ABSTRACT: Phosphorus is still recognized as the element driving the matter cycling in freshwater ecosystems. It is the key nutrient in productivity and eutrophication process of lakes and reservoirs. The bottom sediments cumulatively formed inside and in-shore of lakes play a crucial role in accumulation/sorption of phosphorus organic compounds, as well as in release/desorption of the compounds available for uptake by producers and microbial heterotrophs. These two opposite processes are dependent on the chemical composition of sediments and on the site conditions (like oxygen, pH) in over-bottom layers.

About three hundred of the sediment surface layer samples were taken from the lacustrine habitats in a variety of lakes typical for postglacial landscape (Masurian Lakeland, Poland): profundal and littoral zones in lakes forming a trophic gradient including a humic lake, river/lake ecotone zone and wetland sites adjacent to lake shoreline. The contents of Ca, Fe, Mg, Mn and Al were analysed as well as the amount of total P (TP) and its three basic groups i.e. easily exchangeable, hardly exchangeable and non-exchangeable fractions.

It was found that the sediments of humic lake had the most different, distinct chemical composition and contained very small amounts of Fe, Mn, Mg and Ca – nearly 30 times less than sediments of other, non-humic lakes. These sediments contained the most of organic matter and similar (as in non-humic lakes) amounts of TP whose dominant part (80%) consists of hardly exchangeable organic fraction.

Sediments of lakes forming the trophic gradient along the small (15 km long) river (Jorka River) showed consistent changes in the chemical composition. Sediments of lakes situated up the river system (meso- and meso-eutrophic lakes) had higher content of organic matter and Ca but lower content of TP, Fe and Mg than sediments of lakes in the lower part of the river system (eutrophic and hypertrophic lakes). The content of these elements was also higher in profundal than in littoral sediments. Significantly higher content (40–70%) of non-exchangeable P was found in sediments of eutrophic and hypertrophic lakes than in sediments of meso- and meso-eutrophic lakes (30–60%) in both the littoral and profundal zones.

Sediments of the river-lake-river ecotones (Krutynia River) showed also the consistent changes of element content along the river flow through the lake. The amount of TP was lower in riverine sediments downstream and upstream the lake than in lake sediments. Organic matter and Fe contents were lower and Ca, Mg, Mn and Al contents were higher in river-lake-river ecotones or similar to those in sediments of the lakes from the trophic gradient. Easily exchangeable phosphorus prevailed in lake sediments; TP in riverine sediments was dominated by hardly exchangeable and non-exchangeable forms and was similar to that found in littoral sediments of lakes from the trophic gradient.
Inshore wetland sediments were characterised by a high content of organic matter – higher than in littoral and profundal sediments of lakes forming the trophic gradient. The content of Ca, Mg, Mn and Fe was two to five times lower than in sediments of lakes from the trophic gradient but similar to sediments of humic lake. They also contained less TP than profundal sediments from the trophic gradient and humic lakes but had similar content to littoral and riverine sediments. Almost all phosphorus accumulated in these sediments is associated with a high organic matter deposition.

The study results concern the basic types of lake and lacustrine habitats representative for the postglacial landscape of north and north-east Europe. A significant diversity of sediment origin, chemical composition and phosphorus amount and its potential mobility was found among the sediment types. The wetland and humic sediments appeared to be active in cumulation and stabilisation of P resources while sediment of non-humic, trophic lakes (especially in profundal zones) are the active sites for P release and sorption processes.

KEY WORDS: chemical composition of sediments, phosphorus, fraction of phosphorus, sediments, littoral, profundal, river/lake ecotone, wetland

1. INTRODUCTION

Phosphorus is considered as a crucial element in the functioning and cycling of matter in lake ecosystems (Søndergaard et al. 2001, 2003). Phosphorus present in organic and mineral compounds is still a subject of studies as an element limiting fertility and production of aquatic habitats and thus responsible for eutrophication – the most nuisance process of aquatic environment pollution (Withers and Jarvis 2008).

Phosphorus delivered to a lake undergoes there many complex processes. It is directly incorporated into the trophic chain in a form of soluble compounds (phosphates, low molecular organic compounds) via “microbial loop” and in the primary production of plants (Wetzel 2001). On the other hand, it is removed from cycling due to sedimentation of dead organic (detritus, faeces, tripton) and inorganic (co-precipitates with calcium carbonate and iron hydroxides) particles deposited in lacustrine bottom sediments (Kleeb erg and Schubert 2000, Eckert et al. 2003). This leads to more or less permanent accumulation of phosphorus in sediments in amounts (per 1 m² of lake surface area) much larger than those contained in lake water (Boström et al. 1982).

