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SEDIMENT PHOSPHORUS FORMS AND THEIR ROLE IN LAKE ECOSYSTEMS

SETTEFOSFORI VORMID NING NENDE MÕJU JÄRVEDE ÖKOSÜSTEEMIDELE

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LIST OF ORIGINAL PUBLICATIONS

The present thesis is based on the following papers, which are referred to by Roman numerals in the text. The papers are reproduced by kind permission of the publishers, Springer Science and Business Media (I, III, IV) and Wiley-VCH Verlag (II).

I Nõges, P. & A. Kisand (1999). Horizontal distribution of sediment phosphorus in shallow eutrophic Lake Võrtsjärv (Estonia). Hydrobiologia 409: 167 - 174.

II Nõges, P. & A. Kisand (1999). Forms and mobility of sediment phosphorus in shallow eutrophic Lake Võrtsjärv (Estonia). International Review of Hydrobiology, 84(3): 255 - 270.

III Kisand, A. (2005). Distribution of sediment phosphorus fractions in hypertrophic strongly stratified Lake Verevi. Hydrobiologia 547: 33 - 39.

IV Kisand, A. & P. Nõges (2003). Sediment phosphorus release in phytoplankton dominated versus macrophyte dominated shallow lakes: importance of oxygen conditions. Hydrobiologia 506: 129 - 133.

ABBREVIATIONS

NaOH-RP (H-L):	sodium hydroxide extractable reactive phosphorus fraction according to the method of Hieltjes & Lijklema (1980)
NaOH-RP (Ps):	sodium hydroxide extractable reactive phosphorus fraction according to a modification of the method of Psenner et al. (1988)
BD-RP:	bicarbonate-dithionite extractable phosphorus fraction according to a modification of the method of Psenner et al. (1988)
LOI:	loss on ignition
NRP:	non-reactive phosphorus fraction
P:	phosphorus
Res-P:	residual phosphorus
RP:	reactive phosphorus
SRP:	soluble reactive phosphorus
TP:	total phosphorus
DW:	dry weight
WW:	wet weight
ΣFR:	the sum of measured P fractions

INTRODUCTION

Phosphorus availability is regarded one of the most important factors in determining the water quality of lakes. Numerous studies have shown that a high load of phosphorus leads to high phytoplankton biomass, and therefore to turbid water and often to undesired biological changes (Søndergaard et al., 2003). It is generally acknowledged that phosphorus is often the limiting nutrient in determining algal growth in lakes (Schippers et al., 2006). During the past century the increasing phosphorus load from both agricultural and urban areas has induced rapid eutrophication in a huge number of lakes all over the world, and phosphorus has become one of the most studied elements in aquatic ecosystems.

Sediments are an important part of the lake ecosystem. They not only reflect past and present chemical, physical and biological conditions in the water body but also influence those conditions via nutrient recycling between the sediment and the water. The sediment contains much higher concentrations of phosphorus than the water column of the lake. The return of phosphorus from sediments can considerably affect the lake ecosystem. Knowledge of the mechanisms responsible for P cycling between the sediment and the water column facilitates understanding of the way in which a lake's trophic status is formed and changed and may even indicate ways in which these processes can be controlled.

Phosphorus is present in various chemical forms in lake sediments. These forms differ in their sensitivity to factors causing phosphorus release. One way in which they can be distinguished is by sequential chemical fractionation of sediments and quantification of the phosphorus in the fractions.

The present dissertation is based on studies of phosphorus forms in the sediments of four Estonian lakes. Attention is focused on the sediments of the largest inland Estonian lake, Lake Võrtsjärv, in respect of the distribution of different chemical forms of phosphorus (papers **I, II**). Release of phosphorus from these different forms was studied in the laboratory using sediments from two shallow lakes, Lake Kaiavere and Lake Prossa (paper **IV**). The distribution of sediment phosphorus fractions in stratified lakes was studied and its role discussed using the example of the strongly stratified hypertrophic Lake Verevi (paper **III**).

1. REVIEW OF THE LITERATURE

1.1. Phosphorus accumulation in lake sediments

In many catchments, P loads that originate from human activities exceed natural loading by several orders of magnitude (Schippers et al., 2006). Two major artificial sources of P can be distinguished: (1) point sources and (2) diffuse losses from various agricultural activities. The phosphorus load caused by intensive agriculture is known to have potentially large negative effects on the water quality of lakes. However, owing to the buffering capacity of soils and lake ecosystems, especially the accumulation of the P load in lake sediments, such effects may appear long after intensive agriculture has started. Schippers et al. (2006) concluded that the buffering capacity of lake water was negligible, whereas buffering in the lake sediment postponed the final equilibration of the lake phosphorus for several decades.

Phosphorus can be bound to sediment via sedimentation of particles, biological uptake by sediment biota, physical adsorption, and chemosorption. Phosphorus enters lake ecosystems in particulate or dissolved form. Particulate P can be deposited directly on the sediment whereas dissolved phosphate can be incorporated in the organic material of primary producers and bacteria, eventually sinking to the bottom. Co-precipitation with calcium carbonate or adsorption by iron hydroxides can also cause sedimentation (Gonsiorczyk et al., 1998; Søndergaard et al., 2001). P undergoes numerous chemical and biological transformations in the deposited sediments. Some of it will be permanently buried in the sediment while some may be released and returned to the water column.

In sediments, P can be found in both particulate and dissolved forms. In the upper few centimetres of the sediment the water content may exceed 95% of the wet weight. The amount of P dissolved in the water phase of the sediment, "pore water", is small, often less than 1% of the total P in the sediment. Nevertheless, the phosphorus concentration in the pore water is usually substantially higher than that in the lake water.

1.2. Phosphorus release from sediments

Transport of phosphorus from sediments (except by resuspension) takes place from the comparatively small pool of phosphorus dissolved in the sediment pore water. The size of this pool is regulated by equilibria with particulate phosphorus (Søndergaard et al., 2003). For phosphorus release, two fundamentally different processes must take place. First, the phosphorus must be mobilized from particulate to dissolved form by the action of physical, chemical and biological reactions (desorption, dissolution, ligand exchange mechanisms and enzymatic hydrolysis) and the dissolved P must be transported into the lake. Owing to the concentration gradient between the sediment pore water and the lake water, phosphorus can diffuse from the former to the latter. Factors causing mechanical disturbance of the sediment such as resuspension by wave action, emission of gas bubbles, burrowing by sediment invertebrates, bottom-feeding of fish etc. enable the pore water and lake water to be mixed more intensively, enhancing P release from the sediment (Søndergaard et al., 2003). P may also be transported from the sediment to the lake water in other ways. For example, some phytoplankton species are able to incorporate and store phosphorus in their cells during their resting stages at the bottom of the lake. Thereafter, when they move up to the water column at the beginning of the vegetation period, they take the phosphorus with them (Pettersson et al., 1993).

Phosphorus release is probably controlled by different mechanisms in a eutrophic stratified lake with an anaerobic hypolimnion and a large shallow nonstratified eutrophic lake. The classical model of Mortimer (1941) describes P release from anaerobic sediments due to the reduction of sedimentary ferric iron Fe(III) to ferrous iron Fe(II), leading to the dissolution of both iron and phosphorus adsorbed to iron hydroxides. Shallow lakes are usually well mixed and oxidized throughout the water column. Nonetheless, shallow lake sediments have often been shown to release phosphorus to oxic lake water (Jensen & Andersen, 1992), suggesting that factors other than redox conditions at sediment–water interfaces are involved. The importance of sediment–water interactions is further enhanced in shallow lakes by the high sediment surface:water column volume ratio, which means that the potential influence on lake water concentrations is stronger than in deeper lakes. Direct contact with the photic zone throughout the year and a regular mixing regime guarantee stable and near-optimal conditions for primary production (Nixdorf & Deneke, 1995). The phosphorus pool in the sediment is often more than 100 times greater than that in the lake water, and lake water concentrations are therefore highly dependent on sediment–water interactions (Sondergaard et al., 2003).

At steady state, phosphorus release from the lake sediment is compensated by phosphorus flux from the water column into the sediment. In all oligotrophic lakes and in many eutrophic waters, the net flux of phosphorus on a yearly basis is towards the sediment (Håkanson & Jansson, 1983). In periods when the flux in this direction is reduced or environmental conditions in the sediment change, net P release from sediments can occur, a phenomenon commonly termed *internal loading*.

In order to reverse eutrophication in lakes, much effort has been devoted to reducing the external phosphorus loading. Some lakes respond rapidly to such reductions (Sas, 1989), but phosphorus release from the sediment into the lake water may be so intense and persistent that it prevents any improvement of water quality for a considerable period after loading is reduced (Granéli, 1999). Often lake recovery is delayed by more than 10 years (Marsden, 1989, Jeppesen et al., 2005). Jeppesen et al. (2007) found in a multi-lake comparison that after nutrient loading of shallow lakes was reduced, a new state of equilibrium for phosphorus was typically reached after 10-15 years.

1.3. Phosphorus fractionation

Phosphorus fractions in soils and sediments are characterized by their differential solubility in various chemical extractants. The first attempts to develop a practical analytical technique for separating P compounds in sediments emerged on the basis of the sequential extraction technique developed by Chang & Jackson (1957).The Chang & Jackson procedure yielded the following fractions according to the solvent used in each step: labile P (NH_4Cl), Al-bound P (NH_4F), Fe-bound P (NaOH), Ca-bound P (HCl), reductant-soluble P (CDB) and refractory P (NaOH).Williams and his coworkers identified disadvantages in the Chang and Jackson procedure such as extraction of iron-bound P along with aluminium-bound P using ammonium fluoride, and phosphate resorption due to the formation of calcium difluoride especially in calcium-rich sediments. They suggested several modifications for sediment P fractionation (Williams et al., 1971), leading to fewer fractions: non-apatite P, apatite P and organic P. In addition, dithionite-citrate reagent was found to be ineffective for separating Ca-P from Fe-P because citrate is a strong Ca chelator (Hieltjes & Lijklema, 1980). In more recently developed fractionation schemes for sediments, redox-sensitive P forms such as occluded and reductant-soluble P are no longer distinguished from other forms of inorganic P (Hieltjes & Lijklema, 1980; van Eck, 1982). Psenner et al. (1988) included reductant-soluble P in their fractionation scheme, using extraction by sodium dithionite. Uhlmann et al. (1990) combined the fractionation scheme of Psenner et al. (1988) with hot water extraction in order to determine the portion of polyphosphates among organically bound phosphates.

Phosphorus that is removed during the first one or two steps of a sequential fractionation procedure is usually considered readily available (Gunatilaka, 1988; Psenner et al., 1988). Depending on the strength of the extracting solution and the fractionation method, readily available P has been estimated from such extracts as: 1 M NH_4C1 (Hieltjes & Lijklema, 1980; van Eck, 1982), 0.1 M NaOH (Wildung et al., 1977; Hieltjes & Lijklema, 1980; Ostrofsky, 1987), citrate-bicarbonate-dithionite (Williams et al., 1971) and nitrolotriacetic acid (NTA) (Golterman et al., 1969; Gunatilaka et al., 1988). Ca-bound P (HCl-P) such as apatite was found to be unavailable (Pettersson, 1986; Gunatilaka, 1988), while redox-sensitive Fe-bound P (NaOH-P) may become available under anaerobic conditions (Wildung et al., 1977; Furumai & Ohgaki, 1982; Hosomi et al., 1981). Results obtained from existing fractionation schemes are recognized as analytical estimates of the different forms of P.

An appropriate P fractionation method may provide a way of quantifying reactive and non-reactive P fractions in sediments. Chemical characterization of sediment P in eutrophic lakes provides information about the distribution of various P forms and their potential mobility and bioavailability under prevailing redox potential (Eh) and pH conditions. Lake systems dominated by Fe-bound P, for example, are predicted to release P under anaerobic conditions (Wildung et al., 1977; Hosomi et al., 1981). On the other hand, P solubility in lake systems dominated by Ca-bound P is sensitive to changes in pH. Quantification of reactive and

non-reactive P in lake sediments could therefore be useful for predicting P responses to physico-chemical changes and for understanding internal P cycling (Olila et al., 1995).

A characteristic common to many fractionation methods is that they cannot unambiguously and precisely determine which forms of P are extracted. Thus, the individual P fractions are only defined via the extraction process (i.e. the methods used) and the media with which the sediment sample has been treated. Nevertheless, the extraction methods often yield reproducible results that allow the sediment's phosphorus forms to be described and uniformly interpreted and the dominant binding compounds in a given sediment to be identified (Pettersson et al., 1988). Knowledge of the mechanisms of release of certain phosphorus fractions has led to the development of effective methods for immobilizing phosphorus in sediments (Koschel et al., 2006, Lewandowski et al., 2003; Reitzel et al., 2006; Rydin & Welch, 1998; Schauser et al., 2004; Wauer et al., 2005a; Wauer et al., 2005b). In lake restoration projects, these can be used to reduce phosphorus leakage from such sediments and thus improve the trophic state of the lake.

1.4. Studies of phosphorus fractions in Estonian lake sediments

Studies on phosphorus in sediments were limited to measurements of total phosphorus until the 1990s. Accumulation or release of phosphorus from sediments was discussed on the basis of phosphorus balance calculations (e.g. Loigu & Marksoo, 1982; Nõges et al., 1998; Nõges & Järvet, 1998).

Different forms of phosphorus have been studied in Estonian lake sediments for the past 15 years. The first study revealing more detail about the composition of phosphorus forms in Estonian lakes concerned the sediment in the hypertrophic and polluted Lake Harku (Heinsalu, 1994). Since then, forms of sediment phosphorus have been studied in Estonian lakes from both ecological (Ott et al., 2006a, 2006c) and paleolimnological viewpoints (Kruusement & Punning, 2000), and also in the context of assessment projects to determine possible ways in which polluted lakes in recreationally important population areas might be restored (Ott, 2006b; Ott & Kisand, 2002).

Table 1 summarizes the available data on the P contents and fractional compositions in surface layers of Estonian lake sediments.

Table 1. Total P and P fractions (μg P g^{-1} DW) in the surface sediments of Estonian lakes.

Lake	NH_4Cl-RP	BD-RP	NaOH-RP (Ps)	NaOH-RP (H-L)	NaOH-NRP	HCl-RP	ΣFR	TP	Sediment layer (cm)	Reference
Ruusmäe	1100			1500	2300	300	5200	5200	0-1	Kruusement & Punning, 2000
Köstrejärv	165	317	1840		638	266	3230	4600	0-2	Ott, 2006b
Arbi	323			3100	682	251	4356	4460	0-2	Kisand, unpublished
Harku	116			340	655	621	1732	2340	0-2	Heinsalu, 1994
Martiska	1			369	1141	96	1607	2554	0-2	Kisand, unpublished
Neitsijärv	30			462	698	364	1554	1681	0-5	Galuzo, 2000
Viljandi	140	128	187		268	546	1269		0-2	Ott et al., 2006
Endla	59	365	176		506	78	1184	2200	0-2	Ott, 2006a
Ahnejärv	4			308	752	100	1164	1941	0-2	Kisand, unpublished
Verevi	94			210	401	282	987		0-2	Kisand, 2005
Peipsi	61	168	38		372	230	869		0-1	Kisand, unpublished
Saadjärv	143	140	84		400	93	859	1000	0-2	Ott, 2007
Kuradijärv	8			190	484	95	777	1357	0-2	Kisand, unpublished
Prossa	37	75	61		328	206	737		0-1	Kisand & Nõges, 2003
Liivjärv	29			319	309	55	712	1067	0-2	Kisand, unpublished
Võrtsjärv	31			113	401	157	702	1010	0-2	Kisand & Nõges, 1999
Kaiavere	163	64	80		315	77	699		0-1	Kisand & Nõges, 2003

2. AIMS OF THE STUDY

In the present thesis, the role of fractions of sediment phosphorus was studied in two different types of eutrophic lake ecosystems. The first type represents large shallow non-stratified lakes with frequent sediment resuspension. The second type represents deeper stratified lakes with the formation of an anoxic hypolimnion. The following questions were explored and discussed:

1. What are the main factors determining the distribution of sediment P forms in a large shallow lake? What is the variability of sediment P forms? (**I, II**)

2. What is the potential for P release from sediments in a strongly stratified hypertrophic lake? (**III**)

In addition, the pool of potentially mobile P in sediments from two shallow eutrophic lakes was investigated in a laboratory experiment. The aim was to assess the predictive value of the sediment P fractions for the capacity of sediments to retain or release phosphorus. The following questions were addressed:

3. How do redox conditions influence P release from sediments? Do P fractions have the same release patterns irrespective of the origin of the sediment? According to the hypothesis, the portion of potentially mobile P is determined by the relative amounts of different P fractions in the sediment, and single P fractions originating from two different sediments have the same release pattern under the same redox conditions (aerobic vs. anaerobic). (**IV**)

3. MATERIALS AND METHODS

3.1. Description of the study sites

I present the results of sediment studies on four eutrophic Estonian lakes that differ in size, depth and stratification type.

1. Lake Võrtsjärv (I-II)
The eutrophic Lake Võrtsjärv is located in central Estonia. Its surface area is 270 km^2, its mean depth 2.8 m and its maximum depth 6 m. The lake is exposed to the predominant westerly and south-westerly winds, which owing to its large area cause intense resuspension of sediments (Nõges et al., 1999).
2. Lake Verevi (III)
The hypertrophic Lake Verevi is situated in southern Estonia. Its surface area is 12.6 ha, its mean depth 3.6 m and its maximum depth 11 m. The lake is strongly stratified. In early and warm springs, the stratification may be formed so rapidly that the spring turnover is absent (Ott et al., 2005).
3. Lakes Prossa and Kaiavere (IV)
Both Lake Kaiavere and Lake Prossa are eutrophic, shallow and non-stratifying. Lake Prossa has surface area 33 ha, mean depth 2.2 m and maximum depth 4.2 m. The bottom is largely covered by macrophytes. Lake Kaiavere is a shallow plankton-dominated lake with surface area 250 ha, mean depth 2.8 m and maximum depth 5 m.

