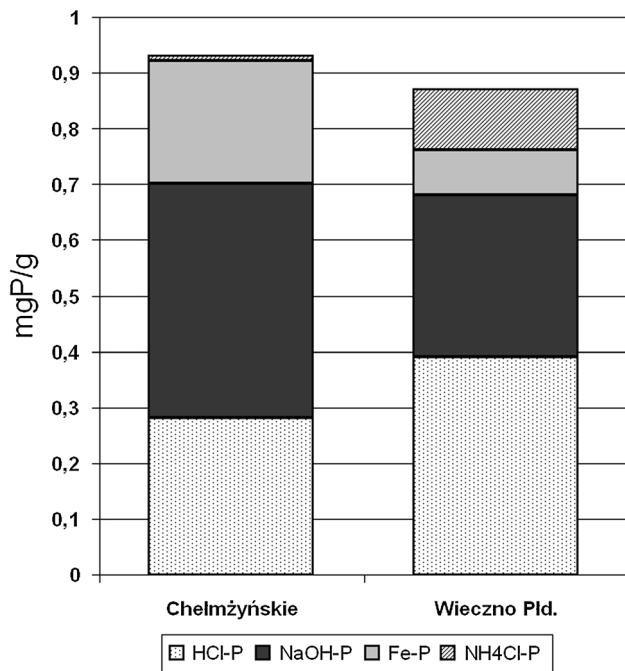


Fig. 5 Phosphorus content in 0.25–0.5 mm P fractions from the Chełmżyńskie and Wieczno Pld. Lakes

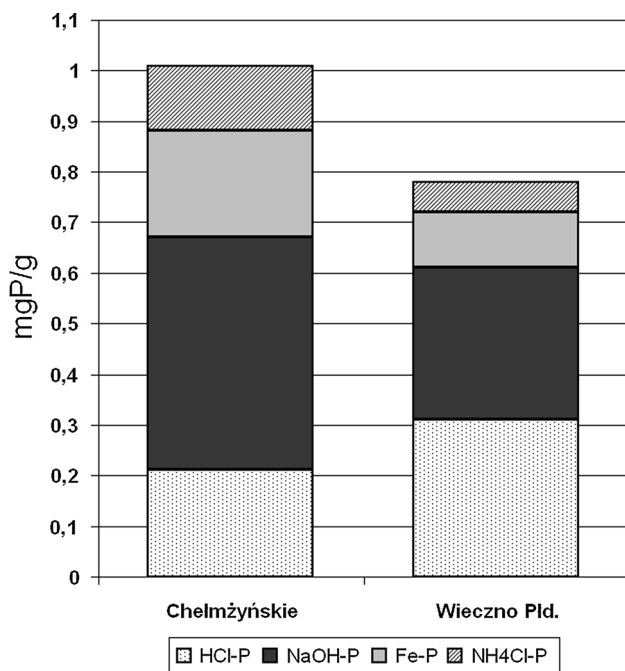


Fig. 6 Phosphorus content in 0.125–0.25 mm P fractions from the Chełmżyńskie and Wieczno Pld. Lakes

this form was predominating in the Chełmżyńskie Lake (Figs. 5, 6). In the Wieczno Pld. Lake, contribution of P bounded with calcium (HCL-P) was either highest (Fig. 5) or comparable (Fig. 6) with NaOH-P fraction (aluminium bounded P) and that amounted to 33 or up to 45 %. These