Returning of mineral phosphorus to cycling is a fundamental process for aquatic ecosystems. Bottom sediments play a crucial role in this process by both binding phosphorus and releasing it to above-bottom waters. The process depends on many properties of the surface sediment layers including:

- chemical – redox potential, pH, the content of iron, calcium, manganese, aluminum and others;
- physical – gradient of P ions at the water/sediment interphase, temperature, resuspension;
- biological – activity of heterotrophic microorganisms, the intensity of organic matter decomposition and mixing by organisms (bioturbation);
- geochemical – the process of diagenesis (a physico-chemical process leading to consolidation of primary loose deposited material) and epigenesis (secondary changes taking place in hardened material and consisting in changes of its structure, mineral composition etc.).
- Phosphorus accumulated in bottom sediments is present in organic and inorganic forms. The latter are often bound to iron, aluminum, manganese, calcium or silt materials (Boström et al. 1982, 1988, Golterman 2004).

Total content of phosphorus in mid-lake and near-shore sediments usually ranges from 0.09 to 0.28% of dry weight and varies depending on environmental factors listed above. This variability depends also on phosphorus fraction i.e. on the type of chemical compound of sediment P (Psener et al. 1991, Golterman 2004).

Stability of Fe- and Mn-bound inorganic forms of phosphorus depend on redox potential and are considered particularly prone to the release. Therefore, they exert an important effect on the so-called internal loading or internal
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The supply of available (for direct uptake by organisms) phosphorus to lake water (Søndergaard et al. 1993, Andersen and Ring 1999, Rydin 2000). Organic forms of phosphorus are considered more resistant to decomposition, less mobile and hence able to build more or less stable fraction in bottom sediments (Böström et al. 1985, Rydin 2000).

The methods of sequential extraction with appropriate reagents are used to determine phosphorus fractions in bottom sediments. These methods are aimed at assessing a potential ability of sediments to release available phosphorus which may help in predicting its variability in lake water (Psenner et al. 1984, Böstrom et al. 1985, Lijklema 1993, Kaiserli et al. 2002, Golterman 2004, Pardo et al. 2004). Only a sum of two or three fractions may be dealt with as a measure of available (easily released) phosphorus resources (Böström et al. 1988, Psenner et al. 1984).

The aim of this paper is to recognise the variability of the content, type and percentage share of P fractions in various river-lake habitats – in profundal, littoral and ecotone (land/water and river/lake) sites. The study involved lakes in a trophic gradient including a humic lake (with enhanced input of humic substances from the catchment) and wetland sites formed at the lake shoreline or surrounding river when it flows in or out of a lake. Collected material represents differentiated pool of sediments associated with lake ecosystems formed under variable conditions of post-glacial landscape now used for agriculture and forestry. The material has different origin, water content, grain size structure of primary substratum (plant material or mid-lake deposits) and chemical composition (organic components versus mineral compounds). Factors of different intensity (oxygenation of overlying waters, temperature) acted upon sediments in situ.
2. STUDY AREA AND SITES

The study was carried out in north-eastern Poland (53°24′–54°22′N, 19°38′–23°31′E) in habitats representing basic types of sediments of lake ecosystems in Masurian Lakeland (north-east Poland). Materials originated from two typical river-lake systems of the Jorka and Krutynia rivers each flowing through several lakes. The study involved also an isolated mid-forest humic lake (Lake Flosek) surrounded by Sphagnum bog – another typical component of lakeland landscape (Fig. 1).

From the Jorka River system (total length 15 km) materials were collected in 4 lakes – from the largest and situated upmost the river course Lake Majcz to the smallest and situated downstream Lake Zełwążek (Table 1). Studied lakes differ in depth, the size and land use of the catchment. Lake Majcz has a forested catchment, lower situated lakes are surrounded by agricultural lands. Analysed lakes markedly differ in the trophic type (chlorophyll a concentration, Secchi disc visibility and total P concentration in summer) from mesotrophic Lake Majcz through meso-eutrophic Lake Głębokie and eutrophic Lake Zełwążek to hypertrophic Lake Jorzec (Table 2). Studied lakes formed a natural trophic gradient of lake ecosystems.

Sediments from profundal and littoral zones of lakes in the Jorka River system were collected in summer of the years 1999–2001. In each of the studied lakes sediments were collected from two sites; in the littoral from a depth of 1.5–2.5 m and from the deepest sites in the profundal (mesotrophic lake – 16 m, meso-eutrophic lake – 34 m, eutrophic lake – 7 m, hypertrophic lake – 11 m) (Fig. 1).

Lake Flosek is situated in the buffer zone of the Masurian Landscape Park. It is a shallow, isolated lake of an area of 4 ha devoid of typical littoral (Table 1). This humic lake close to oligo-mesotrophy has a peatland-forest catchment basin (coniferous forest, Sphagnum bog) (Table 1). Sediments from this lake (called in limnology a dy type) were collected in summer 1993 from 2 sites – from the littoral zone (a depth of 1.5–2.0 m) and from the deepest place (7 m) in the profundal zone.