3.2. Sampling

The sediment samples were collected using a Willner corer. The sediment cores obtained were horizontally sliced into 1-5 cm thick layers; the closer to the sediment surface, the thinner the slices were. To investigate the horizontal distribution of sediment P forms in Võrtsjärv (**I**), 13 sampling sites were chosen to represent different sediment types all over the lake area (Fig. 1). Samples to study vertical distribution of sediment P forms (**II**) were obtained from sampling site No. 13 (Fig. 1). In Lake Verevi (**III**), samples were collected from the eastern part of the lake's deepest bottom area at a depth of 6-8 m in March and June 2001. In 1994 and August 2001, samples were collected close to the deepest point of the lake at the water depth of 9 m. Parallel cores were collected within the distance of 20 m. In Lake Prossa and Lake Kaiavere (**IV**) one sediment core was collected from the deepest bottom areas of the lakes. Samples for measuring SRP in the interstitial water (**II**) were collected in five occasions from June to December 1997.

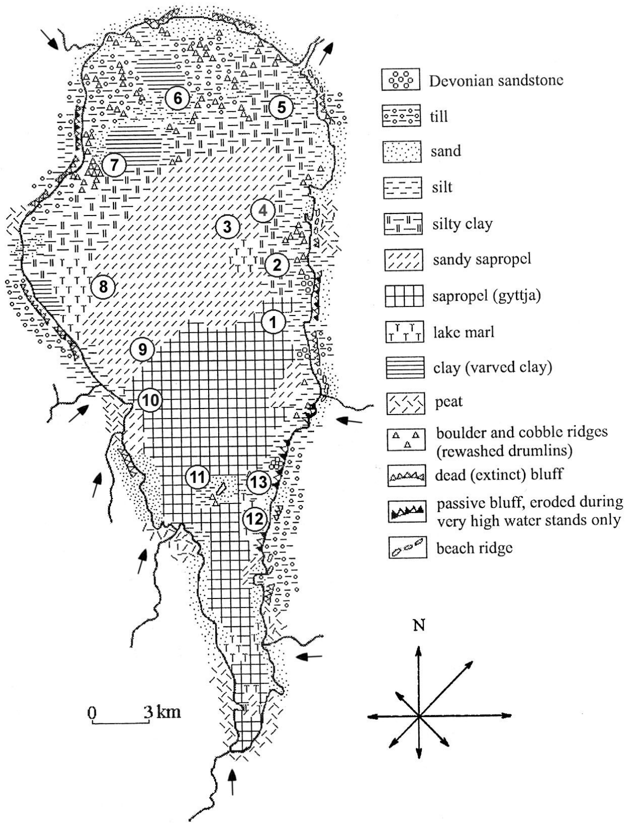

Figure 1. Sediment types (Raukas & Tavast, 2002) and sampling stations in Lake Võrtsjärv. The wind rose is average for the ice-free period (April-October) 1995-1997.

3.3. Laboratory analyses

3.3.1. Phosphorus fractionation

In all studies included in the present thesis, P fractions were analysed in lake sediment samples. The fractionation methods were based on sequential extraction of the wet (raw, untreated) lake sediment. Each solvent dissolves certain compounds together with the phosphorus bound to them. The phosphorus concentrations in each extract ("phosphorus fractions", "phosphorus forms") were determined spectrophotometrically according to Murphy & Riley (1962).

The phosphorus fractionation method of Hieltjes & Lijklema (1980) was used in studies **I-III** (Fig. 2, A) and a modification of the extraction method of Psenner et al. (1988) in studies **III-IV** (Fig. 2, B). The scheme of Hieltjes & Lijklema yielded following fractions, characterized by extraction media:

NH_4Cl-RP	(RP = reactive phosphorus), often termed labile (desorbed, hydrolyzed), loosely bound or adsorbed P. It gives an estimate of the immediately available P. NH_4Cl dissolves small amounts of iron-and aluminium-bound P and affects the solubility of calcium-bound P (Psenner et al., 1988).
NaOH-RP(H-L)	represents the phosphates adsorbed to metal (Fe, Al) oxides and other surfaces, exchangeable against OH^-, and P compounds soluble in bases.
NaOH-NRP	(NRP = non rective phosphorus) is calculated as the difference between total P in the NaOH extract, measured by peroxosulphate digestion, and NaOH-RP. It is assumed to represent the major part of organic and humic P, and also inorganic intracellular polyphosphates of microorganisms (Hupfer et al., 2004).
HCl-RP	represents P bound to carbonates, apatite-P and P released by the dissolution of oxides (not adsorbed to the surface).

An advantage of the scheme of Psenner et al. is the separation of Fe-bound from Al-bound phosphorus by an additional extraction step using the reducing solvent BD (sodium bicarbonate and sodium dithionite). The modification of the original scheme involved the use of 0.1 M NaOH instead of the original 1.0 M NaOH for better comparability with the scheme of Hieltjes & Lijklema. This modification has been used previously by others (e.g. Rydin, 2000). Instead of NaOH-RP(H-L) the scheme of Psenner et al. yielded two fractions:

BD-RP	P bound to redox-sensitive metals (Fe, Mn).
NaOH-RP (Ps)	P adsorbed to Al oxides and other surfaces, exchangeable against OH^-.

3.3.2. Phosphorus release experiment

In the laboratory release experiment (**IV**), 400 mg of wet sediment was enclosed in dialysis bags, which were placed alternatively in oxic or anoxic water. The sediment P fractions were determined by the modified Psenner et al. (1988) method before and after an incubation period of 6 weeks. The steep phosphorus concentration gradient between the inside and outside of the dialysis bags was maintained by replacing the water around the bags once a week. The changes in sediment P fractions were compared between the two different lake sediments and the two different treatments.

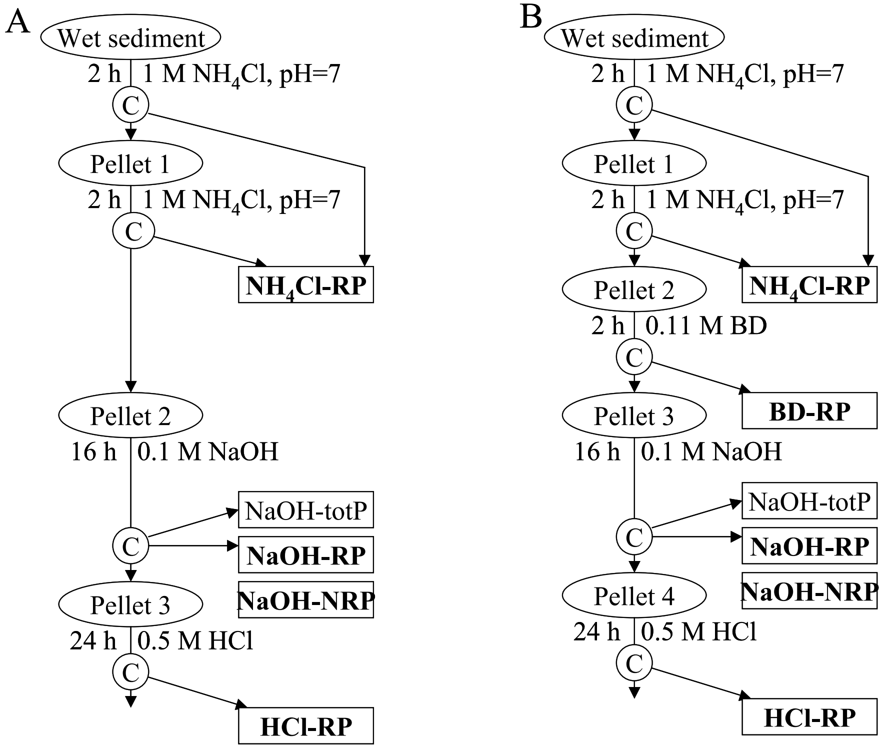

Figure 2. The sequential extraction schemes used in the present studies. A: fractionation scheme according to Hjeltjes & Lijklema (1980); B: the scheme according to Psenner et al. (1988) with the modified NaOH concentration (1 M in the original scheme).

3.3.3. Other sediment analyses

In studies **II, III** the total phosphorus, iron and manganese contents were also determined in the sediment samples. Total phosphorus was measured spectrophotometrically (Murphy & Riley, 1962) after acid digestion of the dried sediment according to Ahlgren & Ahlgren (1976). The iron and manganese contents were measured by atomic adsorption spectroscopy after acid digestion of the dry matter (Ahlgren & Ahlgren, 1976). The dry matter content was determined by drying the wet sediment at 105 °C for 24 h. As a measure of organic content, the loss on ignition (LOI) was calculated from the weight difference before and after heating the dried sediment at 550 °C for 2 h. Further burning of the organic-free sediment at 850 °C for 4 h resulted in weight loss attributable to the emission of carbon dioxide from carbonates. The carbonate content was calculated as the percentage of calcium carbonate per unit weight of dry matter.

To transform concentrations expressed per unit weight of sediment into concentrations per sediment volume or per unit area of lake bottom, the bulk (or wet) densities of the sediments were calculated according to Håkanson & Jansson (1983).

$$\rho = 260/(100+1.6(W+IG^0))$$

where IG^0 = the loss on ignition expressed in percent of total wet weight
W = water content expressed in percent of total wet weight.

In order to measure SRP in the interstitial water (**II**), samplers coated with dialyses membrane tubing (SPECTRA/POR 4) were incubated one week in intact sediment cores. Including replicates (2-3) pore-water analyses were made in 13 cores.

4. RESULTS

4.1. Distribution of sediment phosphorus fractions in a large shallow lake (I - II)

The physical and chemical compositions of the sediment from the large shallow Lake Võrtsjärv proved highly variable. The soft sapropelic sediment in the central and southern lake bottom areas was characterised by a high water content in the raw sediment and a high percentage of organic matter in the dry matter. The dry matter content of the sediment varied from 5% in muddy areas to 60% in the northern sandy-bottom areas (Fig. 3 A). Differences in wind exposure explained 87% of the variability in the DW% (**I**). In contrast to the distribution of DW%, LOI was lowest in the sandy-bottom areas and highest in the lake mud, constituting 1-37% of the sediment dry weight (Fig. 3 B).

The sum of measured P fractions (ΣFR) in the sapropelic samples was about twice that in sandy sediments (Fig. 4 A). However, the opposite picture was obtained when the concentration of phosphorus was expressed per unit lake bottom area or sediment volume. In this case, the sandy and clayey sediment with higher density (i.e. low water and organic matter contents) had considerably more phosphorus per unit volume than the soft organic-rich mud (Fig. 4 B).

There were strong correlations between the general sediment characteristics and the different P fractions. Sediment dry matter content was the most important characteristic, accounting for more than 2/3 of the variability in LOI, bulk density of sediment and all P fractions (Study **I**, Table 3). This variable showed a strong negative correlation with the NH_4Cl-RP, NaOH-RP and NaOH-RP fractions expressed on a dry weight basis; a strong positive correlation was found with the HCl-RP fraction on a volumetric basis (Study **I**, Table 3). The correlation between DW% and ΣFR was negative when the latter was expressed per DW and positive when ΣFR was expressed per sediment volume (Study **I**, Table 3).

The three fractions NH_4Cl-RP, NaOH-RP and NaOH-NRP were positively interrelated, with correlation coefficients ranging from 0.66 to 0.87 ($p<0.001$) HCl-RP correlated negatively with the other fractions on a dry weight basis (r from –0.53 to –0.62, $p<0.001$) and significantly positively with NaOH-RP on a volumetric basis ($r=0.65$, ($p<0.001$).

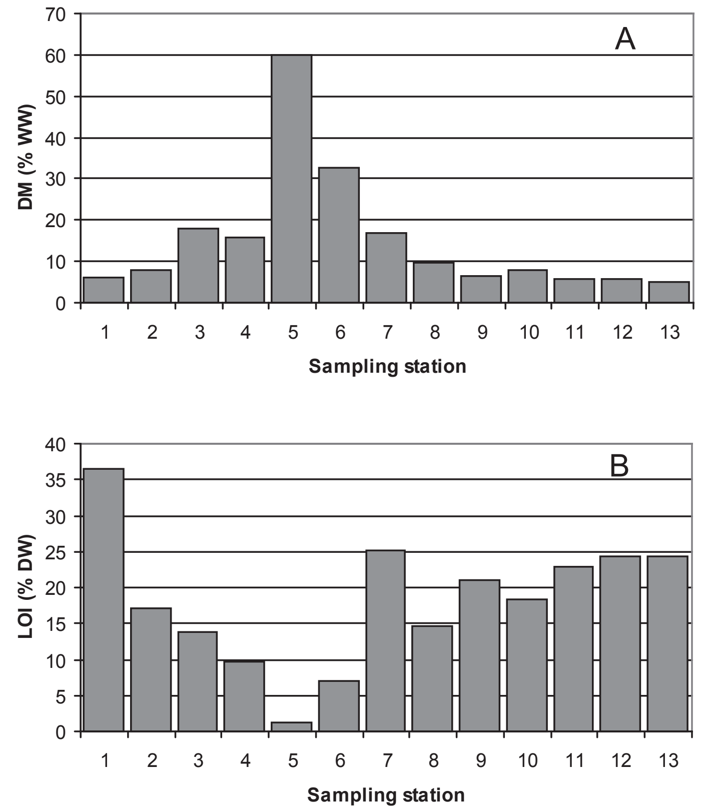

Figure 3. Sediment characteristics in Lake Võrtsjärv. A: Dry weight as percentage of wet weight; B: loss on ignition as percentage of dry weight. Sampling stations are numbered according to Fig. 1.

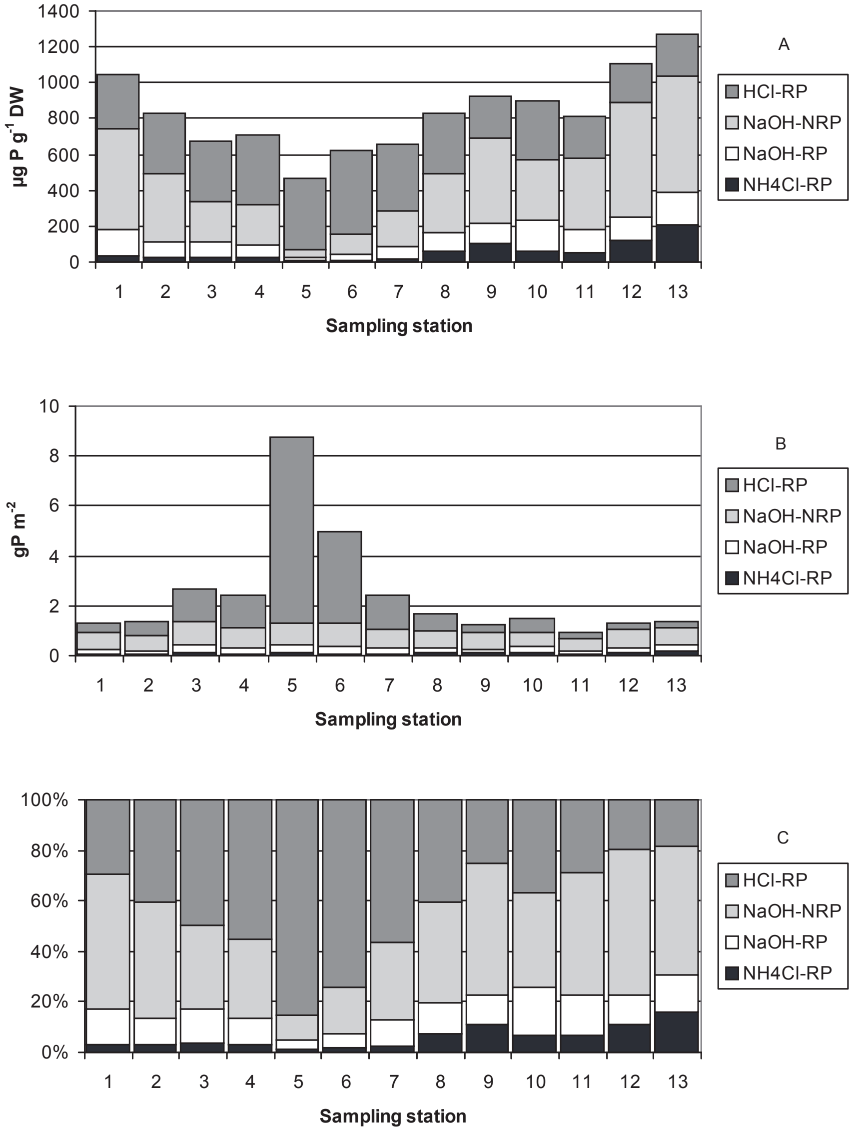

Figure 4. Phosphorus fractions in the sediment of Lake Võrtsjärv. A: P concentration per dry weight of sediment; B: P concentration per sediment volume in the 0-2 cm sediment surface layer; C: relative distribution of P fractions.

Concerning the vertical distribution in the core from sampling site No 13 (Fig. 1), NH$_4$Cl-RP showed the sharpest decrease downcore reaching 10% of its surface value at a depth of 35–40 cm (Study **II**, Fig. 4A). NaOH-RP and NaOH-NRP showed maxima near the sediment surface and a decrease with depth (Study **II**, Fig. 4B, C). HCl-RP was the only fraction increasing with the sediment depth ((Study **II**, Fig. 4D). About one third of TP remained refractory (Study **II**, Fig. 4E).

Temporal changes revealed a significant correlation ($r = 0.80$, $p<0.01$) between the sum of extractable P fractions per sediment dry weight and the changing mean depth of the lake (Study **II,** Fig. 6).

The vertical profile of SRP concentrations in pore-water showed an increase with increasing sediment depth (Study **II,** Fig. 7). In the upper 10 cm the concentrations were usually lower than 10 μg/l and comparable to those in the overlying water. At a depth of 10-15 cm the concentrations were usually higher than 10 μg/l and the maxima occurred in the deepest measured section of 15-20 cm.

As a result of a storm event on 16.09.1996, the date of the lowest water level ever recorded in the lake, the concentration of the SRP increased 23 times, that of TP 4.9 times (Study **II,** Table 3). The nearly 3-times increase in ammonia with a simultaneous decrease in nitrates was an evidence of resuspension reaching deeper anoxic sediment layers. The internal loading caused by the single stormy day amounted to 193 mg SRPm^{-2}, and 377 mg TPm^{-2}.