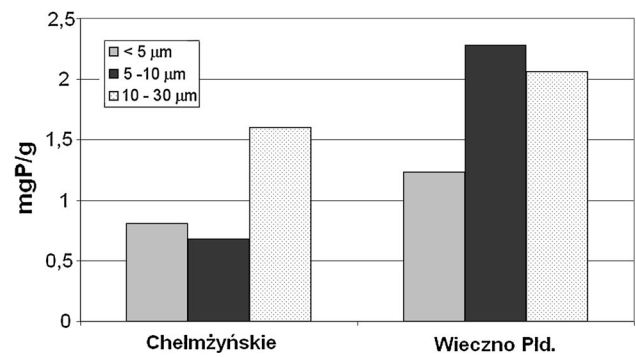


Fig. 7 Total phosphorus content in SPLITT sediment size fractions from the Chełmżyńskie and Wieczno Pld. Lake

pools of P are relatively immobile. The most labile phosphorus fraction (NH₄Cl-P) reached only 1 % in 0.25–0.5 mm fraction in the Chełmżyńskie Lake (Fig. 5) and remained in the range 8–13 % in the Wieczno Lake (Figs. 5, 6). Generally, the content of phosphorus was increasing with the decrease of particle size (Figs. 5, 6). In 0.125–0.25 mm fraction of sediment from the Chełmżyńskie Lake the P total concentration was highest, reaching 1.01 mgP/g.

Generally, a similar trend of TP increase with decreasing particle size is observed in fractions derived by SPLITT system (Fig. 7). However, one should note that total P concentrations in fractions separated by SPLITT were on average by 40 % higher when compared with numbers seen in Figs. 4, 5. The highest TP concentrations, reaching 2.28 mg/g for fraction 5–10 μm, were observed in the case of sediments from the Wieczno Pld. Lake. Unfortunately, mass of fractions was too small to perform SPLITT speciation analysis. It has to be pointed out, that the amount of labile phosphorus (NH₄Cl-P) was considerably higher in non-fractionated material (Fig. 4) than in major fractions (Figs. 5, 6). Such a difference has to be compensated by relatively high share of NH₄Cl-P extractable forms in micrometer size fractions obtained by SPLITT.

Discussion

Increased urbanization and sewage disposal, regulation of wetlands and streams and more intensive farming practices have increased the nutrient loading to many of the lakes world-wide. This has resulted in major changes in the biological structure and dynamics of the lakes and often in a shift from a clear to a turbid state (Sobczyński and Joniak 2013; Schindler 2012; Fisher et al. 2009; Smal et al. 2005). Phosphorus generally enters aquatic ecosystems sorbed to soil particles that are eroded into lakes, streams, and rivers. (Sharpley 2006). The sediment-bound phosphorus includes P associated with soil particles and organic material eroded

during flow events and constitutes 60–90 % of P transported in surface runoff from most cultivated land (Sharpley 2006). Much of P runoff occurs during major erosion-causing storms (Pionke et al. 1997). Potential P pollution of aquatic ecosystems is thus strongly influenced by watershed land use and the concentration of P in watershed soils. Factors that increase erosion or the amount of P in the soil should be considered as strengthening the potential P runoff to downhill aquatic ecosystems (Daniel et al. 1994; Sharpley et al. 1994). As proven by Sobczykński and Joniak (2009a, b), even at negligible impact of diffuse outflow, the shallow lake ecosystem functioning can be substantially disturbed by exclusive long-term impact of point source discharges.

The catchment area of the Chełmżyńskie Lake is by 26 % smaller than that of the Wieczno Płd. Lake, but that smaller watershed is characterized by (1) 1.5 times larger relative contribution of arable land, (2) presence of urban settlements, and industry which are non-existent in catchment of the Wieczno Płd. Lake, (3) 3.5 times lower contribution of forested area as compared with the catchment of Wieczno Płd. Lake, (4) twice as high contribution of TC, and by 1.5 times higher contribution of IC in comparison with values found in the Wieczno Płd. (Table 5). These parameters may be indicative for stronger anthropogenic pressure in the Chełmżyńskie Lake. On the other hand, one should be aware of the fact that potentially more polluted waters draining the catchment of the Chełmżyńskie Lake feed nearly 4 times larger volume of this lake as compared with the volume of the Wieczno Płd. Lake (Table 1). The fact is that the Wieczno Płd. Lake is much more sensitive, as algal blooms are more frequent and extensive, the latter confirmed by low Secchi depth readings (Table 2). So, the reasons of such a situation must be sought out somewhere else, not only in land cover/use, even if these parameters are commonly known as primary driving forces of excessive N and P emission, leading to eutrophication.