Sediments were also collected from two lakes situated in the upper part of the Krutynia River system. Lake Kujno is one of the smallest and shallow lakes crossed by the river. It is a eutrophic lake of an agricultural-forest catchment (Table 1). Lake Gant is one of the deepest lakes of the system, a meso-eutrophic lake situated in forested catchment basin (Table 1). Sediments from two transitional river-lake-river zones of these lakes were collected in 5 sites: 1) in the river 100 m above the river inlet to a lake, 2) at the river inlet to a lake, 3) in the lacustrine part above the river outlet from a lake, 4) at the river outlet from a lake, and 5) in the river 100 m downstream from the outlet. Sediments so collected produced natural series formed by the river of directionally decreasing water flow. Sediment cores from these lakes were collected in summer 1992.

Material from inshore wetland habitats was collected at the shores of Lake Majcz and

Table 1. Characteristics of studied lakes and their catchment basins (from various sources).

<table>
<thead>
<tr>
<th>Morphometric data</th>
<th>Jorka river catchment</th>
<th>Krutynia river catchment</th>
<th>Lake without outflow</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>53°45′–53°53′N and 21°25′–21°33′E</td>
<td>53°36′–53°57′N and 21°04′–21°35′E</td>
<td>53°44′N and 21°25′E</td>
</tr>
<tr>
<td>Area (ha)</td>
<td>174</td>
<td>46</td>
<td>12</td>
</tr>
<tr>
<td>Depth max. (m)</td>
<td>16.4</td>
<td>34.3</td>
<td>7.4</td>
</tr>
<tr>
<td>Depth mean (m)</td>
<td>6.0</td>
<td>11.8</td>
<td>3.7</td>
</tr>
<tr>
<td>Shoreline (m)</td>
<td>7850</td>
<td>4100</td>
<td>1810</td>
</tr>
<tr>
<td>Total catchment (km²)</td>
<td>17.07</td>
<td>12.17</td>
<td>76</td>
</tr>
<tr>
<td>Land use</td>
<td>forest</td>
<td>agricultural</td>
<td>agricultural</td>
</tr>
</tbody>
</table>

(1) Hillbricht-Ilkowska (2002); (2) Hillbricht-Ilkowska and Wiśniewski (1996); (3) Hillbricht-Ilkowska et al. (1998)
Lake Jorzec typically covered by belt-shaped plant communities (nitrophilous vegetation, alder woods, sedges and reed) and agricultural use (meadows or arable fields) of nearby grounds (Fig. 2). The site at Lake Jorzec (28–30 m wide) is covered by 20–30 years old alder wood with belt-shaped Circaeo-Alnetum vegetation 10 to 12 m wide and Carici acutiformis-Alnetum (8–20 m wide) with moss, sedges and reed in the herb layer. The site at Lake Majcz (23 m wide) is overgrown by Urtica dioica (5 m), by young alder wood Carici acutiformis-Alnetum (13–18 m) and Carice-tum acutiformis (4–5 m) with sedges, reed and Nupharo-Nymphaeetum from the lake side (Kloss and Wilpisze wska 2002). Peat forms an upper soil layer in both sites (Rzep ecki 2002).

Sediments from inshore wetland habitats adjoining lakes Majcz and Jorzec were collected in summer of the years 1999 and 2000. Sediments were collected in each habitat from one site in a zone directly contacting lake waters (Fig. 2).

3. METHODS

3.1. Field study

Intact sediment cores 15–20 cm thick together with overlying water (c. 1 L) were taken with plexiglass tubes (diameter c. 10 cm and surface area of 52 cm²) using modified Kajak’s sampler. Three to four cores further used for chemical analyses and phosphorus fractionation were taken from every site. In total, 238 sediment cores were taken from lakes and other lacustrine habitats. Water and organic matter content and concentrations of Fe, Mn, Ca, Mg, Al, total phosphorus (TP) and its fractions were determined in the lab.

3.2. Laboratory study

3.2.1. Analyses of basic components | of sediments

Water content in a 5 cm sediment layer was determined by comparison of fresh weight and that after drying at 105°C for 24 hours (APHA 1971). Organic matter content (OM) in sediments was determined as the loss on ignition at 450°C for 4 hours (after regeneration of carbonates) of a sample previously dried at 105°C for 24 hours (APHA 1971).

Percent content of Ca, Mg, Fe, Al, and Mn in bottom sediments and in sediments from wetland habitats was determined by the flame AAS in material dried, homogenised and subjected to a mild digestion in 3M HCl (Parker 1972, Bengtsson and Persson 1978). Total phosphorus in sediments was determined spectrophotometrically with the molybdenum blue method after preliminary mineralization acc. to Golterman and Clymo (1978). Basic components of sediments were analysed in three repetitions.
3.2.2. Analysis of phosphorus fractions in sediments

The method of sequential chemical fractionation elaborated by Psenner et al. (1991) was used to determine which forms of phosphorus take part in P transformations in sediments. Phosphorus fractions were analysed in the top 5 cm layer of intact sediment cores. Fractions were analysed in three repetitions by taking c. 50 cm³ of sediment from each of the three cores and separating it for 15 minutes in a MPW 25050 centrifuge at 1700 g. Half a gram of centrifuged material was used to determine particular P fractions.