4.2. Distribution of sediment phosphorus fractions in the strongly stratified hypertrophic lake (III)

The concentration of TP reached the value of 1.5 mg g^{-1} DW in the sediment depth of 5-10 cm and declined more than 1.5 times by the depth of 40 cm in the sediment core sampled in August 1994 (Study **III**, Fig. 1). In the uppermost layers of the Lake Verevi sediment, NaOH-NRP (organic P) dominated while HCl-RP (apatite-P) became dominant in somewhat deeper layers below 7 cm (Fig. 5). NaOH-RP(H-L) exceeded the concentration of NH_4Cl-RP. NaOH-RP(Ps) was the smallest fraction in upper 7 cm. Its concentration was roughly two times lower than that of BD-RP. NH_4Cl-RP was the smallest of all fractions measured according to Hieltjes & Lijklema (1980). In August 2001, the extreme concentration of NH_4Cl-RP (526 µg g^{-1} DW) appeared in the depth of 4-5 cm constituting 39% of the sum of all P fractions in that sediment layer (**III**).

The P content in upper 40 cm of the hypolimnetic bottom was calculated on the bases of the data from August 1994 (Study **III**, Table 1). 5 cm thick surficial sediment layer contained only half of the P amount present in the 5-10 cm sediment layer. A gradual decrease of P amount appeared below 10 cm.

There were 300 kg of potentially mobile phosphorus fractions (NH_4Cl-RP, BD-RP, NaOH-NRP) in the upper 10 cm of the sediment layer of the hypolimnetic bottom sediment (40% of lake bottom area).

4.3. Phosphorus release experiment (IV)

The sediments of Lake Kaiavere and Lake Prossa had similar phosphorus concentrations: the initial sums of all phosphorus fractions were 697 and 737µg P/g DW, respectively. After the six week dialysis, the Lake Kaiavere sediment lost a quarter (26%) of its P content under oxic conditions and a half (49%) under anoxic conditions (Figure 6). The Lake Prossa sediment lost around 40% of its P content under both oxic and anoxic conditions (38% and 42%, respectively).

The initial sedimentary phosphorus compositions differed between the lakes mainly in two fractions. The Lake Kaiavere sediment contained more than twice as much NH_4Cl-RP (160 µg Pg^{-1}DW) as the Lake

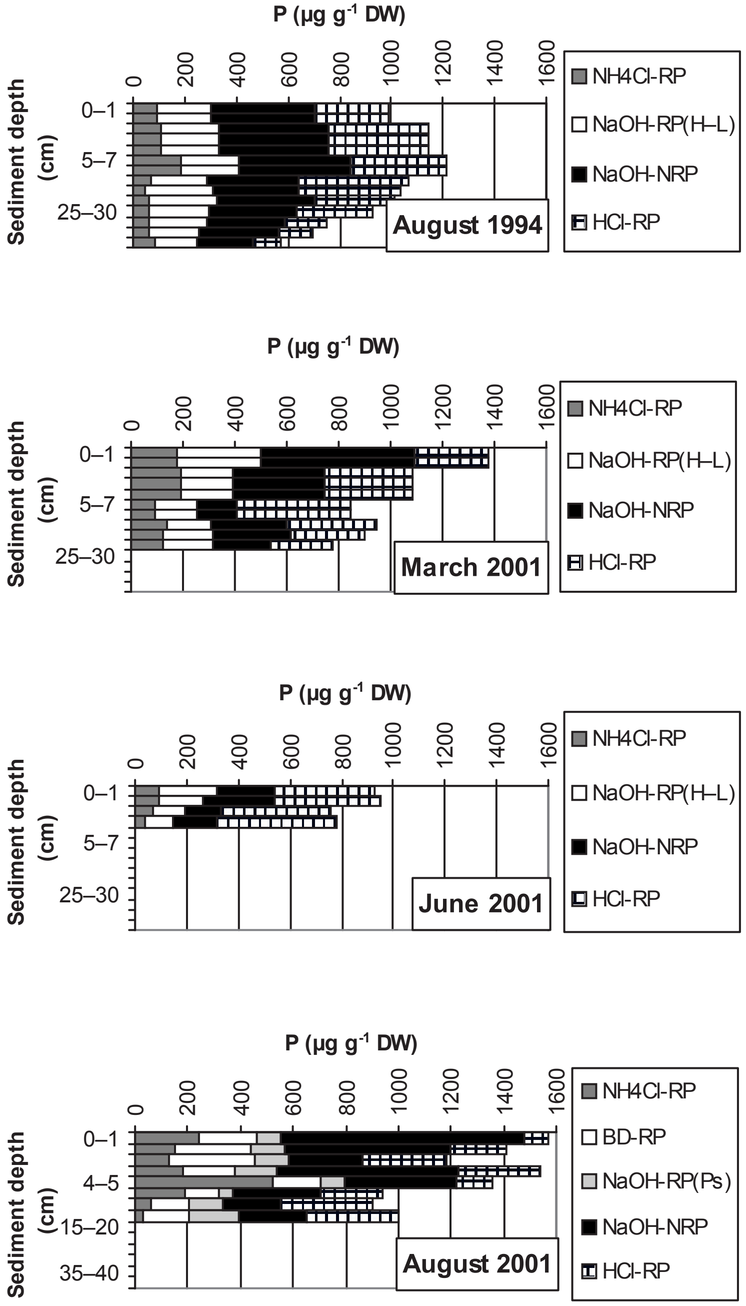

Figure 5. Distribution of phosphorus fractions in the sediment of Lake Verevi. H–L = determined according to Hieltjes & Lijklema (1980); Ps = determined by the modified scheme of Psenner et al. (1988).

Prossa sediment (75 µg Pg^{-1}DW). On the other hand, the Lake Prossa sediment had three times more HCl-RP than the Lake Kaiavere sediment (206 and 75 µg Pg^{-1}DW, respectively). The concentrations of the other fractions were similar in the two lakes. The dominant fraction in both sediments was NaOH-NRP (315-330 µg Pg^{-1}DW); BD-RP and NaOH-RP were each 60-80 µg Pg^{-1}DW. In the Lake Kaiavere sediment the release of P from each fraction was generally higher under reduced than oxidized conditions (Fig. 7). In the Lake Prossa sediment the average concentration of P released as NaOH-RP, NaOH-NRP and HCl-RP was slightly higher in the anoxic environment than in the oxic. However, the differences between the oxic and anoxic treatments were statistically significant only for NH$_4$Cl-RP, NaOH-NRP and HCl-RP in the Lake Kaiavere sediment and for NH$_4$Cl-RP and NaOH-RP in Lake Prossa.

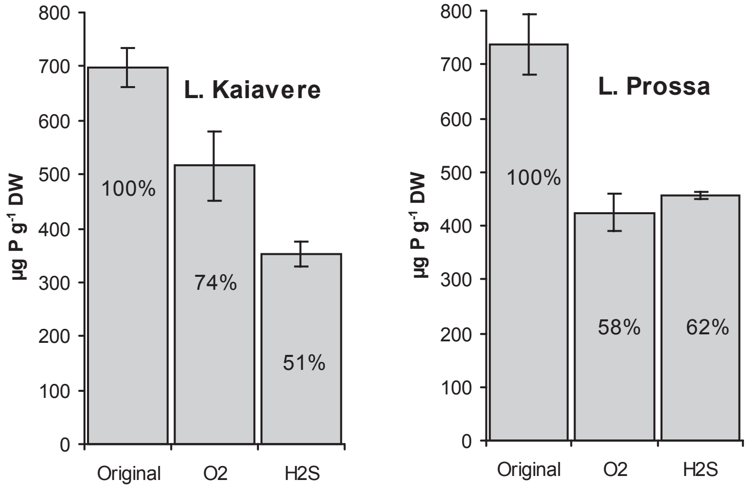

Figure 6. Phosphorus concentration in the sediment of L. Kaiavere and L. Prossa before and after oxic (O$_2$) and anoxic (H$_2$S) treatments.

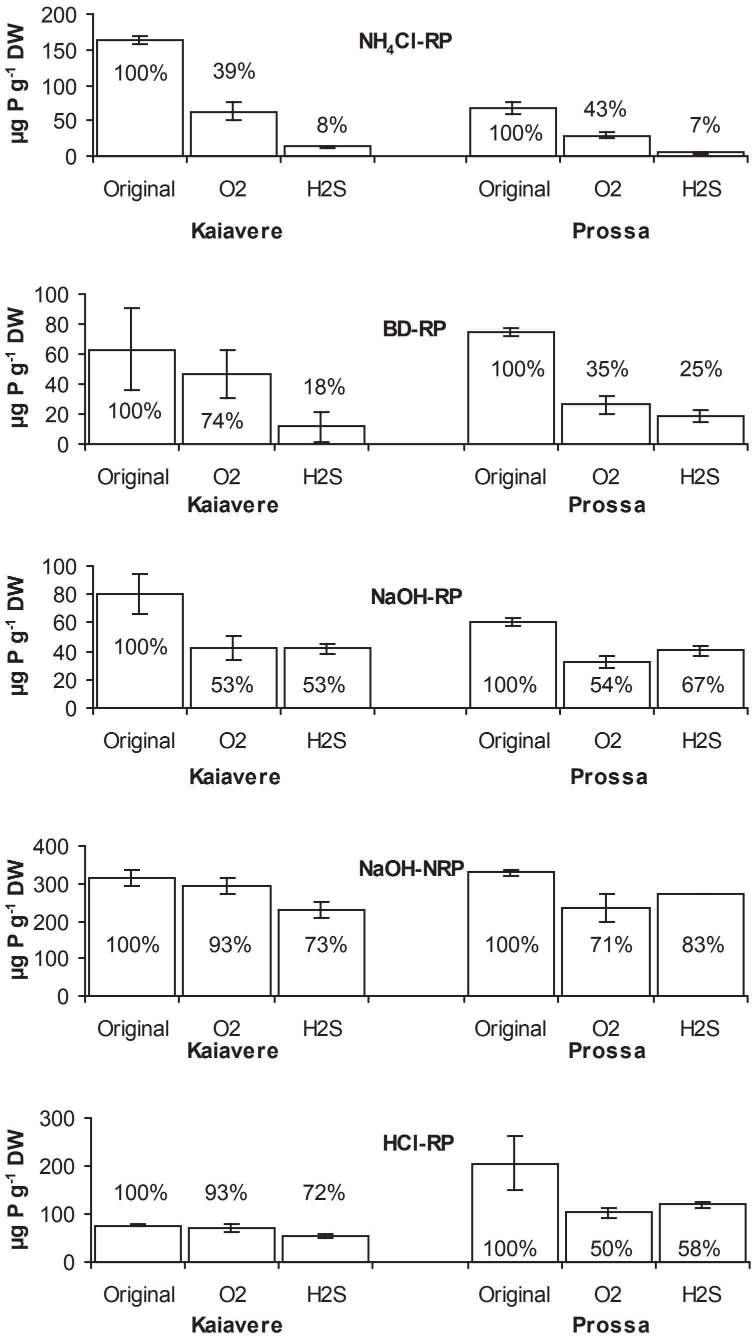

Figure 7. Sediment P fractions (±St. Dev.) before and after incubation in oxic (O$_2$) and anoxic (H$_2$S) conditions in Lake Kaiavere and Lake Prossa.

5. DISCUSSION

5.1. Distribution of sediment phosphorus in a large shallow lake (I-II)

The bottom of Lake Võrtsjärv is covered with different sediment types, as reflected in the range of dry matter contents of the sediment (from 5% to 60% of WW). In most sediment studies, concentrations are expressed on a dry weight basis. In ecological studies, sediment P concentration is often expressed per lake surface area or lake volume. Kamp-Nielsen (1983) showed that it would be appropriate to express the sediment P concentration as the amount of P per sediment volume or per area covered by sediment, specifying the sediment depth considered that is in direct contact with the water column. The present data, from highly variable sediment types, clearly demonstrate the differences between volumetric and dry weight-based sediment phosphorus concentrations. In the data from Lake Võrtsjärv, the statistical significance and even the direction of several correlations between phosphorus forms and other sediment characteristics changed when volumetric concentrations instead of dry weight-based concentrations were used (**I**).

The type of inorganic matter in surface sediments depends first of all on the mineralogy of the soils in the watershed and on bottom deposits in erosion areas. During replacement, sediments are sorted by grain size while the chemical composition of the inorganic compartment is less affected. The differences in the mineralogical composition within one lake should be much smaller than those in lakes situated in different watersheds. This is also true of the organic matter composition, which depends on the ratio of autochthonous to allochthonous sources of organic matter.

In Lake Võrtsjärv, there are strong covariations between the horizontal distribution of sediment phosphorus forms and other sediment characteristics. The dry matter content of the surface 10 cm sediment explained 72-96 % of the spatial variability of separate phosphorus fractions and 87 % of the differences in total phosphorus.

Until resuspension concernes the oxidized sediment surface layers having a similar SRP content with the overlaying water, no increase in the water phosphate pool occurs. SRP can be additionally adsorbed on the fine-grained particles if there are free adsorption sites (Wisniewski, 1995). Internal SRP loading may occur when resuspension reaches deeper anoxic sediments with high P concentration in pore-water (Peters & Cattaneo, 1984). In L. Võrtsjärv the daily release of SRP ($45.2 \cdot 10^3$ kg) during the storm exceeded the annual external P load to the lake ($21.8 \cdot 10^3$ kg of SRP, $35.4 \cdot 10^3$ kg of TP; Järvet, 1997).

Seasonal changes in sediment P content were inconsistent with mass balance calculations and can be attributed to sediment redistribution caused by resuspension in decreasing water levels. During heavy storms at low water level in Lake Võrtsjärv, large internal SRP loadings may occur that exceed the annual load from the watershed. Thus, water level fluctuations can be critical for P release due to enhanced resuspension of sediments. Søndergaard et al. (1992) found in a laboratory experiment with sediment from the shallow wind-exposed Lake Arresø that the release of P from resuspended sediments was 20-30 times greater than from undisturbed sediment. Lake Arresø has about twice as much total P in the dry matter of the sediment, a high proportion of NH_4Cl-RP (0.32 mg P g DW^{-1} in upper 2 cm) and a low Fe/P ratio. In Lake Võrtsjärv, the NH_4Cl-RP concentrations were one or two orders of magnitude lower in most sampling sites for horizontal variability. These comparatively low NH_4Cl-RP concentrations can be explained by the high Fe/P mass ratio in the Lake Võrtsjärv sediment. According to Jensen et al. (1992), a Fe/P ratio above 15 in an oxidized sediment would be able to control the release of SRP to the overlying water column. During heavy storms at low water level, deeper anoxic sediment layers are also denuded in Lake Võrtsjärv.

In large and shallow polymictic lakes the bottom sediments are continuously stirred up and washed throughout the ice-free period, preventing accumulation of labile P. In large shallow lakes with lower relative depth the sediment is in close contact with the water column. Therefore the potential for internal phosphorus loading and the resilience of ecosystem recovery after the removal of external P sources is much less than in smaller lakes with greater relative depth (Nõges et al., 2007).

5.2. Sediments as internal phosphorus sources in a highly eutrophic lake (III)

Lake Verevi is highly eutrophic today, notwithstanding the moderate external phosphorus load. The significant rise in phosphorus concentrations in the hypolimnion during stagnation periods indicates that the high P content in the lake water is probably maintained by P supply from the sediments (Nõges, 2005). The total phosphorus content of the Lake Verevi sediment (1.6 mg g-1 DW) was low in comparison to other stratified and eutrophic lakes in Estonia such as the nearby Lake Arbi (average for upper 35 cm 4.04 mg/g^{-1} DW), Lake Martiska (average 2.6 mg/g^{-1} DW (unpublished data) and Lake Ruusmäe (average 5.2 mg/g^{-1} DW) (Kruusement & Punning, 2000). The sediment P concentration in Lake Verevi was similar to those in shallow and eutrophic lakes such as Lake Võrtsjärv (average for upper 50 cm 0.78 mg/g^{-1} DW) (Nõges & Kisand, 1999).

Easily degradable organic P can be regarded as potentially mobile, and P adsorbed to iron surfaces becomes highly available under anaerobic conditions (Pettersson, 1998). Under anoxic conditions, Fe(III) is reduced to Fe(II). As a result, both iron and adsorbed phosphorus are converted to soluble form (Søndergaard et al., 2003). NH_4Cl-RP, NaOH-NRP and BD-RP can be considered potentially available phosphorus fractions (Rydin, 2000), i.e. parts of those fractions can be released into the lake water under appropriate conditions. Our calculations (**III**) revealed that potentially mobile fractions constitute about 300 kg of P in the upper 10 cm of the hypolimnetic bottom sediment, which represents 40% of the total lake bottom area. The actual percentage of P to be released cannot be determined on the basis of P fractions. The high concentrations of labile phosphorus fraction indicated the low binding capacity of phosphorus by lake sediment. Therefore there is high risk of internal load of phosphorus from 40% of lake bottom area owing to sediment and hypolimnion anoxia (**III**).

Lake Verevi is stratified for most of the year. Phosphorus, released from sediments, accumulates in the hypolimnion, often resulting in more than ten-fold concentration of this nutrient compared to that in the epilimnion (Ott et al., 2005a). Since water mixing by wave action does not play an important role in Lake Verevi, P can spread into the upper water column only during water circulation events in spring and autumn. These events are followed by algal blooms (Kõiv & Kangro, 2005). Some of the P is likely to be assimilated from the water column by macrophytes as Lake Verevi has a relatively small area, so relatively significant phosphorus uptake by littoral zone vegetation could be suspected. When planktonic organisms decay, P is released into both the water column and the sediments. Pettersson (1998) studied the P content in suspended matter, settling particles and sediment of the stratified eutrophic Lake Erken, and showed that phosphorus-rich material in the water released P on its way down to the sediment, and that there was further release from the sediment. That is probably also the case in Lake Verevi; most of the organic material was trapped in the epi-, meta- and hypolimnion and was degraded before it ever reached the sediments (Ott et al., 2005b). The remaining material reaches sediments and returns in part to the water column.

5.3. Predictive value of phosphorus fractions (IV)

The pool of potentially mobile phosphorus in the L. Kaiavere sediment under anoxic conditions was twice that under oxic conditions. This result is in good agreement with other release experiments in which oxic and anoxic conditions were compared (Rydin, 2000). According to the classical theory, phosphorus in the BD-RP fraction is potentially mobile owing to the reduction of Fe(III) to Fe(II), which results in dissolution of both iron and phosphorus bound to iron (Søndergaard et al., 2003). Rydin (2000) even found in his experiment with oxic and anoxic water percolating through the sediment of Lake Erken that more than 90% of the BD-RP was released under anoxic conditions.