Phosphorus release mechanisms in lakes

At a process-oriented level, the P release from sediments represents only one part of the whole lake internal P turnover because particulate P is continuously converted into dissolved P in all lake compartments (Hupfer and Lewandowski 2008). Phosphorus can be released from the sediment depths as low as 20 cm (Søndergaard et al. 2003) but the upper 10–15 cm layer of sediments is actively involved in physicochemical exchange with the water column. Lake sediments can be very different and highly variable regarding chemical composition. Parameters such as dry weight, organic content, and content of iron, aluminum, manganese, calcium and other elements with

capacity to bind and release phosphorus may all influence sediment–water interactions (Søndergaard et al. 1996).

Hupfer and Lewandowski (2008) further prove that (a) P retention of the lake sediment strongly depends on sediment characteristics and land use of the catchment, (b) the presence of redox-insensitive P-binding systems such as $\text{Al}(\text{OH})_3$, irreducible Fe(III) minerals can enhance the P retention and completely prevent P release even in case of anoxic conditions, (c) alternative release mechanisms such as a dissolution of calcium-bound P and decomposition of organic P under both, aerobic and anaerobic conditions are often more important than redox driven by Fe-coupled P cycle, (d) role of bacteria in P cycling is of importance because they affect P cycling not only by altering the redox conditions but also by releasing P during mineralization of organic matter. Studies of Boström et al. (1982) and Jensen and Andersen (1992) show that shallow lakes have often demonstrated phosphorus release to oxic lake water, suggesting that other factors than redox conditions at the sediment–water interface are involved. Søndergaard et al. (2003) emphasize the importance of high sediment surface: water column ratio in shallow lakes, which means that the potential influence on lake water concentrations is stronger than in deeper lakes.

The maximum and the average depths in the Chełmżyńskie Lake equal to 27.1 and 6.1 m, whereas in the Wieczno Płd. they reach 4.1 and 2.2 m (Table 1). Though P concentration in interstitial waters was by ca. $8 \mu\text{gP}/\text{dm}^3$ higher in the Wieczno Płd. Lake, P concentrations in water column did not differ very much in both lakes (Table 4). Very shallow and only by 30 % smaller (by surface) Wieczno Płd. Lake, as compared with the Chełmżyńskie Lake, is characterized by a high sediment surface, water column and by large active bottom. Role of these parameters in supply in epilimnetic waters in shallow lakes has been emphasized by Søndergaard et al. (2003) and Kowalczevska-Madura et al. (2010). Thus, more frequent and intense algal blooms in the Wieczno Płd. Lake in summer and autumn can be explained by the morphology of the lake but also by much higher content of phosphorus in the fractions below $30 \mu\text{m}$ (Fig. 7). These particles in the case of a shallow reservoir can be quite easily resuspended and P released into the water column and in the conditions of strong water mixing may be responsible for the seasonal increase in eutrophication of the reservoir. In deep lakes, the nutrients potentially released from the sediment are accumulated in the often oxygen-poor hypolimnion during summer and thus become difficult to access for primary producers. In contrast, in shallow lakes the well-mixed conditions create an immediate interaction between the sediments and the photic zone's pools of nutrients and primary producers during the whole growth season. In shallow and wind-exposed lakes frequent

resuspension may also result in an overall summer accumulation of organic matter in the lake, as decomposition primarily occurs in the water column. In less wind-exposed lakes, sedimentation is permanent over most of the lake bottom and the sediment content of nutrients is more uniform (Nixdorf and Deneke 1995).

Based on our findings, we are of the opinion that shallowness of the Lake Wiczno Płd. favors water mixing causing resuspension of fine particles, which results in enhanced P internal cycling and thus P availability for primary producers. Much higher content of phosphorus in the fractions below 30 μm in the Wiczno Płd. than the Chełmżyńskie Lake supports our statement.

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