The method of direct chemical fractionation allows distinguishing three basic groups of P fractions differently prone to release from the total pool of the element:

1. easily exchangeable phosphorus involves three fractions. The first is a fraction extracted with 1M NHCl (pH = 7) (NHCl-RP). It contains loosely bound phosphorus also known as labile phosphorus. It is most easily available part of sediment P which may be used directly by plants and microorganisms. The second is a fraction extracted with 0.5 M sodium dithionate (NaSSO solution buffered by NaHCO) (BD-RP). It contains phosphorus associated mainly with metal (e.g., Fe, Mn) hydroxides. In the natural environment phosphorus from this fraction is released from sediments to water under conditions of reduced oxygen concentrations. The fraction of phosphorus extracted by 1M NaOH (NaOH-RP) represents the element adsorbed by metal (Fe, Al) oxides. In the natural environment this fraction is easily available to plants and microorganisms.

2. hardly exchangeable phosphorus contains two fractions determined after preliminary mineralization. The fraction extracted with 0.5 M sodium dithionate (NaSSO solution buffered with NaHCO) (BD-NRP) contains organic P whose stability depends on redox conditions. The fraction extracted with 1M NaOH (NaOH-NRP) contains phosphorus associated with microorganisms (together with polyphosphates) and part of organic P associated with detritus and humic substances. It may be released in the effect of microbial activity.

3. non-exchangeable phosphorus contains two fractions. That extracted with 0.5M HCl (HCl-P) is associated mainly with carbonates and includes P from apatite and P released during total dissolution of metal oxides. This fraction may be mobilised from sediments only after rapid changes of pH. The last fraction contains non-exchangeable, residual P together with part of organic phosphorus (P-res.). Its content is calculated from the difference between total P and the sum of reactive phosphorus fractions (RP) mentioned above. It is assumed that phosphorus contained in this fraction can not be mobilised or re-cycled in the effect of physical, chemical or biological processes taking place in lacustrine habitats.

4. Dissolved reactive phosphorus (DRP) in each of analysed fractions was determined spectrophotometrically with the molybdenum blue method after filtering the extract through glass fibre filter Whatman GF/F (Golterman and Clymo 1978).

STATISTICA software package v. 6 (StatSoft, Inc. 2003) was used to statistical assessment of the obtained results. Statistical tests (Student t-test, ANOVA) for the significance of differences between means for analysed datasets were calculated at P <0.05.

4. RESULTS

4.1. Chemical composition of bottom sediments of studied lakes and lacustrine habitats

Mean content of chemical components in four groups of sediments showed consistent and significant differences between lakes and habitats in the trophic gradient of lakes and in the set of river-lake-river sediments (Figs 3–10).

Water content of an upper 5 cm sediment layer in studied groups of lakes ranged from 50 to 97% fresh weight (Fig. 3). The highest water content was found in bottom sediments
of the type dy from both littoral and profundal zone of humic lake. Other sediments contained from 40 to 90% of water. More water (70–83%) was found in profundal sediments of lakes from the trophic gradient, in inshore wetland sediments and in sediments from river-lake system (40–90%) than in littoral sediments (20–70%) (Fig. 3).

Organic matter content varied between 10 and 83% of dry weight of sediments (Fig. 4). The highest content of organic matter (c. 80%) was characteristic for dy sediments in humic lake and inshore sediments of wetland habitats. Much less organic matter was found in profundal sediments of lakes across the trophic gradient (25–31%) and in sediments

Fig. 3. Water content (% of fresh weight) in four groups of sediments (A–D) from various lakes and habitats (Data for humic lake and the lakes along the Krutynia River after Wiśniewski and Rzepecki 1996, Rzepecki 1997).

Fig. 4. Organic matter content (% dry wt.) in four groups of sediments (A–D) from various lakes and habitats (Data for humic lake and for the lakes along the Krutynia River after Wiśniewski and Rzepecki 1996, Rzepecki 1997).
of the lake-river system of the Krutynia River (11–23%). Littoral sediments of lakes in the trophic gradient showed smaller content of organic matter (<20%) than profundal sediments (>25%) where it significantly decreased from meso- (45%) to hypertrophic (25%) lake (Fig. 4).

Fig. 5. Calcium content (% dry wt.) in four groups of sediments (A–D) from various lakes and habitats (Data for humic lake and the lakes of the Krutynia River system after Wiśniewski and Rzepecki 1996, Rzepecki 1997).