NaOH-RP is considered to be stable under changing redox conditions. In our study, roughly half the NaOH-RP was released under both oxic and anoxic conditions. A different release pattern was found in the dominant NaOH-NRP fraction. In some studies, NRP is considered not to be a mobile P fraction (Boström et al., 1982; Petersson et al. 1988). In contrast, Rydin (2000) found that a 1 cm thick layer of the surface sediment from Lake Erken released five times more phosphorus under reduced than oxidised conditions, the maximum loss being about half the original NaOH-NRP pool. Uhlmann et al. (1990) suggest that polyphosphates can be extracted in NaOH-NRP.

A potentially mobile portion of the calcium-bound P was included in the HCl-RP in the sediment of Lake Prossa but not in Lake Kaiavere. This fraction released about half the phosphorus in the sediment of the calcareous macrophyte-dominated lake, while it remained comparatively stable in the sediment of the plankton-dominated lake. Redox conditions made only a minor contribution to this difference. HCl-RP is considered to consist mostly of apatite (Boström et al., 1982, Psenner et al., 1988). However, Pettersson et al. (1988) stress that in calcareous sediments, P can be bound to calcium without having to be in the form of apatite. Phosphorus can be adsorbed on the surface of calcium carbonate. L. Prossa has a large proportion of HCl-RP in its sediments. This pool can be supported by phosphorus adsorbed to calcite crusts, which can be seen on Chara stems in L. Prossa. The process of formation of such crusts is well-known (Graneli & Solander, 1988).

Ammonium chloride, used in the first steps of the sequential extraction, dissolves calcium carbonate and releases phosphorus adsorbed to calcite (Pettersson et al., 1988). Pettersson & Istvanovics (1988) demonstrated that up to three times more phosphorus was extracted from the calcareous L. Balaton sediment when the ammonium chloride extraction step was repeated eleven times instead of twice, as in the schemes of Hieltjes & Lijklema (1980) and Psenner et al. (1988). In the calcareous L. Prossa sediment the second ammonium chloride extraction yielded as much reactive P as the first. Hieltjes & Lijklema (1980) included fractionation with ammonium chloride in order to dissolve calcium carbonate and thus prevent adsorption of the phosphorus extracted with NaOH to calcium carbonate, in which case it would be finally extracted as HCl-RP. In the L. Kaiavere sediment the amount of extracted P declined three-fold in these two steps. Two successive extractions with ammonium chloride may not have been sufficient to remove all the calcium carbonate, so some of the phosphorus in the HCl-RP may be readsorbed P instead of apatite P. This readsorbed P could constitute the mobile part of the HCl-RP fraction.

In many sediment studies connected to water management or lake restoration, researchers need to estimate the maximum (or potential) release of sediment P under certain conditions (e.g. oxic and anoxic). Sediment phosphorus fractions are considered to give more information for predicting potential phosphorus release.

However, we face uncertainties when predicting P release on the basis of the distribution of P forms alone, because we do not know what proportion of the P could be liberated from the given fraction of the particular sediment. Potential sediment phosphorus release from a particular fraction may differ between lakes despite similar oxygen conditions. Comparison of P release from the sediments of Lakes Kaiavere and Prossa showed that, even if exposed under identical environmental conditions, the fractionation steps do not necessarily release similar proportions of phosphorus. Hence, differences in sediment composition play a very important part in the pattern of release of phosphorus fractions, so P fractions alone are not sufficient to predict the release of P from sediments.

6. CONCLUSIONS

According to the Water Framework Directive of EU, good ecological status of all surface water bodies should be achieved by 2015. For many lakes this challenging goal requires the improvement of trophic status and management of the phosphorus load. In addition to external point and non-point P sources, P release from sediments may provide a substantial portion of the total P loading. Thus, P stored in sediments due to previous intensive human activity may support a high lake trophic level for decades. Studies on P fractions improve the understanding of factors influencing P cycling between lake sediment and water. Knowledge about the distribution of sediment P fractions with different mobilities helps to develop the most appropriate and cost-effective methods for lake restoration. Sediment P could be converted to stable forms alternatively, suitable environmental conditions could be created to maintain the stability of P fractions in the sediment. The different aspects of sediment phosphorus and its mobility addressed in present study have revealed that:

1. Strong covariation between the horizontal distribution of sediment phosphorus forms and other sediment characteristics was found in the large shallow eutrophic Lake Võrtsjärv. The dry matter content of the top 10 cm of the sediment explained 72-96 % of the spatial variation of the separate phosphorus fractions and 87 % of the differences in total phosphorus (**I**). In shallow lakes, water level fluctuations can be critical for P release due to enhanced resuspension of sediments. During heavy storms at low water level in Lake Võrtsjärv, large internal SRP loadings from deeper anoxic sediment layers may occur that exceed the annual load from the watershed (**II**).

2. In the highly eutrophic and strongly stratified Lake Verevi, the high concentrations of the labile phosphorus fraction indicated that the lake sediment had a low binding capacity for phosphorus. Therefore there is high risk of internal loading of phosphorus from 40% of the lake bottom area (**III**).

3. Information on the distribution and amounts of P fractions is not always sufficient to predict the amount of P that could be released from the sediment. Release experiments could be essential because the potential for release of a single phosphorus fraction from the sediment may differ between lakes despite similar oxygen conditions. In our study the two lake sediments had different sensitivities to oxygen conditions. In the calcareous macrophyte-dominated Lake Prossa the same amounts of phosphorus were released under both oxic and anoxic conditions, whereas in the plankton-dominated Lake Kaiavere twice as much phosphorus was released under anoxic than oxic conditions (**IV**).

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SUMMARY IN ESTONIAN

Fosfor on paljudes veeökosüsteemides primaarproduktsiooni limiteerivaks biogeeniks. Inimtegevuse mõjul on veekogude fosforikoormus oluliselt kasvanud, tuues kaasa järvede kiirenenud eutrofeerumise. Põhjasetteil on oluline roll järvede fosforiringes: setted võivad kas siduda või vabastada fosforit, mõjutades selle biogeeni hulka järvevees ja seega ka primaarproduktsiooni ning veekogu üldist troofsust. Fosfor esineb järvesetetes erinevate keemiliste vormidena, mille eristamiseks kasutatakse järjestikusel ekstraheerimisel põhinevat fraktsioneerimist. Sette fosforifraktsioonide uuringud aitavad mõista, millised tegurid mõjutavad selle olulise biogeeni ringet sette ja vee vahel. Euroopa Liidu Veepoliitika Raamdirektiiv on seadnud eesmärgiks saavutada aastaks 2015 kõigi pinnaveekogude hea või väga hea seisund; paljude järvede jaoks tähendab see nõue muuhulgas ka järve fosforikoormuse alandamist. Selle ülesande täitmisel võib aga takistuseks osutuda fosfori sisekoormus järvesetetest.

Käesoleva doktoritöö põhiosaks olevate uuringute tulemused on esitatud neljas teadusartiklis, mis käsitlevad fosfori vormide jaotumise seaduspärasusi ning resuspensiooni mõju suure madala järve ökosüsteemile (artiklid **I, II**), settefosfori mõju hüpertroofse kihistunud järve ökosüsteemile (artikkel **III**) ning fosfori vabanemist settest erinevates hapnikuoludes (artikkel **IV**).

Suure madala järve settefosfori fraktsioonide jaotumist ning rolli veeökosüsteemis uuriti Võrtsjärve näitel. Madalatele, tuultele avatud kihistumata järvedele on iseloomulik sette sage resuspensioon, mille käigus kujunevad järvepõhjal välja setete erosiooni- ja akumulatsioonialad. Uuringutes **I** ja **II** ilmnesid järgnevad seaduspärasused:

- Fosforifraktsioonide jaotus korreleerub hästi sette kuivainesisaldusega (**I**). Kõrgema kuivainesisaldusega settepiirkonnas (erosioonialade liivakad ja savikad setted) domineerib apatiitne P, väiksema kuivainesisaldusega setetes aga orgaaniline fosfor.
- Pindmiste settekihtide poorivee fosforisisaldus on võrdlemisi madal (**II**). See seletub ühelt poolt sette läbisegamisega resuspensiooni käigus, mis ei lase välja kujuneda teraval kontsentratsioonigradiendil järve vee ja sette poorivee vahel. Teisest küljest on Võrtsjärve sette raua ja fosfori massisuhe (>26) piisavalt kõrge selleks, et siduda fosforit aeroobses settekihis. Sügavamates settekihtides on poorivee fosforikontsentratsioon kõrgem; madala veetaseme ning tugeva lainetuse korral võib resuspensioon puudutada ka anaeroobseid settekihte. Sellisel juhul järvevette sattuv fosfori hulk võib ületada järve aastase väliskoormuse.

Sügavas kihistunud kõrge troofsusega järves viib fosfori vabanemine settest hüpolimnioni fosforisisalduse tõusule. See fosfor on primaarprodutsentidele kättesaadav peamiselt järvevee tsirkulatsiooniperioodidel. Käesolevas töös hinnati hüpertroofse Verevi järve settefosfori potentsiaalset mobiilsust fosforifraktsioonide abil.

- Vaatamata sette mõõdukale üldfosfori sisaldusele viitas labiilse fosfori kõrge kontsentratsioon hüpertroofses kihistunud Verevi järves sette küllastumisele fosforiga ning fosfori vabanemisele anaeroobsest järvepõhja piirkonnast (**III**).
- Hüpolimneetilise sette (40% järvepõhja pindalast) 10 cm paksuse pinnakihi potentsiaalselt mobiilsetes fosforifraktsioonides sisaldus 300 kg P (**III**).

Laboratoorses katses kahe madala eutroofse järve setetega tõstatati küsimus, kas aeroobsest ning anaeroobsest settest vabaneva fosfori hulk on määratud sette fosforifraktsioonide jaotusega. Uuringu tulemusena leiti:

- Madala kalgiveelise makrofüüdijärve settest vabanes ühepalju fosforit nii aeroobsetes kui anaeroobsetes tingimustes. Madala planktonijärve settest vabanes anaeroobsetes tingimustes kaks korda rohkem fosforit kui aeroobsetes tingimustes. Need erinevused ei olnud määratud ainult sette algse fosforifraktsioonide jaotusega; olulised on ka muud erinevused sette koostises, mis mõjutavad fosforifraktsioonide potentsiaalset mobiilsust (**IV**).
- Fosfori sisekoormuse täpsemaks hindamiseks peaks lisaks sette fosforifraktsioonide jaotuse ning koguse määramisele kaasama ka fosfori vabanemiskatsed (**IV**).

Sette P fraktsioonide erineva potentsiaalse mobiilsuse uurimise praktiliseks väljundiks on mitmesuguste järvetervenduslike meetodite väljatöötamine, mille puhul settefosfor viiakse stabiilsesse vormi või luuakse järves tingimused, mis soodustavad settes olemas olevate P vormide stabiilsust. Ka Eestis on mitmeid järvi, mille hea seisundi taastamiseks oleks hädavajalik saada kontrolli alla fosfori sisekoormus setetest. Taolised projektid nõuavad detailseid settefosfori eeluuringuid: milline on settevormide vertikaalne ja horisontaalne jaotus järves, millised on domineerivad settefraktsioonid, kas sette fosforisidumisvõime on ammendatud. Kuigi fosfori vormide uuringute tulemusel on loodud efektiivseid meetodeid setteist pärineva fosforivoo tõkestamiseks, jääb reaalselt väga paljude tervendamist vajavate järvede seisund veel pikaks ajaks parandamata: varasemate aasta(kümne)tega järvedesse kogunenud fosfori püsiv sidumine setetesse või eemaldamine järvest on majanduslikult kulukas.

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I

PUBLICATIONS

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Horizontal distribution of sediment phosphorus in shallow eutrophic Lake Võrtsjärv (Estonia)

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Key words: lake morphometry, wind fetch, sediment phosphorus fractionation

Abstract

Effective wind fetch and lake width in the dominating wind direction accounted for 87% of the observed spatial variability of sediment dry weight in large (270 km^2), shallow (mean depth 2.8 m) eutrophic Lake Võrtsjärv, Estonia. Focusing of lighter sediments to more sheltered bottom areas was reflected also in the horizontal distribution of sediment phosphorus forms which correlated strongly (R^2 from 0.72 to 0.96) with the dry matter content of the surficial 10 cm sediment. Loosely bound (NH_4Cl-RP), Fe- and Al-bound (NaOH-RP), and organic phosphorus (NaOH-NRP) revealed strong positive intercorrelation (r^2 from 0.72 to 0.87). Ca-bound phosphorus (HCl-RP) correlated negatively with the three former fractions. In contrast to the other fractions, CHl-RP correlated better with general sediment characteristics, such as dry weight, bulk density and loss on ignition, when volumetric concentrations were used. Relatively constant HCl-RP content per dry weight in sediments of different grain size suggests that Ca-bound phosphorus was included in the particle matrix, apatite probably forming its major part. As apatite belongs to a heavier crystalline fraction, it is more resistant to resuspension. Therefore, HCl-RP was the overwhelming form of phosphorus in erosion areas, where its volumetric concentration was up to 30 times higher than in organic-rich soft sediments.

Introduction

Sediment trap studies in shallow lakes (Andersen & Lastein, 1981; Bengtsson et al., 1990; Behrendt & Nixdorf, 1993; Wisniewski, 1995) show a predominating role of sediment resuspension in sedimentation flux. Grain size and specific gravity determine shear stress at which the particles can be resuspended. Thus, smaller and lighter particles will be washed out and transported to deeper, sheltered basins, while larger or heavier particles remain at erosion sites. As phosphorus can be bound to organic and mineral compounds in several forms, selective transport causes its continuous redistribution in lakes.

During resuspension events, as a rule, large amounts of soluble reactive phosphorus are released from sediments (Boström et al., 1982; Søndergaard et al., 1992). Still, depending on the saturation level and fractional composition of P in sediments, resuspension of fine-grained matter may result in the expansion of phosphate adsorption sites, thus enhancing phosphorus sedimentation (Wisniewski, 1995). Knowledge of the fractional composition can help evaluate the potential of a particular sediment to adsorb or release phosphorus when conditions, such as pH or dissolved oxygen concentration, change (Marsden, 1989). Strong correlations were found between phosphorus species, organic matter, mean grain size and concentration of iron in Lake Erie (Williams et al., 1976) and in 66 lakes in eastern North America (Ostrofsky, 1987). This reveals that the quality and quantity of sediment phosphorus can be predicted, to some extent, on the basis of a few simple variables.

The objective of this study was to examine the horizontal distribution of phosphorus forms in surficial bottom sediments of Lake Võrtsjärv and to associate it with formation of the spatial pattern of more general sediment characteristics, such as sediment dry weight, bulk density and loss on ignition.

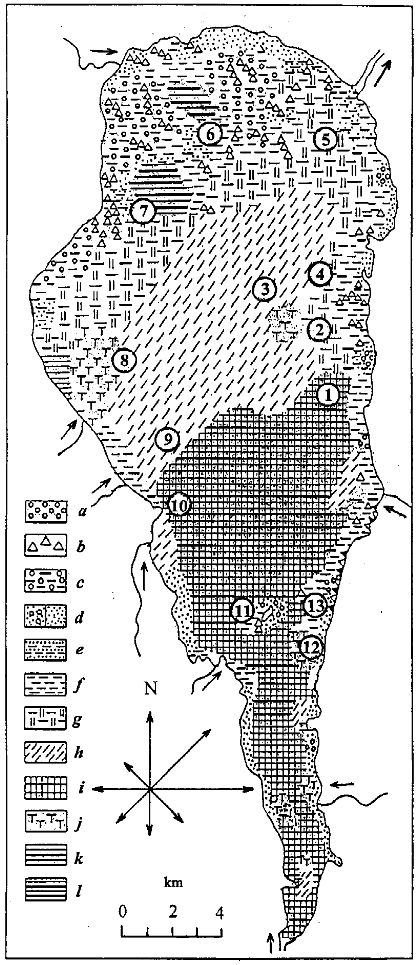

Figure 1. Distribution of bottom sediments in L. Võrtsjärv (Raukas, 1995). (a) devonian sandstone; (b) boulder accumulations; (c) till; (d) sand, silty sand and gravelly sand; (e) sandy silt and silty sand; (f) silt and sandy silt; (g) silty clay; (h) sapropelic silty clay; (i) sapropel, often with a high mineral content; (j) lake marl; (k) clay; (l) varved clay. Numbers denote sampling stations. The wind rose is average for the ice-free period (April–October) 1995–97.

Material and methods

Sediment samples were taken with a Willner corer on June 17, 1996 (13 cores all over the lake, see Figure 1), and sliced into subsamples of 0–2, 2–5 and 5–10 cm. The dry weight of sediment (DW%) was determined after drying at 105 °C during 24 h. We estimated the content of organic matter (IG%) as loss on ignition at 550 °C during 2 h. The bulk density of sediment (ρ) was calculated using the formula of Håkanson & Jansson (1983):

$$\rho = 100^{*}\rho_m/(100 + W + IG^0)(\rho_m - 1), \qquad (1)$$

where ρ_m is the density of inorganic particles taken equal to 2.6, W is the water content of sediment, IG^0 is the organic content (ignition loss at 550 °C) expressed as a percentage of total wet weight.

Sediment phosphorus fractionation was performed in triplicates according to the extraction scheme of Hieltjes & Lijklema (1980). Raw sediment was extracted in consecutive steps with NH_4Cl, NaOH and HCl solutions. After centrifugation at 3000 rpm for 10 min, the concentration of soluble reactive phosphorus was measured from the supernatant according to Murphy & Riley (1962). In addition to the obtained reactive phosphorus (RP) fractions (NH_4Cl-RP, NaOH-RP and HCl-RP), the amount of NaOH-non-reactive phosphorus (NaOH-NRP) was calculated as the difference between total P in the NaOH supernatant (NaOH-TP) and NaOH-RP. NaOH-TP was measured according to Murphy & Riley, op. cit. after persulphate digestion.

Linear (Pearson) correlation analysis and linear regression analysis were applied. As most sediment characteristics demonstrated a log-normal distribution, correlation analysis was carried out using log-transformed values. The parameters of three sediment layers of 0–2, 2–5 and 5–10 cm were included in the analysis as separate cases.

In order to evaluate the influence of wind action to sediments, we measured the length of the axis of wind direction from a particular station upwind up to intersection with the lake shore, as well as the length of 7 radials at 6° intervals on either side of the axis. Effective fetch was calculated after Gons et al. (1986) as the sum of 15 products of length (x_i) and the square of the angle between the radial and the axis of wind direction (α_i) divided by the sum of their cosines (13.5):

$$F = \Sigma x_i(\cos\alpha_i)^2/13.5 \qquad (2)$$

Data on wind direction we obtained from Tõravere Meteorological Station located at a distance of 20 km from the lake.

Site description

Eutrophic Lake Võrtsjärv is located in Central Estonia. It has a surface area of 270 km^2; mean depth is 2.8 m and maximum depth is 6 m. Due to its large area, this shallow lake is exposed to the predominating westerly and south-westerly winds which cause intense resuspension of sediments (Nõges et al., 1999). The distribution map of bottom sediments in L. Võrtsjärv (Figure 1) shows a classical pattern where lighter and small-grained fractions (sapropel and sapropelic silty clay) are eroded from shallow, more exposed areas and transported to deeper or sheltered bottoms. Boulders, till, gravelly sand and sand dominate in the sediments of erosion areas. In L. Võrtsjärv, one cannot find accumulation bottoms *sensu* Bengtsson et al. (1990), i.e. areas where erosion never occurs. Transportation bottom represents about 2/3 of the area of lake bottom and is covered with soft deposits, rich in organic matter, lying on lake marl. The latter is denuded in places close to the western shore and in the southern part of the lake. The thickness of sapropel and marl layers increases southwards reaching 7 and 4.7 m, respectively (Veber, 1973). Varved clay lying under marl is exposed in places in the northern part of the lake.

Results

The dry matter content of the uppermost sediment layer (Figure 2A) varied from 5–6% in muddy areas (St. 1, 9, 11, 12, 13) to 60% in sandy area (St. 5). Horizontal variability of DW% in sediments could be attributed to differences in wind exposure. Effective wind fetch and the lake width in the dominating wind direction accounted for 87% of the observed differences in DW% (Table 1). The determination coefficient (R^2) of the model did not increase much on including the depth of sampling stations (ranging from 1.6 to 5.0 m) or fetch of the westerly wind, which were refused as insignificant in step-wise variable selection procedure.

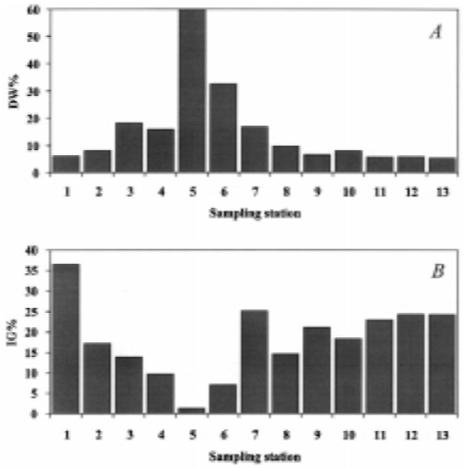

Figure 2. Dry matter content in fresh sediment (DW%; A) and dry weight loss on ignition (IG%; B) in the 0–2 cm sediment surface layer in L. Võrtsjärv.

Loss on ignition (IG%) formed 1–37% of sediment dry weight. We measured the smallest IG% at St. 5 (Figure 2B). The bulk density of fresh sediment varied from 1.02 to 1.57 g cm^{-3}.

The sum of measured P fractions (ΣFR) made up 0.06–0.10% of sediment dry weight. Soft sediments of the central and southern parts contained twice as much P as sandy sediments in northern areas (Figure 3A). A totally different pattern was revealed when P content in the 0–2 cm sediment layer was expressed per square metre of lake bottom (Figure 3B). Owing to the low content of organic matter and water, the sediment of erosion bottom had a considerably higher bulk density than the sediment of southern areas. Thus phosphorus content per unit area (or unit volume) was much higher in sandy and silty sediments of Sts. 5 and 6 in the northern lake part.

NH_4Cl-RP was the smallest P fraction in all types of sediments making up 1–16% of ΣFR (Figure 3C). Its concentration varied from 7 to 206 μg g DW^{-1}. The concentration of this most mobile fraction, expressed both per DW and per unit volume, was the highest at Sts. 12 and 13 near the deepest point of the lake (Figure 3A, B).

NaOH-RP, representing Fe- and Al-bound P, accounted for 3–19% of ΣFR. Its concentration ranged from 15 μg g DW^{-1} in a sandy area (St. 5) to 180 μg g^{-1} in a deep lake part (St. 13). Variation was lower

Table 1. Summary of linear regression for sediment dry matter content (DW%) as a dependent variable

Independent variable	Coefficient	Std. error	*t*-value	Significance level *p*
Intercept	−6.557	5.768	−1.137	0.284960
Fetch of SW wind, km	3.282	0.460	7.140	0.000054
Length of SW-NO cross section of lake, km	5.149	0.777	6.629	0.000096
Length of W-O cross section of lake, km	−6.589	1.050	−6.274	0.000145

Number of observations=13; R=0.950; R^2=0.902; adjusted R^2=0.869; model significance P <0.00007; standard error of estimate=5 615.

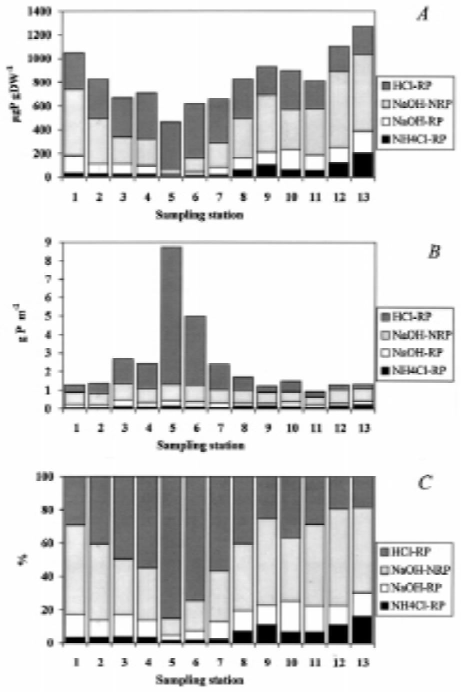

Figure 3. The amount of sediment phosphorus by fractions expressed per dry weight (A), per square metre (B) and per sum of fractions (C) in the 0–2 cm sediment surface layer in L. Võrtsjärv.

Table 2. Variation coefficients (standard deviation/average) of phosphorus fractions in the 0–2 cm sediment layer on wet weight, dry weight, volumetric and percentage basis

Fraction	Per WW	Per DW	Per volume	Per ΣFR
NH_4Cl-RP	0.52	0.52	0.48	0.75
NaOH-RP	0.28	0.47	0.32	0.34
NaOH-NRP	0.15	0.54	0.19	0.36
HCl-RP	1.18	0.23	1.44	0.48
ΣFR	0.65	0.22	0.88	–

when its concentration was expressed per unit wet weight (WW) or per unit volume of sediment (Table 2). The uppermost 2 cm of sediment contained 0.14–0.36 g m^{-2} of NaOH-RP, with higher values in the sandy northern part of the lake (Figure 3B).

NaOH-NRP constituted nearly 60% of P in soft sediments. The concentration of this fraction was highly variable ranging from 47 μg g DW^{-1} in the northern part to 647 μg g DW^{-1} in the soft sediment of the deep area. At the same time, the concentration of NaOH-NRP, expressed on a square metre basis, had the lowest variability. Maxima (0.90 g m^{-2} at Sts. 3, 5 and 6) exceeded minima (0.45 g m^{-2} at St. 11) only by a factor of 2.

Wetzel (1975) defined calcareous sediments as those containing >30% of $CaCO_3$. According to this criterion, sediments of L. Võrtsjärv are non-calcareous. Nevertheless, $CaCO_3$ content is quite high. In muddy sediment (St. 13), carbonates made up 14.4%, whereas Ca accounted for 8.6% of sediment dry weight (K.-D. Wolter, unpublished data). The concentration of HCl-RP in these sediments was low (0.25–0.5 g m^{-2} in the 0–2 cm sediment layer). In sandy areas, Ca-bound P contributed up to 85% of P fractions and reached its maximum there in absolute terms (462 μg g DW^{-1} at St. 6, and 7.4 g m^{-2} in the 0–2 cm layer at St. 5). The content of HCl-RP per sediment dry weight was rather uniform, ranging from 214 to 462 μg g^{-1} at different sampling stations (Figure 3A). However, its variability per unit volume was the highest (Table 2).

We found strong correlations between general sediment characteristics and different phosphorus fractions (Table 3). Sediment dry matter content (DW%) was the most important characteristic accounting for more than 2/3 of variability of loss on ignition, bulk density of sediment, as well as all P

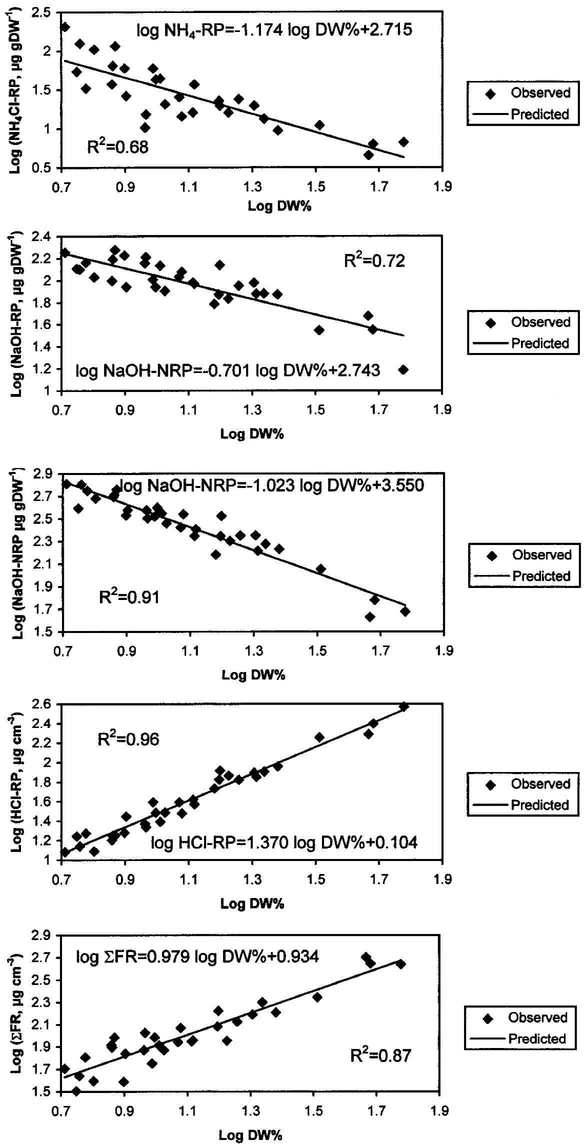

Figure 4. Correlations of different phosphorus fractions with the dry matter content of sediments in the 0–2, 2–5 and 5–10 cm sediment layers in L. Võrtsjärv.

Table 3. Correlations between log-transformed sediment characteristics. Underlined: $P < 0.001$ (to save space, the logarithm is omitted in the variable's names)

		DW%	IG%	ρ	Per dry weight					Per volume			
					NH_4Cl-RP	NaOH-RP	NaOH-NRP	HCl-RP	ΣFR	NH_4Cl-RP	NaOH-RP	NaOH-NRP	HCl-RP
IG%		$\underline{-0.82}$											
ρ		$\underline{0.90}$	$\underline{-0.94}$										
Per dry weight	NH_4Cl-RP	$\underline{-0.81}$	$\underline{0.58}$	−0.38									
	NaOH-RP	$\underline{-0.84}$	$\underline{0.82}$	$\underline{-0.68}$	$\underline{0.71}$								
	NaOH-NRP	$\underline{-0.94}$	$\underline{0.83}$	$\underline{-0.62}$	$\underline{0.84}$	$\underline{0.87}$							
	HCl-RP	$\underline{0.67}$	$\underline{-0.54}$	0.49	$\underline{-0.62}$	$\underline{-0.53}$	$\underline{-0.59}$						
	ΣFR	$\underline{-0.80}$	$\underline{0.62}$	−0.42	$\underline{0.83}$	$\underline{0.81}$	$\underline{0.89}$	−0.36					
Per volume	NH_4Cl-RP	0.34	−0.22	0.30	−0.31	−0.15	−0.27	0.06	−0.18				
	NaOH-RP	$\underline{0.70}$	−0.47	$\underline{0.59}$	$\underline{-0.60}$	−0.40	$\underline{-0.66}$	0.37	$\underline{-0.52}$	$\underline{0.66}$			
	NaOH-NRP	$\underline{0.52}$	−0.40	0.48	−0.50	−0.28	−0.46	0.29	−0.33	$\underline{0.80}$	$\underline{0.84}$		
	HCl-RP	$\underline{0.98}$	$\underline{-0.81}$	$\underline{0.88}$	$\underline{-0.80}$	$\underline{-0.86}$	$\underline{-0.93}$	$\underline{0.73}$	$\underline{-0.82}$	0.23	$\underline{0.65}$	0.43	
	ΣFR	$\underline{0.93}$	$\underline{-0.76}$	$\underline{0.86}$	$\underline{-0.80}$	$\underline{-0.75}$	$\underline{-0.86}$	$\underline{0.65}$	$\underline{-0.73}$	$\underline{0.59}$	$\underline{0.85}$	$\underline{0.75}$	$\underline{0.90}$

fraction. This variable was strongly negatively correlated with NH_4Cl-RP, NaOH-RP and NaOH-NRP fractions expressed on a dry weight basis; a strong positive correlation was found with the HCl-RP fraction on a volumetric basis (Figure 4). Correlation between DW% and ΣFR was negative, when the latter was expressed per DW, and positive, when ΣFR was expressed per sediment volume.

The three fractions, NH_4Cl-RP, NaOH-RP and NaOH-NRP, were positively interrelated, with correlation coefficients ranging from 0.66 to 0.87. HCl-RP behaved differently revealing negative correlations with the other fractions on a dry weight basis (r from −0.53 to −0.62) and a significant positive correlation with NaOH-RP on a volumetric basis (r=0.65).

Discussion

According to Enell & Löfgren (1988), the dry matter content of organic surface sediments in freshwater ecosystems is usually 1–5%. In the accumulation bottoms of 23 Swedish lakes sediments contained 4–22% of dry matter (Pettersson, 1986). At seven stations in Lake Balaton, DW% fell into the range of 22–32% (Pettersson & Istvánovics, 1988). As the sediments of both erosion and transportation bottoms were included in the present study, the range of dry matter content (5–60%) for L. Võrtsjärv was much wider. Sediment replacement explains spatial differences observed in most of the sediment characteristics. The variable included in the regression model demonstrated the principal role of the wind and lake morphometry in the formation of the spatial pattern of DW%. Although one can intuitively associate wind fetch more to wave induced shear stress and the length of the cross sections of the lake to the shear stress caused by currents, it is impossible to provide a causal explanation to the model arguments. Flow fields simulated for L. Võrtsjärv (Kivimaa et al., 1998) revealed strong compensating currents across wind-protected shores almost in case of all wind directions.

Surface sediments of L. Võrtsjärv can be characterized as phosphorus-poor. Adding of refractory P (on average 30% of TP for L. Võrtsjärv; not measured in this study) to the measured fractions yields a TP content of 0.9–1.4 mg gDW^{-1}. For comparison, in 66 lakes of Eastern North America P content of surficial sediments ranged from 1.3 to 9.2 mg gDW^{-1} (Ostrofsky, 1987). According to Holtan et al. (1988), phosphorus content varies from 0.01 mg gDW^{-1} or less in sandy, coastal sediments up to 10 mg gDW^{-1} in iron- and carbonate-rich gyttja. In several data sets analyzed by Ahl (1988) the minimum and maximum P contents, excluding the extremes, fell into the range of 0.03–4.0 mg gDW^{-1}.

In most sediment studies, concentrations are expressed on a dry weight basis. In ecological studies, sediment P concentration often has to be transformed to lake surface area or lake volume. As was shown by Kamp-Nielsen (1983), it would be appropriate for this purpose to express concentration as the amount of P per sediment volume or per sediment area, specifying the considered sediment depth. Our data demonstrate clearly differences between volumetric and dry weight based phosphorus concentrations in the sediment. Several correlations between phosphorus forms and other sediment characteristics changed their statistical significance or even polarity when volumetric concentrations were applied instead of dry weight based concentrations.

The type of inorganic matter in surface sediments depends first of all on the mineralogical composition of soils in the watershed and on bottom deposits in erosion areas. During replacement, sediments are sorted out by grain size, but the chemical composition of the inorganic compartment is less affected. At least, differences in the mineralogical composition within one lake must be much smaller than in case of lakes situated in different watersheds. The same is valid for organic matter composition, which depends on the ratio of autochthonous to allochthonous sources. The large variety of sediment types in L. Võrtsjärv represents a continuum of mixtures which differ from each other in the proportion of inorganic and organic components. This proportion is reflected by the dry matter content of sediment. A specific binding of different P fractions to either the inorganic or the organic component accounts for the large number of strong correlations found between phosphorus forms and the dry matter content of sediment. This effect is enhanced by a different degree of consolidation of sediments. In more minerogenic sediments of erosion bottoms, the heavy inorganic component causes high volumetric concentrations of all phosphorus fractions, so that the volumetric concentration of even the NaOH-RP fraction ('organic-P') was the highest in sand.

The proportion of NH_4Cl-RP among phosphorus fractions was quite large in L. Võrtsjärv compared with several American (Ostrofsky, 1987) and Swedish lakes (Pettersson, 1986) for which the phosphorus fractionation technique of Hieltjes & Lijklema (1980) was applied. As shown by Pettersson et al. (1988), in carbonate-rich sediments Ca-bound P does not necessarily occur the apatite form. NH_4Cl dissolves $CaCO_3$ and releases P which is adsorbed to calcite. Starast (1982) regarded coprecipitation of phosphates and 4–8-fold supersaturated calcite during the vegetation period as the main factor controlling phosphorus concentration in the water of L. Võrtsjärv. A large proportion of the NH_4Cl-RP fraction, originating evidently from dissolved calcite in L. Võrtsjärv, could be the reason why its correlation with NaOH-RP (r=0.72) was lower compared with the results obtained from the study of 66 American lakes (Ostrofsky, 1987) where these fractions were most strongly interrelated (r=0.90).