Fig. 6. Iron content (% dry wt.) in four groups of sediments (A–D) from various lakes and habitats (Data for humic lake and the lakes of the Krutynia River system after Wiśniewski and Rzepecki 1996, Rzepecki 1997).
Calcium content in dry matter of sediments ranged from 1 to 30% (Fig. 5). The lowest content of Ca was found in dy sediments of humic lake (c. 5%), in inshore wetland habitats (c. 3%) and in sediments from the outlet river sections of both lakes in the Krutynia River system (c. 2%). Several times higher content of calcium was noted in both littoral and profundal sediments of lakes from the trophic gradient (8–29%) and in sediments from two lakes of the Krutynia system (10–30%) apart from those in the river outlet zones (Fig. 5). In the littoral and profundal of mesotrophic lake calcium content was the highest (up to 29%), decreased in meso-eutrophic lake (9.5 and 19%, respectively) and in eutrophic lake (8 and 11%) and increased again in hypertrophic lake to 19% in littoral sediments and to 26% in profundal sediments. Calcium content in lake-river system of the Krutynia River was smallest in riverine sediments upstream the lakes (c. 2%) and increased in subsequent sites to achieve maximum in sediments from the river outlet from a lake (25–30%) (Fig. 5). Iron content in studied sediments ranged from 0.1 to 2.7% of dry weight (Fig. 6). The lowest content (c. 0.2%) was found in littoral and profundal sediments of humic lake, the highest (up to 2.7%) – in profundal sediments of lakes in the Jorka River system (Fig. 6). In the latter lakes profundal sediments contained more Fe than littoral sediments and the sediments from hypertrophic lakes showed significantly higher Fe contents as compared with lakes of lower trophic status (2.2–2.7 vs 0.1–1%). Higher content of iron was also found in wetland sediments of inshore lake zones (c. 1%) and lower (<0.5%) in sediments of the river-lake and lake-river zones of the Krutynia River (with the exception of in-lake site where Fe content in sediments reached 1.1%) (Fig. 6).

Magnesium content varied from 0.06 to 0.46% of dry sediment weight. The lowest Mg content was found in humic lake and in the Krutynia riverine sediments at the inlet and outlet from lakes (0.1–0.25%). The highest contents (0.2–0.46%) were recorded in sediments from lakes of the Jorka River system. As in the case of Ca and Fe content, slightly (but significantly – \( P < 0.05 \)) higher magnesium content was found in littoral than in profundal sediments of lakes in the trophic gradient and the highest content in sediments from hypertrophic lake compared with lakes of lower trophic status (Fig. 7). In wetland inshore sediments magnesium content was equal to c. 0.2% dry weight i.e. much less than

![Fig. 7. Magnesium content (% dry wt.) in four groups of sediments (A–D) from various lakes and habitats (Data for humic lake and the lakes of the Krutynia River system after Wiśniewski and Rzepecki 1996, Rzepecki 1997).](image-url)
in lake sediments. In the river-lake zones magnesium content varied in a way similar to that of iron. The lowest content of Mg (c. 0.1%) was found in riverine sediments up- and downstream lakes and higher in the lacustrine part of transitory zones in both lakes of the Krutynia River system (Fig. 7).

Manganese content in sediments of the four groups of lakes showed the variability very similar to that of Mg, Fe and Ca. It ranged from 0.1 × 10⁻³ to more than 1.6 × 10⁻³% of dry weight (Fig. 8). The lowest content of Mn was noted in sediments of humic lake (0.4–0.6 × 10⁻³%) and in wetland inshore sediments (<0.4 × 10⁻³%); the highest – in profundal sediments of lakes from the trophic gradient. In river-lake zones the lowest Al content was noted in riverine sediments downstream the lakes (c. 0.05%) and the highest – upstream the lakes and in sediments of the lacustrine part of transitory zones (c. 0.1–0.15%) (Fig. 9).

4.2. The content of total phosphorus in various types of sediments

The content of total phosphorus in the upper 5 cm sediment layer of studied lakes and habitats differed significantly between particular habitats (littoral, profundal) and between lakes of different trophic status (Fig. 10).

Sediments of humic lake contained from 0.8 to 1.1 mg TP g⁻¹ dry wt. in profundal and littoral sediments, respectively. The content of total P in profundal sediments was similar to that found in non-humic lakes though lower than in lakes situated downstream the Jorka River (Fig. 10).
Mean TP content in littoral sediments of lakes in the trophic gradient was lower than in profundal sediments and significantly increased with trophic status of lakes – in the littoral from 0.1 to 0.9 mg TP g⁻¹ dry wt. and in the profundal from 1.0 to 1.7 mg TP g⁻¹ dry wt. (Fig. 10). Mean TP content in bottom sediments was as a rule lower in meso- and meso-eutrophic lakes than in eutrophic and hypertrophic lakes (0.1–0.6 and 0.7–1.7 mg TP g⁻¹, respectively). The highest content of sediment TP was found in hypertrophic lake situated

![Graph A. Lakes of the trophic gradient along the Jorka River](image1)

![Graph B. Humic lake](image2)

![Graph C. Inshore wetland habitats](image3)

![Graph D. River-lake-river zones of the Krutynia River system](image4)

Fig. 9. Aluminum content (% dry wt.) in three groups of sediments (A–D) from various lakes and habitats (Data for humic lake and the lakes of the Krutynia River system after Wiśniewski and Rzepecki 1996, Rzepecki 1997) Note: no data for group C – inshore wetland habitats.