Broberg & Persson (1988) interpreted the strong covariation, found frequently between NaOH-RP and NaOH-NRP fractions, as an indication for Al- and Fe-bound P being partly coupled to humic matter. In L. Võrtsjärv, both P fractions correlated best with dry matter content in sediment and had almost equally strong correlations with organic matter content. A similar behaviour of Fe-bound P and 'organic P' fractions in Lake Võrtsjärv supports the idea of Broberg & Persson (1988) that the P content of small particles is high due to their high surface to volume ratio. P content on a DW basis varies as follows: sand<silt<clay<organic sediment (Ahl, 1988), but as shown by Williams et al. (1976), relationships between mean grain size and these P forms is strongly curvilinear.

HCl-RP correlated negatively with three other P fractions. In contrast to the latter, correlations between HCl-RP and general sediment characteristics were stronger when volumetric concentrations were used. The relatively constant amount of HCl-RP per sediment dry weight, irrespective of differences in grain size, suggests that extraction by NH_4Cl removed effectively surface-bound (adsorbed to calcite) phosphorus and that the HCl-RP fraction consisted of Ca-bound phosphorus included in the particle matrix. Although different phosphorus minerals, formed in diagenetic processes, can contribute to this fraction (Pettersson et al., 1988), apatite is probably the most important among them. As apatite belongs to the heavier crystalline fraction (Broberg & Persson, 1988), it is more resistant to resuspension. This explains the overwhelming dominance of the HCl-RP fraction in erosion areas.

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Forms and Mobility of Sediment Phosphorus in Shallow Eutrophic Lake Võrtsjärv (Estonia)

key words: shallow lake; sediment phosphorus fractions; mass balance; resuspension; pore-water

Abstract

The surficial sediment (0–10 cm) of shallow eutrophic Lake Võrtsjärv (Estonia) was characterized by an acid insoluble residue of 50% dry weight and low nutrient, Fe and Mn content. Among phosphorus (P) fractions (HIELTJES and LIJKLEMA, 1980), NaOH-NRP amounted on an average to 50%, HCl-RP to 30%, NaOH-RP to 16%, and NH_4Cl-RP to 4% of their sum. Seasonal changes in sediment P content were inconsistent with mass balance calculations and could be attributed to sediment redistribution caused by decreasing water level. High Fe/P ratio (26–30) and the aeration of surficial sediment by frequent resuspension kept phosphate adsorbed. Low pore-water SRP (commonly $<10\ \mu g\ l^{-1}$) usually prevented phosphate release from surficial sediment. However, a storm in September 1996 (max. wind speed 16 m s^{-1}) which coincided with the extremely low water level in the lake (mean depth 1.44 m), denuded deeper anoxic sediment layers and caused a SRP release of 193 mg P $m^{-2}\ d^{-1}$.

1. Introduction

Frequent disturbance by waves and bioturbation, generally high temperatures and vigorous bacterial activity lead us to anticipate high rates of phosphorus (P) release from shallow lake sediments. However, these rates are difficult to measure in non-stratified lakes because dispersal by mixing and rapid uptake of ortophosphate by algae and bacteria precludes the development of concentration gradients needed for release rate estimates by common mass-balance approach (BOSTRÖM *et al.*, 1982). Attempts to estimate release rates by monitoring temporal changes in sediment P pool have also been unsuccessful because P concentrations in sediments are generally too high to be remarkably affected by release (SØNDERGAARD, 1990). Sediment resuspension, common in shallow lakes, can affect the concentration of soluble reactive phosphorus (SRP) in opposite ways depending on the saturation of sediments with P and the redox potential (MARSDEN, 1989). Consequently, the role of shallow sediments in the nutrient budget of lakes is not well understood, largely for lack of a suitable method for the estimation of P release rates. Up to now, only a miscellaneous approach to the question of seasonal P release with simultaneous application of different methods can give us an insight into the potential mobility of P and indicate the timing of release.

In L. Võrtsjärv where, due to frequent sediment disturbance, the matter exchange on the sediment-water interface exceeds the matter exchange between the lake and its watershed by an order of magnitude (NÕGES *et al.*, 1998), the main question is, what mechanisms control the retention of P in the lake and the aerobic P release. This research describes the vertical distribution and seasonal changes of P fractions (measured according to HIELTJES and LIJKLEMA, 1980) and pore-water P concentrations. A new budget-based approach to the estimation of processes in P cycle in a non-stratified lake was applied to seasonal data from Lake Võrtsjärv.

2. Site Description

Lake Võrtsjärv (Fig. 1) is a large (270 km^2), shallow (long-term mean depth 2.7 m) lake located in Central Estonia. Devonian sandstone forms the baserock of the lake bottom denuded in the northern part of the lake and covered partially with gravelly sand and boulders from the Pleistocene and Holocene. Due to the shallowness the lake is lacking a real accumulation area *sensu* HÅKANSON (1977), and the deeper parts can be classified as transportation bottom which are subjected to periodic resuspension during storms. A transition from sandy silt, silt, silty clay to gyttja, often with a high mineral content, characterizes the transportation bottom southwards from the erosion areas (RAUKAS, 1995). In the southern part of the lake two thirds of the bottom are covered with gyttja. Lake marl lying under the gyttja layer is denuded in places. The mean thickness of these layers is 1.74 m and maximum 7.6 m in the narrow southern part of the lake (VEBER, 1973).

Water renewal proceeds about once a year. The mainly cultivated drainage area exceeds the area of the lake about 12 times. The lake has 6 main inflows and one outflow (Fig. 1) which discharges to Lake Peipsi. Due to a restricted outflow, the changes in the water level have large seasonal and interannual amplitudes, both about 1.5 m. The absolute water level ranged from 34.6 to 32.1 m above sea level during the studied period corresponding to the mean depth range from 3.4 (May 1995) to 1.4 m (Sept. 1996). The lake is eutrophic, characterized by an annual mean total nitrogen (TN) concentration of 2 mg l^{-1} and a TP concentration of about 50 μg l^{-1}.

3. Material and Methods

TP and SRP were measured in non-filtered water samples taken from the lake and from the inflows weekly in 1995 and biweekly in 1996. For TP measurements the persulfate oxydation was used followed by molybdenium blue technique. Particulate P (PP) was calculated as the difference between TP and SRP. The PP compartment might contain also colloidal P in humic complexes which do not give the molybdenium blue reaction in standard SRP analysis.

The P budget calculations are described in detail in NÕGES *et al.* (1998). The external budget (EB) for both years was calculated as the difference between external loading and efflux. The net budget (NB) showing the changes in the lake P pool not explained by EB was calculated only for 1995 (Fig. 3) using the daily values of the lake volume (V) and interpolated P concentrations (C):

$$NB = (C_{t(n)}V_{t(n)} - C_{t(n-1)}V_{t(n-1)}) - EB \qquad (1)$$

Samples of the soft sediment from the stationary station (A Fig. 1) were taken with a WILLNER corer in 1–6 replicates on 9 occasions from August 1994 to July 1996. Samples were sliced into subsamples of 0–2, 2–5, and 5–10 cm. The water content of the sediment was determined after drying (105 °C, 24 h), the organic matter content by the dry weight loss on ignition (LOI, 550 °C, 2 h). Sediment P fractionation was performed in triplicates according to HIELTJES and LIJKLEMA (1980). Sediment was extracted in four following steps with three solutions: NH_4Cl, NaOH and HCl. From these solutions the concentration of SRP was measured using the molybdenium-blue reaction. The extraction yields the following fractions, characterized by the extraction media:

1. NH_4Cl-RP (RP = reactive phosphorus), often termed labile (desorbed, hydrolyzed), loosely bound or adsorbed P. It gives an estimate of the immediately available P. NH_4Cl dissolves small amounts of iron- and aluminium-bound P and affects the solubility of calcium-bound P (PSENNER *et al.*, 1988).
2. NaOH-RP represents the phosphates adsorbed to metal (Fe, Al) oxides and other surfaces, exchangeable against OH^-, and P compounds soluble in bases.
3. NaOH-NRP (NRP = non reactive phosphorus) is calculated as the difference between total P in the NaOH extract, measured by peroxosulphate digestion, and NaOH-RP. It is assumed to represent the major part of organic and humic P. Existing methods for determination of organic P in lake sediments do not include any "labile" organic P. Between 50 and 80% of the total organic P has been proposed to consist of high molecular weight humic-fulvic complexes (BOSTRÖM *et al.*, 1982).

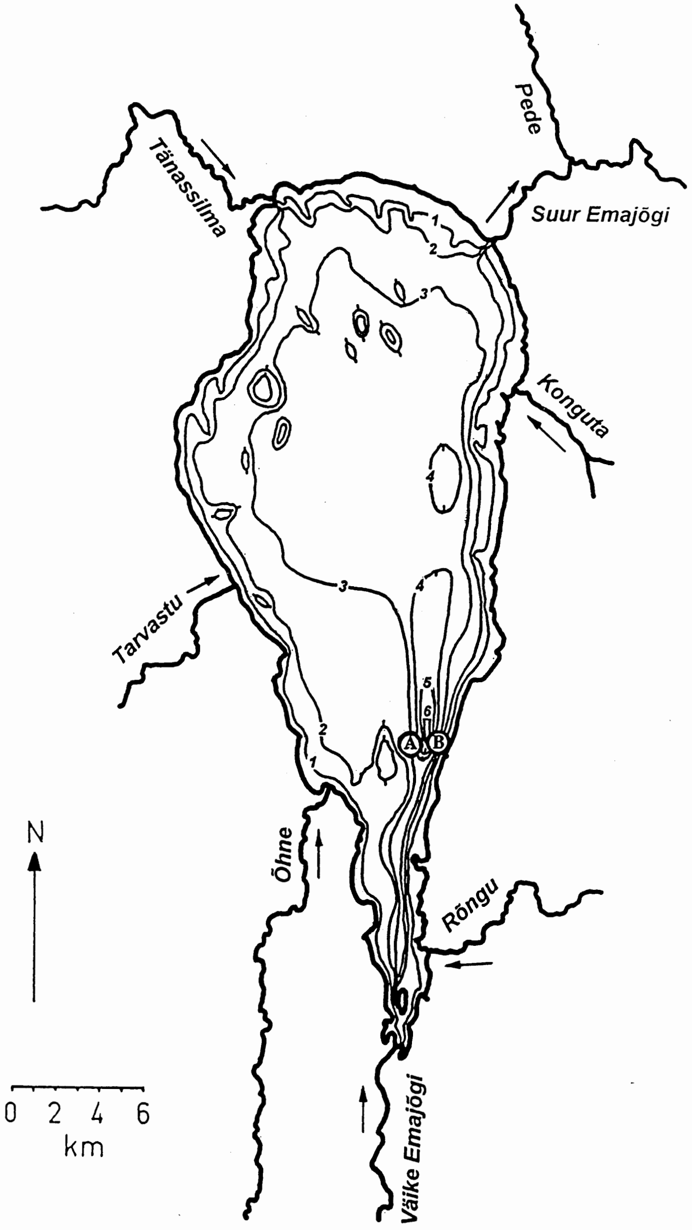

Figure 1. Bathymetric map of L. Võrtsjärv and the sediment sampling stations. 1–6 – depth isolines at mean water level; A – stationary sediment sampling station; B – sampling station in May 1993.

4. HCl-RP represents P bound to carbonates, apatite-P and P released by the dissolution of oxides (not adsorbed to the surface). It may contain traces of hydrolyzed organic P (Psenner *et al.*, 1988).

TP was measured in the mixed acid (H_2SO_4 + HNO_3 + $HClO_4$) digest of the dry sediment (Ahlgren and Ahlgren, 1976). Refractory P was calculated as the difference between TP and the sum of extractable P fractions (Sum FR).

In May 1993, one sediment core was taken from sampling station B (Fig. 1) and analyzed in the laboratory of Technical University of Berlin, departement of Limnology. In this series TP, Fe and Mn were measured after digesting 250 mg of the sample with 5 ml 7 N HNO_3 (140 °C, 0.5 h). TP was measured in the digest according to Murphy and Riley (1962) and metals by using atomic absorption spectrometry (AAS). The acid insoluble residue of the sediment was calculated by subtracting the main acid soluble ions (Ca, Mg, Na, K, Fe and Mn) from the residue of ignition at 900 °C (Wolter, 1992). The residue of ignition at 900 °C does not contain carbonate any more, the formation of oxides in the sample (e.g. CaO) by the ignition process is taken into consideration by the calculation. The concentration of carbonates was calculated as the difference between losses on ignition at 550 °C and 900 °C (Wolter, *op. cit.*). The general sediment characteristics and part of the results of elemental analysis are first published in the present paper (W. Ripl, K.-D. Wolter, with permission).

In August 1994, an additional core from station A was sliced in 5 cm layers down to 50 cm to study the vertical distribution of P fractions. From this core also the concentration of Fe and Mn was determined by AAS after mixed acid digestion (Ahlgren and Ahlgren, 1976).

Samples for measuring SRP in the interstitial water were collected on five occasions from June to December 1997. Pore-water samplers coated with dialysis membrane tubing (SPECTRA/POR 4, cut off 12,000–14,000 D, Spectrum Medical Industries Inc.) were incubated one week in intact sediment cores at *in situ* temperature. Including replicates (2–3) pore-water analyses were made in 13 cores.

4. Results

4.1. Sediment Composition

The sediment of the gyttja area is formed of autochthonous organic deposits mixed with silioceous and calcareous components flushed from the drainage area or eroded from the mainly mineral bottom of the northern part of the lake. Analyses of vertical cores (May 1993 and August 1994) made in different laboratories gave consistent results (Fig. 2). The loss on ignition (LOI) made up about one quarter of sediment dry weight (DW). The inorganic compartment was large, especially, the proportion of acid insoluble residue which constituted from 45 to 60% DW (not shown). The sediment could be characterized as nutrient-, iron- and manganese-poor. The Fe:P ratio by weight was high and increased downcore (Fig. 2).

4.2. Mass Balance of Phosphorus

The TP external budget for 1995 (Fig. 3A) reflected the hydrological regime of the lake. The TP pool increased during the first half of the year together with the rising water level. From April to August, PP constituted one half of the external load (not shown) that could be attributed to the increased load of humic substances. The maximum of the EB in May was caused by the second flood peak while the flow in the outflowing river was reversed during two weeks. During lowering of the water level in the second half of the year, the efflux of TP dominated over the influx. Annual retention constituted 28% of the 0.2 g m^{-2} external load.

The net budget of TP (Fig. 3B) showed a frequently alternating and rather balanced P exchange at the sediment-water interface. The amplitude of NB exceeded that of EB nearly by an order of magnitude. Besides the sediment-water exchange, the net budgets of PP and SRP (Fig. 3C, D) include also the transformation processes within the water column caused

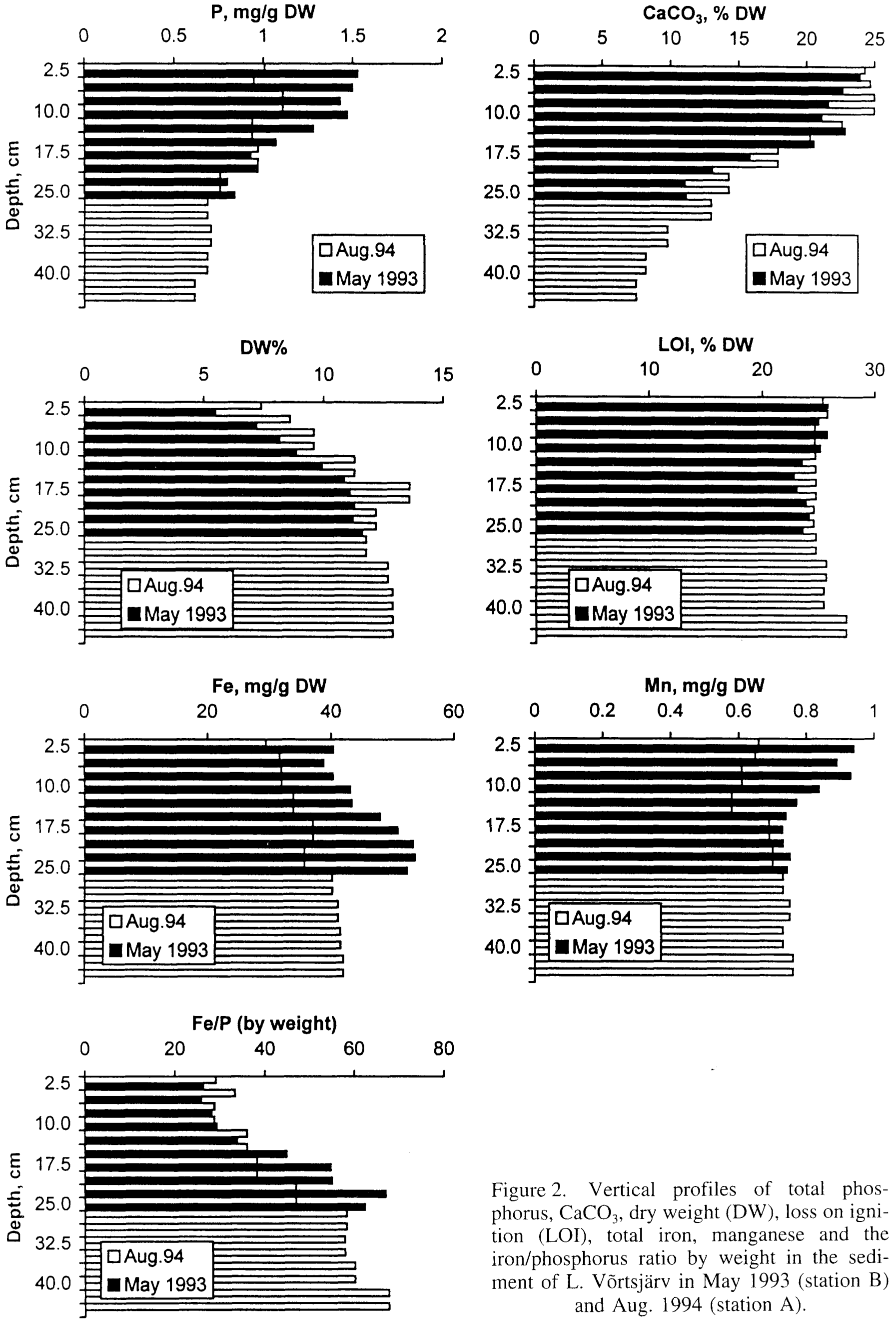

Figure 2. Vertical profiles of total phosphorus, $CaCO_3$, dry weight (DW), loss on ignition (LOI), total iron, manganese and the iron/phosphorus ratio by weight in the sediment of L. Võrtsjärv in May 1993 (station B) and Aug. 1994 (station A).