![Graph A. Lakes of the trophic gradient along the Jorka River](image5)

![Graph B. Humic lake](image6)

![Graph C. Inshore wetland habitats](image7)

![Graph D. River-lake-river zones of the Krutynia River system](image8)

Fig. 10. Total phosphorus content (mg g⁻¹ dry wt.) in four groups of sediments (A–D) from various lakes and habitats (Data for lakes of the Krutynia River system after Wiśniewski and Rzepecki 1996, those for humic lake – after Rzepecki 1997).
downstream the Jorka River both in the littoral (0.9 mg TP g⁻¹ dry wt.) and in the profundal (c. 1.7 mg TP g⁻¹ dry wt.) (Fig. 10). Mean TP content in sediments of inshore wetland habitat was similar to that in littoral sediments of the Jorka lakes and ranged from 0.9 to 1.0 mg TP g⁻¹ dry wt. (Fig. 10).

The range of TP contents in sediments of the river-lake-river system (0.6–1.3 mg TP g⁻¹) was similar to that in littoral sediments of lakes from the trophic gradient (Fig. 10). TP in riverine sediments above and below the lakes was lowest (c. 0.7 mg TP g⁻¹) and increased to achieve maximum in lacustrine part of the transitory zone (c. 1.3 mg TP g⁻¹). TP content in bottom sediments of lakes from this system was similar to that in lakes of the trophic gradient along the Jorka River (Fig. 10).

4.3. The content of phosphorus fractions in various types of sediments

Percent content of the groups of P fractions differed between lakes, habitats (littoral-profundal) and between sediments of lakes from the trophic gradient and sediments of the river-lake-river system (Figs 11–14).

Sediments of humic lake showed a high content of non-exchangeable and hardly exchangeable P, whose main fraction was organic (BD-NRP, NaOH-NRP) and residual (P-resid.) phosphorus. These fractions contributed in 80% to total P in littoral sediments but only in 40% in profundal sediments. Phosphorus associated with carbonates and apatite P (HCl-P) assigned to non-exchangeable forms had 1–3% share in the TP pool. Reverse situation was noted in profundal sediments of this lake where the easily exchangeable form prevailed (up to 60%). The main component in this group was the fraction adsorbed on metal oxides (NaOH-RP). Other fractions of easily exchangeable phosphorus contributed much less to the total P content. Phosphorus released from sediments under reduced conditions (BD-RP) constituted up to 10% and labile P (NHCl-P) – up to 9% of TP (Fig. 11).

Lacustrine sediments of the trophic gradient along the Jorka River, both littoral and profundal, showed directional changes in the content of particular P fractions (Fig. 12).

Non-exchangeable P (30–71%) and hardly exchangeable P (20–57%) dominated phosphorus pool in both littoral and profundal sediments of these lakes. Significantly higher content (40–70%) of non-exchangeable P was found in sediments of eutrophic and hypertrophic lakes than in sediments of meso- and meso-eutrophic lakes (30–60%). This regularity was true for both littoral and profundal sediments. Non-exchangeable phosphorus fraction associated with carbonates and apatite-P (HCl-P) showed a large variability and was higher in littoral sediments (12–30%) than in profundal sediments (5–13%) of most of the lakes (Fig. 12).

Opposite changes were noted in the content of hardly exchangeable phosphorus in sediments of lakes from the Jorka River trophic gradient. More phosphorus of this fraction was found in sediments of meso- and meso-eutrophic lakes (40–60%) than in eutrophic and hypertrophic lakes (20–40%) in both the littoral and profundal. The group of
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hardly exchangeable phosphorus was dominated by organic P and humic P (NaOH-NRP). Its content ranged from 12 to 43% of total P in all studied habitats of lakes along the Jorka River. The second fraction from this group was redox-dependent organic P fraction (BD-NRP) whose contribution varied from 4 to 15% of the total P in littoral and profundal sediments (Fig. 12).

The share of easily exchangeable P in lacustrine sediments of the Jorka River system varied from 9 to 23% in both littoral and profundal sediments. It did not, however, show directional changes along the trophic gradient (Fig. 12). A large variability of P fraction absorbed by metal oxides (NaOH-RP) and that released under reduced conditions (BD-RP) (2–12% and 3–14%, respectively) was found in the easily exchangeable group of P fractions. The share of BD-RP fraction was higher only in meso-eutrophic and hypertrophic lakes (14 and 12%, respectively) and the share of NaOH-RP fraction was significantly higher in profundal sediments of hypertrophic lake (12%) than in other lakes (4–8%).