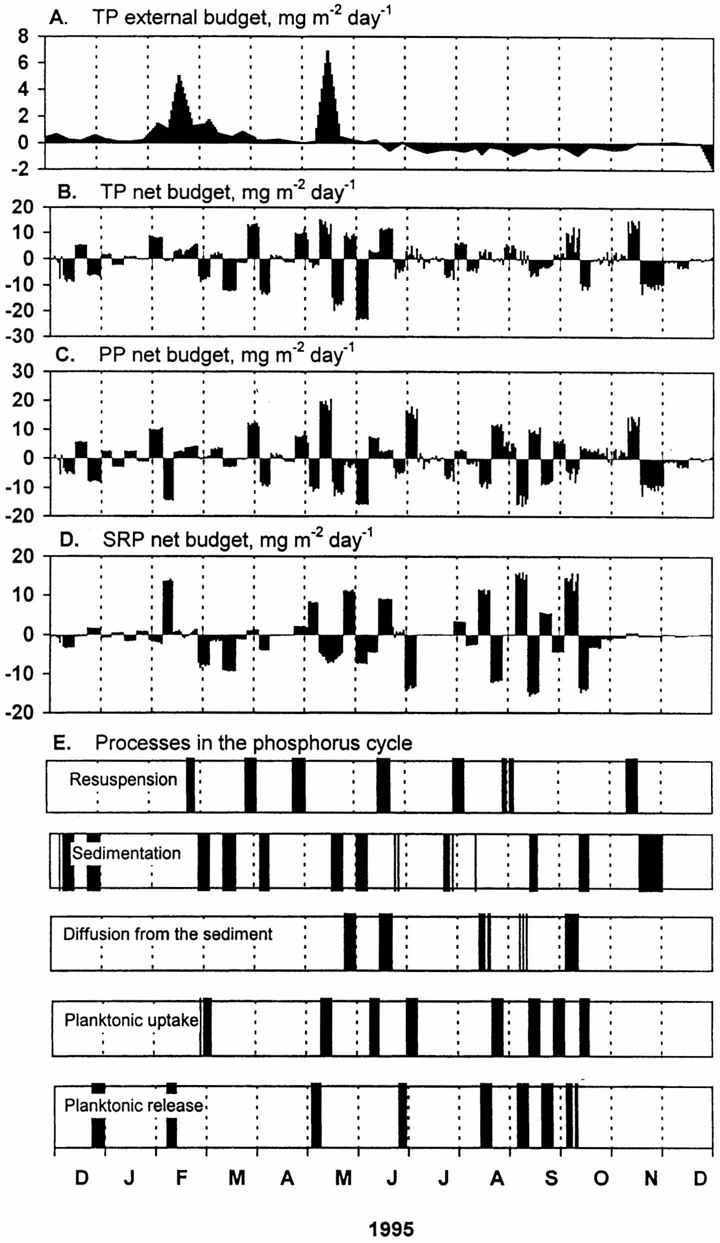

Figure 3. Phosphorus budget of L. Võrtsjärv and the predominating processes in the phosphorus cycle in 1995. A – external budget of total phosphorus (TP); B – net budget of TP; C – net budget of particulate phosphorus (PP); D – net budget of soluble reactive phosphorus (SRP); E – periodicity of dominating processes in the phosphorus cycle revealed by the data filtration technique (description in the text).

by planktonic uptake and release. In order to interprete these changes, a model was created (Fig. 3E) provided that:

1) a negative TP net budget shows the prevailing of sedimentation over resuspension

$$\text{sedimentation} = [NB_{TP} < 0] \qquad (2)$$

2) cases of simultaneous positive values in SRP and PP net budgets were treated as resuspension

$$\text{resuspension} = [NB_{PP} > 0 \text{ and } NB_{SRP} > 0] \qquad (3)$$

3) positive values in TP net budget caused predominantly by SRP were taken as release from the sediment by diffusion

$$\text{diffusion} = [NB_{TP} > 0 \text{ and } NB_{SRP} > NB_{PP}] \qquad (4)$$

4) an increase in PP exceeding the increase in TP pool indicates a transformation of SRP to PP within the water column and was taken for planktonic uptake

$$\text{planktonic uptake} = [NB_{PP} > 0 \text{ and } NB_{PP} > NB_{TP}] \qquad (5)$$

5) an increase in SRP exceeding the increase in TP pool gives evidence of a release of SRP from the PP compartment in the water column as a result of phytoplankton exudate release, decay, or zooplankton grazing

$$\text{planktonic release} = [NB_{SRP} > 0 \text{ and } NB_{SRP} > NB_{TP}] \qquad (6)$$

The resuspension-like situations when PP and SRP increased simultaneously, occurred irregularly from February to November (Fig. 3E). Sedimentation peaks occurred about one month after periods of large external loadings and after ice formation. The model showed a possible diffusional leakage of SRP during a much shorter period, from the end of May to the first half of October. Planktonic uptake followed regularly, with one week lag, the periods of planktonic release.

4.3. Sediment Phosphorus Fractions

As an average 70% of TP in the gyttja sediment was extractable by the fractionation technique. NaOH-NRP formed about one half of the sum of extractable P fractions in the uppermost 0–10 cm layer (Table 1). HCl-RP and NaOH-RP were the second and third largest fractions. NH_4Cl-RP was the smallest and the most variable one among all fractions.

Table 1. Number of samples, mean values, standard deviation and variation coefficient of sediment P fractions as measured at Station A in L. Võrtsjärv.

	Temporal series from Aug. 94 to Jul. 96				**Small-scale spatial series in Jul. 96**			
	Number of samples*	Mean µg/g DW	Std. Dev. µg/g DW	CV %	Number of samples*	Mean µg/g DW	Std. Dev. µg/g DW	CV %
NH_4Cl-RP	84	42	39	94	88	27	9	32
NaOH-RP	92	151	71	47	85	81	29	36
NaOH-NRP	85	413	149	36	69	457	111	24
HCl-RP	91	257	88	34	87	230	19	8
SUM FR.	74	831	241	29	67	796	102	13

* All correct replicates included. The numbers are different due to excluded outliers

4.3.1. Vertical Distribution

In the 50 cm core taken in August 1994, NH_4Cl-RP showed the sharpest decrease downcore reaching 10% of its surface value at a depth of 35–40 cm (Fig. 4A). NaOH-RP and NaOH-NRP fractions showed maxima near the sediment surface (2–10 cm) and an exponential decrease with depth (Fig. 4B, C). HCl-RP was the only fraction increasing with the sediment depth (Fig. 4D). About one third (15–43%) of TP remained refractory (non-extraxtable) by the extraction technique used (Fig. 4E, F).

In the seasonal course NH_4Cl-RP was always highest in the sediment top layer (Fig. 5), although no statistically significant differences could be found between 0–2 and 2–5 cm layers. The concentration of NH_4Cl-RP and NaOH-NRP in the 2–5 cm layer was significantly ($p < 0.05$) higher than in the 5–10 cm layer. The difference between 0–2 and 5–10 layers was highly significant ($p < 0.001$) for both fractions and, additionally, for the sum of extractable P fractions ($p = 0.003$).

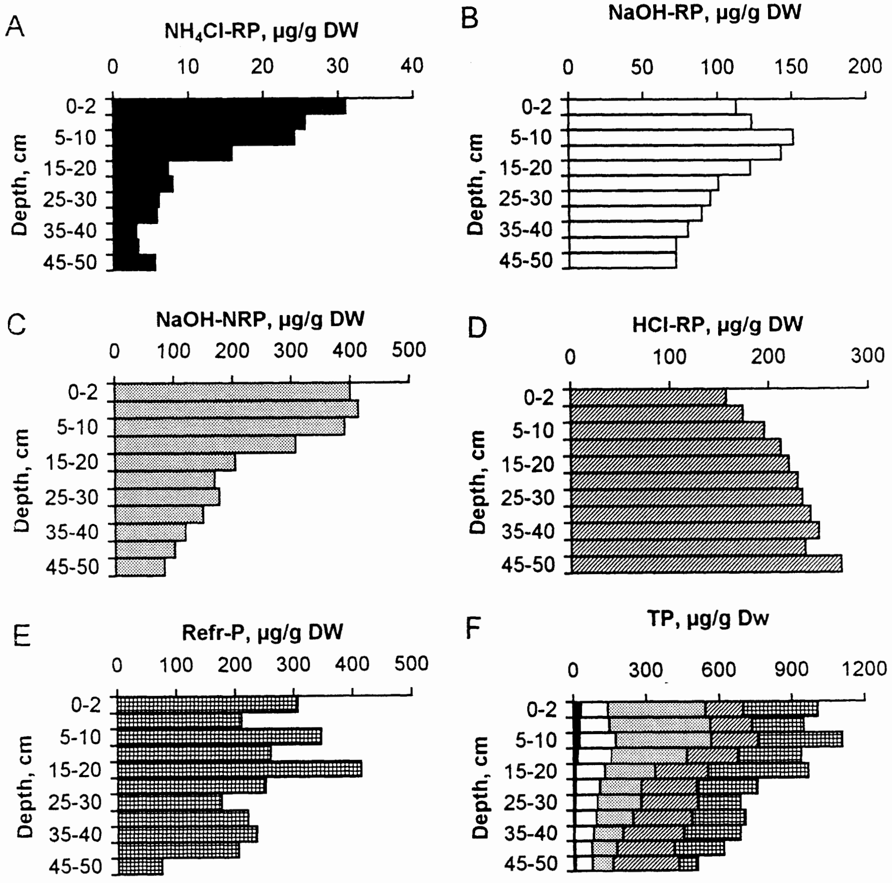

Figure 4. Vertical distribution of P fractions in the sediment of L. Võrtsjärv (station A; Aug. 1994).

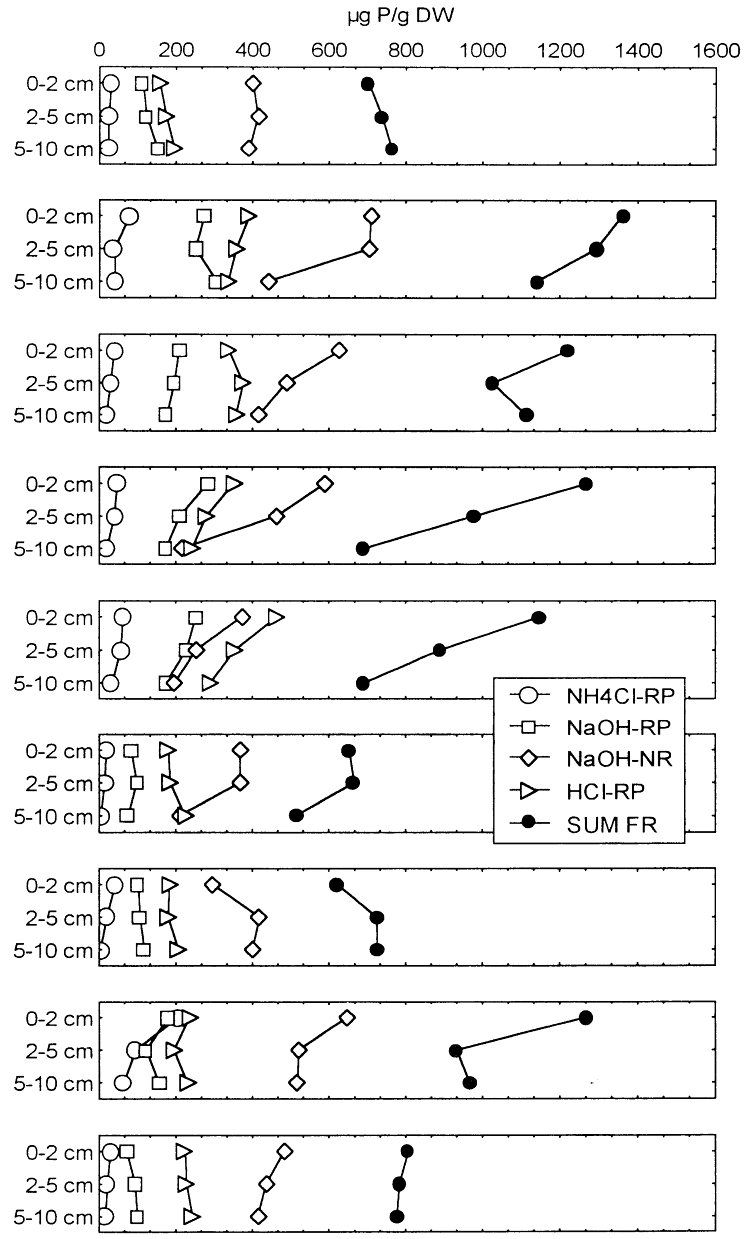

Figure 5. Temporal changes in sediment P fractions and their sum (SUM FR) as recorded at sampling station A in L. Võrtsjärv from Aug. 1994 to July 1996.

Table 2. Significance (p) of interannual differences in concentrations of sediment P fractions at Station B in L. Võrtsjärv (Kruskal-Wallis median test).

Years	NH_4Cl-RP	NaOH-RP	NaOH-NRP	HCl-RP	SUM FR
1994–95	0.0679	0.0711	0.0704	0.0786	0.0761
1994–96	0.5591	0.0773	0.5690	0.0820	0.5691
1995–96	0.0001	0.0000	0.2978	0.0000	0.0010

4.3.2. Small-Scale Horizontal Variability

Six cores taken on 24.07.96 around Station A with 20–30 m distances from each other showed a much smaller variability in P fractions than the cores taken seasonally on nine occasions from the same station (Table 1). This allows us to talk about temporal changes in sediment P fractions.

4.3.3. Temporal Changes

Figure 5 reveals remarkable dynamics of the major P fractions, exceeding the extent of the vertical and the small-scale horizontal variability. Due to small number of observations in 1994, the difference between this year and and the others could not be proved statistically (Table 2). Comparing the years 1995 and 1996, only the concentration of organically bound P (NaOH-NRP) remained almost at the same level. The concentrations of NH_4Cl-RP, NaOH-RP and HCl-RP were significantly higher in 1995 compared with data from 1996. Also the sum of extractable P fractions was significantly higher in 1995 (1050 ± 224 µg/g DW *versus* 776 ± 152 µg/g DW in 1996). The difference in P content in the 0–10 cm sediment layer between these two years amounted to 2.13 g/m^2. The simultaneous increase in the water column TP pool (0.13 g/m^2) was too small to explain the large loss from the sediment. A significant correlation ($r = 0.80$, $p < 0.01$) was found between the sum of extractable P fractions per sediment dry weight and the changing mean depth of the lake (Fig. 6).

4.4. Phosphorus in Pore-Water

Despite the large variability of SRP concentrations in pore-water (0–384 µg/l), the vertical profile was similar on all occasions showing an increase with increasing depth (Fig. 7). In the upper 10 cm the concentrations were usually < 10 µg/l and comparable to those in the overlying water. Only on 16. 10. 97, SRP concentrations from 43 to 146 µg/l were measured in the upper layers. At a depth of 10–15 cm the concentrations were usually higher than 10 µg/l and the maxima occurred in the deepest measured section of 15–20 cm.

With one exception (on 04. 11. 97) SRP concentrations in the lake during sampling were higher than those measured in the pore-water sampler after exposition.

4.5. The Effect of Storms on Water Quality

On 16. 09. 96, the date of the lowest water level ever recorded in the lake (mean depth 1.44 m), a north wind (16 m/s) affected strongly most of the chemical and hydrobiological characteristics of the lake (Table 3). Compared with the last measurement made before the

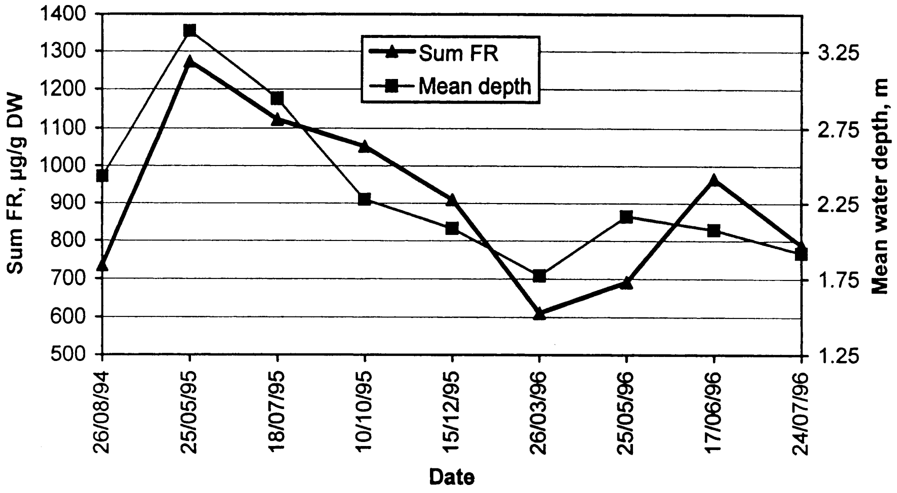

Figure 6. Seasonal course of mean water depth in L. Võrtsjärv and of P concentration (Sum FR – sum of extractable P fractions) in the 0–10 cm sediment layer at sampling station A from Aug. 1994 to July 1996.

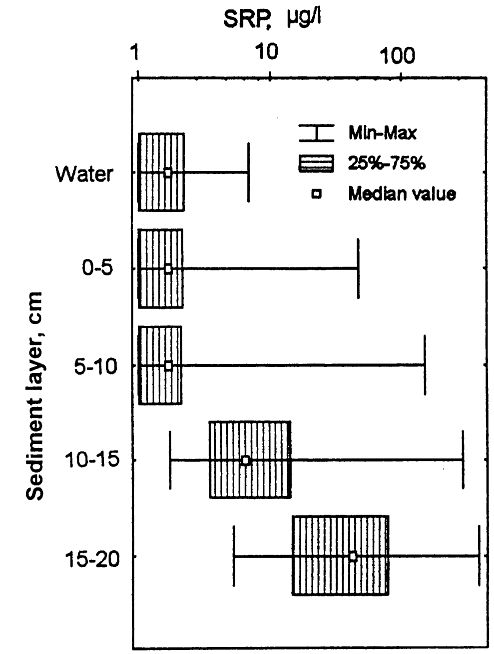

Figure 7. Box and whiskers plot by quartiles of SRP concentration in sediment pore-water and in the overlying water as measured in 13 sediment cores taken from sampling station A in L. Võrtsjärv from June to December 1997.