Loosely bound phosphorus (NHCl-P) was the smallest of the easily exchangeable P fractions. Its share varied from 0.4 to 3% of the total P in littoral and profundal sediments (Fig. 12).

Inshore wetland sediments in habitats adjoining lakes were dominated (30–50%) by hardly exchangeable forms of phosphorus whose main part was composed (in 10–30%) of organic and humic P fractions (NaOH-NRP), and by non-exchangeable phosphorus composed mainly (30–70%) of residual P. The sum of these two fractions was equal to c. 90%. The share of exchangeable phosphorus was small ranging from 5 to 12% and its basic form was NaOH-RP fraction (3–7%) (Fig. 13).

The share of particular P fractions in sediments of the river-lake-river system differed between particular sites (Fig. 14). The dominating phosphorus form in sediments within transitory zones, in the river up- and downstream the lakes and in the river outlet from lakes was non-exchangeable phosphorus which, together with hardly exchangeable P, constituted 57 to 92% of TP in sediments. Phosphorus associated with carbonates and
apatite P (HCl-RP) in particular sites of transitory zones made up to 27% of TP in both lakes. Easily exchangeable P dominated (in 70%) in lacustrine sediments at the river outlet from lakes. Its main parts were the fraction released under anoxic conditions (BD-RP) and phosphorus associated with metal oxides (NaOH-RP) (up to 35%). The smallest part of easily exchangeable phosphorus was the fraction of loosely bound P (NHCl-P). In riverine sediments its share was c. 1% but at the river inlet to and outlet from the lake and in lacustrine sediments it increased to 5% (Fig. 14).

5. DISCUSSION

The groups of sediments distinguished in this paper showed a set of consistent features indicating some regularities though the latter are separate and characteristic for each of the studied habitats.

Most distinct composition had the sediments of humic lake (in limnology named “dy” sediments) which contained very small amounts of Fe, Mn, Mg and Ca – nearly 30 times less than sediments of other, non-humic lakes (Boström 1984, Young and Harvey 1992, Hörnström et al. 1993). These sediments contained the most of organic matter and similar (as in lakes of the trophic gradient) amounts of TP whose dominant part (80%) was hardly exchangeable organic fraction. In such lakes the organic P fraction is
mainly composed of humic substances delivered from surrounding catchment basin often covered by coniferous forests. Phosphorus in these substances is usually bound indirectly with metals (e.g. Fe$^{3+}$) combined in humic complexes (Díaz-Espejo et al. 1999). This is a characteristic feature of such lakes commonly found among boreal lakes (Bostrom 1984, Pettersson and Olsson 1986).

Sediments of harmonic, non-humic lakes (type gttja like those from the Jorka River system) had different chemical composition. First of all they showed higher TP content markedly increasing in profundal sediments from mesotrophic to hypertrophic lake. Sediments of these lakes had typically high, though variable, content of Fe, Mn, Ca, Mg and organic matter. Changes in sediment TP content from meso- and meso-eutrophic lakes (situated in the upper part of the system) to hypertrophic lake (situated downstream the river course) were accompanied by changes in the content of elements mentioned above. Sediments of lakes situated up the river system had higher content of organic matter and Ca but lower content of TP, Fe and Mg than sediments of lakes in the lower part of the river system. The content of these elements was also higher in profundal than in littoral sediments.

Lower contents of Ca and Fe in littoral compared with profundal sediments of lakes in the trophic gradient are worth noticing since this finding is opposite to results reported by other authors (Williams et al. 1976, Koschel et al. 1983, Kairesalo and Matilainen 1994). They explain higher Ca content in littoral sediments by precipitation of CaCO$_3$ at high pH due to intensive photosynthesis of macrophytes, and particularly of stoneworts.

Fig. 14. The content of fractions and functional groups of phosphorus compounds (% of total P) in sediments of the river-lake-river system of the Krutyenia River (Data for lakes after Wiśniewski and Rzepecki 1996).
(Characeae) (Crawford 1977, Blindow 1992). The reason for lower content of these elements in studies of lakes may be in morphometric features of these lakes. The lakes are small but nevertheless morphologically diverse – lake shores are strongly inclined and hence profundal zone is much deeper than the littoral. Such shape of lake bottom enforces sediments focusing in the deeper, profundal zone (Håkansson and Jansson 1983 after Górnia 1996, Håkansson 1994). Poorly developed littoral zone in relation to the whole lake basin (20–40%) differentiates the lakes presented in this paper from those studied by other authors, which is probably the reason for larger accumulation of Ca, Fe and organic matter in profundal sediments.

The content of phosphorus fractions also differed between littoral and profundal sediments. Kairesalo and Matilainen (1994) reported higher content of P fractions associated with Ca in littoral than in profundal sediments. Andersen and Ring (1999) estimated Ca-bound phosphorus fraction at 26% in littoral sediments and at 18% in profundal sediments. The same fraction estimated in this study was similar and varied between 4 and 30%. In most of the lakes significantly higher content of this fraction was found in littoral than in profundal sediments. This may be explained by adsorption and co-precipitation of phosphorus with calcium carbonate which forms in the period of intensive photosynthesis (Koschel et al. 1983). Nürnberg (1988) was of the opinion that in lakes of relatively high Ca concentration in water (> 11 mg L^-1) P binding predominates over P release. The process is important since at anaerobic conditions (when Fe-bound phosphorus is released to water from sediments) Ca may additionally retain phosphorus in sediments (Brunberg et al. 2002, Kufel and Kufel 2002). Moreover, many studies indicate that such combination of P with Ca belong to a hardly exchangeable P fraction (Williams and Mayer 1972, Pettersson and Istvánovics 1988).

The content of easily exchangeable P fraction was significantly lower in littoral than in profundal sediments of lakes along the trophic gradient (except for meso-eutrophic lake). This finding may be explained by a lack of significant impact of littoral vegetation or a lack of rooted macrophytes that could aerate upper sediment layer and hence increase the amount of phosphorus bound to metal (Fe, Mn) hydroxides (Christensen and Andersen 1996, Andersen and Ring 1999).

Sediments of the river-lake-river system showed directional changes in the content of particular elements. Lacustrine sediments were richest in analysed elements than riverine sediments down and upstream the lakes. Organic matter and Fe contents were lower and Ca, Mg, Mn and Al contents were higher or similar to those in sediments of the lakes along the trophic gradient. The content of total phosphorus in sediments of the system was similar to that found in littoral sediments of the Jorka lakes. The former showed, however, lower contents of TP, and its hardly exchangeable and non-exchangeable fractions in riverine sections than in lacustrine sites.

Easily exchangeable phosphorus prevailed in lacustrine sediments; TP in riverine sediments was dominated by hardly exchangeable and non-exchangeable forms. Such a pattern in river-lake-river habitats is determined mainly by surrounding area and by water velocity which result in the increased share of mineral forms (medium and coarse-grained products of soil erosion) in riverine sections and the increased accumulation of organic matter in lacustrine sediments (Wiśniewski and Rzepecki 1996).

Inshore wetland sediments behaved differently from typical lake sediments. They were characterised by a high content of organic matter – higher than in littoral and profundal sediments of lakes along the trophic gradient. The content of Ca, Mg, Mn and Fe was from two to five times lower there than in sediments of lakes along the trophic gradient but similar to that in sediments of humic lake. They also contained less TP than profundal sediments of the gyttja and dy type but had similar content to littoral and riverine sediments. As in the case of profundal and riverine sediments, non-exchangeable and hardly exchangeable P fractions dominated TP content in wetland inshore sediments. Almost all phosphorus accumulated in these sediments is associated with a high organic matter deposition (Reddy and D’Angelo 1994, Carlyle and Hill 2001). Higher
temperatures prevailing there in the summer period enhance the production of bacteria and swamp/aquatic vegetation and thus increase the content of phosphorus in organic matter. This is the reason of the increased pool of organic phosphorus potentially susceptible to release (Watts 2000a, b, Khoshsanesh et al. 2002).

6. CONCLUSIONS

The composition of sediments and their potential role in the cycling of phosphorus – the basic element in aquatic ecosystems – were evaluated in the study for different lacustrine habitats of lakes created by glacier 13 million years ago. Therefore the results are representative for various lake habitats from north and north-eastern Europe.

The main source of variability of analyzed parameters of sediments and their role in the ecosystem processes remains the origin and conditions of sediments formation due to their location inside and close to the lake.

The pattern of these parameters in sediments suggests that high release of phosphorus should take place in habitats with high share of easily exchangeable phosphorus but the most important mechanism of phosphorus binding is depended on Fe and Mn content and in turn – on oxygenic conditions in sediment and in the water over. The lacustrine sediments at the river outlet from lake and profundal sediments of lakes of the trophic gradient belong to this type of habitats.

Habitats in which non-exchangeable phosphorus dominated should be the sites of strongest accumulation. The inshore wetland sediments and sediments of humic lake belong to this type.

The study results will be compared (Rzepecki, in preparation) with the apparent rates of release/adsorption P processes in the study lakes evaluated in experimental research (Rzepecki 1997, 2002).

ACKNOWLEDGEMENTS: I am very grateful to professor Anna Hillbricht-Ilkowska for her help during the work and many valuable suggestions and comments. I thank Ms Krystyna E. Gromadka for excellent technical assistance.

7. REFERENCES


The dynamics of phosphorus in lacustrine sediments


Received after revision April 2010