Table 3. Wind velocity and water characteristics before (03. 09.), during (16. 09.) and after (01. 10.) a storm in L. Võrtsjärv in 1996 as measured at Station B (wind data from the meteorological station Tõravere).

Parameter / date	**03/09/96**	**16/09/96**	**01/10/96**
Mean wind velocity, m/s	2.5	7.3	3
Maximum wind velocity, m/s	8	16	10
Suspended solids, mg/l	19	140	49
Secchi depth, m	0.55	0.15	0.3
SRP, µg/l	6	140	25
TP, µg/l	68	330	130
NH_4^+, mgN/l	0.012	0.031	0.02
NO_x^-, mgN/l	0.251	0.152	0.165
TN, mg/l	1.0	2.0	2.0
Chlorophyll *a*, µg/l	37	105	92
Phytoplankton biomass, mg/l	72	65	61

storm, the concentration of SRP increased 23 times, that of TP 4.9 times, and the amount of suspended solids 7.4 times. Secchi depth decreased 3.7 times reaching the smallest value (0.15 m) ever registered in the lake. As phytoplankton biomass remained almost on the previous level, the nearly three times increase in chlorophyll *a* concentration was accounted for by a rather high chlorophyll content (47.5 ± 13.8 µg/g) per sediment dry weight. The nearly 3-times increase in ammonia with a simultaneous decrease in nitrates was an evidence of resuspension reaching deeper anoxic sediment layers, the sites of denitrification.

The internal loading caused by the single stormy day amounted to 193 mg SRP/m^2 and 377 mg TP/m^2. Assuming a similar increase in the whole lake (234 km^2 at that time), the amount of SRP increased by $45 \cdot 10^3$ kg and that of TP by $88 \cdot 10^3$ kg.

5. Discussion

Over extended periods such as an annual cycle there is a net deposit of P in the sediment also in most eutrophic lakes (Boström *et al.*, 1982) while as a rule more than 50% of the external load accumulates in the sediment (Lijklema, 1985). As a result of the collapse of soviet agricultural system and the decreasing trend of precipitations during the last decade, the annual external P load to L. Võrtsjärv has almost continuously decreased from $100 \cdot 10^3$ kg in 1987 to $35 \cdot 10^3$ kg in 1996 (Järvet, 1997). P retention amounted to 59% of the load during the high-water period of 1988–1991 (Nõges and Järvet, 1998) but decreased to 28% in 1995 when the water level rapidly dropped (Nõges *et al.*, 1998). In spite of smaller load in 1995 ($61 \cdot 10^3$ kg *versus* $82 \cdot 10^3$ kg in 1988–91) more P was flushed out of the lake ($44 \cdot 10^3$ kg *versus* $33 \cdot 10^3$ kg in 1988–91). Obviously, the retention capacity of the lake is much more dependent on the extent and frequency of sediment disturbance (determined by the water level) than on the external loading.

The "filtration" of the budget by using logical premises (Eq. 2–6) enabled to find out the most probable periods for occurrence and dominance of the processes involved in the P cycle. However, besides its cognitive value the model has several limitations. Because most of the processes take place simultaneously in nature, but some of them (sedimentation and resuspension, planktonic uptake and release) are mutually exclusive by model conditions, the gaps do not necessarily mean interruptions of the processes. The results are of a qualitative character and their reliability is dependent first of all on the rightness of the premises, but also on the extent of measured differences.

Large fluctuations in P net budgets seem to be typical of wind subjected shallow lakes. In L. Grosser Müggelsee (mean depth 4.9 m, TP 3.5 mg/g DW at sediment surface), a period of P release started from May but was characterized by a steady alternation of intervals with low and high P release rate (Kleeberg and Kozerski, 1997). A close relationship between the Fe/P release ratio and the subsequent effectiveness of phosphate scavening by ferric oxohydroxide immediately after the positive redox-turnover described by Gunnars and Blomqvist (1997) may cause rapid fluctuations in SRP budget when mixing conditions change. Fluctuations in P budget of L. Võrtsjärv are caused first of all by the highly variable nature of the resuspension-sedimentation cycle. The resuspended PP is rapidly deposited when the wind ceases but the simultaneous drop in dissolved oxygen concentration in the bottom layer (Nõges and Nõges, 1998) can affect the mobility of redox sensitive P. In the 3 m deep L. Arresø, resuspension occurred about 50% of time, while the resuspended particles had a relatively high settling velocity and on average, a relatively short residence time in the water column of 7 hours (Kristensen *et al.*, 1992). The combination of hydrodynamic factors with changing chemical conditions and high P recyling rate by biota complicates to prove the dependence of P release on wind within a range of moderate wind velocities.

Compared to several published datasets of TP in lake sediments (Nürnberg, 1987; Ostrofsky, 1987; Holtan *et al.*, 1988) the sediment of L. Võrtsjärv with its maximum 1–1.5 mg P g DW^{-1} falls to the lower boundary of the reported range. One reason for the low concentration not only of P, but also of Fe and Ca, is the high content of acid insoluble residue (mainly silica) in gyttja sediments which "dilutes" the dry matter. Nürnberg (1987) considers TP concentrations a suitable basis to predict release rates from anoxic sediments, but several investigations have revealed results that contradict to this statement. In aerobic sediments no correlations between sediment TP and P release could be found (Boström *et al.*, 1982). The TP content and immobilization in the sediment is mostly related to the import of P and proportions of its binding partners (Gunnars and Blomqvist, 1997), but can be strongly affected by changes in pH (Søndergaard, 1988) or formation of iron sulphides (Morse *et al.*, 1987; Caraco *et al.*, 1993).

The decrease in sedimentary P concentrations with sediment depth, observed also in L. Võrtsjärv, Holtan *et al.* (1988) explained 1) by increased concentration in the recently settling material, 2) by a delay in mineralization of the recently settled material, and 3) by resorption or precipitation of P diffusing from the deeper sediment layers, where oxygen depletion reduces redox potential and sorption capacity. Starast (1982) considers the coprecipitation of phosphates together with 4–8-fold supersaturated calcite during the vegetation period to be the main factor controlling the P concentration in L. Võrtsjärv. Under saturated conditions one mole of carbonate can precipitate per each mole of CO_2 removed by photosynthesis (Lijklema, 1985). If no other adsorption sites are available, most of this phosphate will desorb and return to the overlying water. In this case the peaks of both, dissolved and sorbed phosphates, will be found at or near the sediment surface as described by Holtan *et al.* (1988). In L. Võrtsjärv NH_4Cl-RP and pore-water SRP showed opposite vertical distribution, the first having its maximum but the latter its minimum in the sediment top layer. Golterman (1988) demonstrated that phosphate adsorbed to calcite can be transferred to iron hydroxides the amount of which will control the equilibrium between sorbed phosphates and pore-water SRP. A similar process can be assumed in L. Võrtsjärv.

The shape of the pore-water SRP profile in L. Võrtsjärv was similar to this described by Enell and Löfgren (1988) as typical for eutrophic sediments during turnover, i.e. for sediments with oxic top layer. Principally, this kind of distribution may form as a result of frequent wash-out of the surficial sediment layers while an equilibrium is reached between pore-water and overlying water. In this case a continuous diffusional release can be assumed, and the pore-water SRP concentrations ought to increase rapidly after cessation of sediment mixing. The incubation period of 7–10 days used for dialysis ought to be sufficient to restore a dissolved phosphate distribution, characteristic of undisturbed sediment. As the pore-water SRP profile measured by means of dialysis still demonstrated a minimum at the sediment surface and no leaching to the overlying water, an immobilization of P in the 0–10 cm top layer was obvious.

Beginning from the classical works of Mortimer (1941, 1942), iron complexes are the most frequently quoted factor determining P mobilization in the sediment. They have a key position even in calcareous sediments (Löfgren, 1987). Holdren and Armstrong (1986) stated that the oxidation of ferrous iron prevents P moving from the sediment solid phase into the pore-water, if the atomic Fe/P ratio in the interstitial water is higher than 1.8. Gunnars and Blomqvist (1997) summarizing published Fe/P ratios for marine and freshwater ecosystems show that the predominant Fe/P surface complexation ratio of ferric hydroxide is 2, hence, for Fe/P ratios lower than 2 in the dissolved phase the available iron is in too short supply to bind all dissolved phosphate. Jensen *et al.* (1992) suggested that a Fe/P ratio by weight of 15 in the oxidized sediment would be able to control release of SRP to the overlying water column if pH of the sediment surface is less than 8.0. Referring to Lijklema (1977) the authors stated that at $pH > 8$ the saturation of the sorption sites on $FeOOH \cdot H_2O$ begins at a Fe/P ratio by weight of about 25. In spite of the relatively low iron concentration in L. Võrtsjärv surface sediment, the Fe/P ratio ranging from 26 to 30 could probably be able to keep phosphates adsorbed in the undisturbed sediment. However, due to the strong dependence of the adsorption-desorption equilibrium on pH (Boström *et al.*, 1982; Søndergaard, 1988, 1990), phosphate liberation may occur when sediment particles are carried to the water column having pH between 8.0 and 8.8 in L. Võrtsjärv. The SRP release during summer revealed by the net budget was most probably caused by intensive mineralization of P associated with fresh organic deposits.

The effect of storms on the redistribution of sediments in shallow lakes was clearly demonstrated by Bengtsson *et al.* (1990). The authors showed that a single storm may distribute more bottom material than the total annual resuspension caused by frequent but smaller wind events. Until resuspension concernes the oxidized sediment surface layers having a similar SRP content with the overlying water, no increase in the water phosphate pool occurs. SRP can be additionally adsorbed on the fine-grained particles if there are free adsorption sites (Fitzgerald, 1970; Wisniewski, 1995). In Lake Memphremagog Peters and Cattaneo (1984) found a significant difference in TP concentrations between calm and windy days, but the turbulence had no effect on SRP concentrations. However, the authors admit that internal SRP loading may occur when resuspension reaches deeper, anoxic sediments with high P concentration in pore-water. In L. Võrtsjärv the daily release of SRP ($45.2 \cdot 10^3$ kg) during the storm exceeded the annual external P load to the lake ($21.8 \cdot 10^3$ kg of SRP, $35.4 \cdot 10^3$ kg of TP, Järvet, 1997).

The sensitivity of P release on meteorological conditions, especially wind velocities and direction, makes shallow lakes more unpredictable compared to stratified lakes whereas very substantial variations can occur between years (Marsden, 1989). However, the interannual difference in sediment P content in L. Võrtsjärv (2.13 g m^{-2} in the 10 cm top layer) could not be explained by release. Extrapolating this value to the externally homogenous gyttja area of the lake (~90 km^2), gives a difference of $192 \cdot 10^3$ kg in annual mean sediment P pools. This value is clearly unrealistic, as the external budget for 1995 showed an efflux of only $44 \cdot 10^3$ kg P and there was almost no increase in the water column P pool. There can be two explanations for this contradiction: either the results of the measurements were incorrect, or the changes were of a local character and, hence, not representative for the whole area. The latter assumption is supported by the significant correlation found between the sum of P fractions per sediment dry weight and the water level. Probably, the large changes in the water level caused redistribution of sediments while the status of the sampling area changed: the place belonging to the accumulation bottom at high water level was strongly eroded at low water level. This denuded the deeper sediment layers with a lower P content. An objection to this hypothesis is the similar behaviour of NaOH-RP and HCl-RP in the time series ($r = 0.88$). Assuming the denudation of deeper layers, NaOH-RP ought to decrease but HCl-RP to increase in a vertical profile.

6. Conclusions

1. The extremely low pore-water SRP concentration in the surficial sediment, indicating a small potential phosphate release during most of the year, could be attributed to the high Fe/P ratio and to the oxidation of the surficial sediment by frequent resuspension.
2. At heavy storms that denude the deeper anoxic sediment layers, large internal SRP loadings may occur that exceed the annual load from the watershed.
3. The variable water level in L.Võrtsjärv is responsible for the alternation of erosion and deposition processes in the gyttja area, homogenous by appearances, resulting in the formation of local changes in sediment composition.

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Distribution of sediment phosphorus fractions in hypertrophic strongly stratified Lake Verevi

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Abstract

Lake Verevi is a hypertrophic and strongly stratified (partly meromictic) small temperate lake. Vertical distribution of sediment phosphorus fractions as well as iron, manganese, organic matter and calcium carbonate of the deep bottom sediment was determined. The study focused on the ecologically important layer of the sediment [<20(45) cm]. In the uppermost layers of the sediment, NaOH-NRP (organic P) dominated while HCl-RP (apatite-P) became dominant in some deeper layers below 7 cm. Extremely high concentrations of labile phosphorus fraction (NH_4Cl-RP) indicated the low binding capacity of phosphorus by lake sediment. Due to sediment and hypolimnion anoxia, the internal load of phosphorus in this lake is most likely. Potentially mobile phosphorus fractions (NH_4Cl-RP, BD-RP, NaOH-NRP) formed 301 kg in upper 10 cm thick sediment layer of hypolimnetic bottom sediment (40% of lake bottom area).

Introduction

Phosphorus is the key element of eutrophication processes in many lakes. Phosphorus supply to the euphotic zone depends on the external load and also on the tendency of sediments to retain or release phosphorus. The intensity of water mixing and stratification play an important role in this process. Stratification may lead to anoxic conditions, lowered pH and accumulation of nutrients in both hypolimnion and surface sediments of eutrophic lakes.

Total phosphorus concentration is a poor measure of the potential phosphorus release from sediments. Chemical fractionation of sedimentary phosphorus has served as a tool to predict the phosphorus binding capacity of sediments under different environmental conditions. In most cases, the potential internal load is the matter of interest.

The aim of present study was to determine the distribution of phosphorus fractions and other chemical properties of surface sediments in hypertrophic strongly stratified and partly meromictic Lake Verevi. The special emphasis of the study was focused on the upper 20 cm of sediment, which could take part in nutrient exchange between the water column and bottom.

Study site

Hypertrophic hard-water Lake Verevi is situated in South Estonia, within the borders of town Elva. General description of the ecosystem as well as detailed information on the location and bathymetry of the lake is presented by Ott et al., (2005a, 2005b). The lake has a surface area of 12.6 ha, maximum depth of 11 m, mean depth of 3.6 m and theoretical water residence time on an average 0.5 times per year. The deepest part of the lake is situated in the middle of the southern part of the lake while the narrow northern part is shallow and largely covered by macrophytes. The lake is strongly stratified and during winter covered by ice. In early warm springs, the stratification may be formed so rapidly that the spring turnover is absent. The lake is sheltered from winds and no marked water mixing due to wave action occurs.

The lake, especially its shallow northern part is rich in springs. The upper layer of sediment in the northern part is soft greyish-green calcareous mud. In the southern part, the upper 30–50 cm thick sediment layer consists of H_2S-rich greenish-black mud, apparently being formed in anoxic conditions. In 1989, the phosphorus content of the surface sediment of Lake Verevi was determined with the depth resolution of 20 cm (Rummi et al., 1991). The lowest phosphorus value of 0.4 mg g^{-1} of dry sediment (DW) has been reported from the northern part of the lake, the highest concentration from the middle area of the southern part was 1.4 mg g^{-1} DW.

Materials and methods

Field work

Sediment samples were collected using Willner core sampler in four occasions: August 1994 (one core, length 45 cm), March 2001 (two cores, 15 and 25 cm long), June 2001 (two cores, both 4 cm long) and August 2001 (both cores 15 cm long). In March and June 2001, samples were collected from the eastern part of the lake's deepest bottom area at a depth of 6–8 m. In 1994 and August 2001, samples were collected close to the deepest point of the lake at the water depth of 9 m. Parallel cores were collected within the distance of 20 m.

The cores were sliced immediately after sampling. The slicing intervals were following: 0–2 cm, 2–5 cm, 5–10 cm in 1994, 0–2 cm, 2–5 cm, 5–7 cm, 7–10 cm in March 2001 and 0–1 cm, 1–2 cm, 2–3 cm, 3–4 cm, 4–5 cm, 5–7 cm, 7–10 cm in June and August 2001; deeper than 10 cm, all cores were sliced with 5 cm intervals. The samples were kept in closed plastic bags in an icebox until they could be stored at 4 °C (normally within 1 h after sampling). The laboratory analyses began 1 week after sampling in 1994 and on the following day in 2001.

Laboratory analyses

The concentrations of dry matter and phosphorus fractions in the sediment were analysed. Additionally, in 1994, the concentrations of organic matter, carbonates, iron, manganese and total phosphorus were measured.

The concentration of dry matter of the sediment was calculated from weight difference before and after drying of triplicate samples at 105 °C for 24 h. The bulk density of the sediment was calculated according to Håkanson & Jansson (1983), enabling to determine the phosphorus amount in certain sediment volume.

The concentration of organic matter of the sediment was determined by the loss of weight during ignition at 550 °C for 2 h. Ignition residue was further ignited at 825 °C for 4 h. The loss of weight was ascribed to the emission of carbon dioxide serving as a basis for calculation of the carbonate concentration.

Manganese and iron concentrations were measured using Atomic Adsorption/ Flame Emission Spectroscopy (AA/FES, Shimadzu AA-670) after digestion of dry sediment in 7 M HNO_3. The content of total phosphorus was determined spectrophotometrically according to Murphy & Riley (1962) after boiling of dry sediment in mixed acids (conc. H_2SO_4, HNO_3, $HClO_4$).

Sediment phosphorus fractionation was performed in triplicates according to Hieltjes & Lijklema (1980) at the first three sampling cases. Sediment was extracted in four following steps with three solutions: NH_4Cl, NaOH and HCl. From these solutions, the concentration of soluble reactive phosphorus was measured according to Murphy & Riley (1962). The following fractions were gained:

1. NH_4Cl-RP (RP = reactive phosphate) – labile, loosely bound or adsorbed P.
2. NaOH-RP represents the phosphates adsorbed to metal (Fe, Al) oxides and other surfaces, exchangeable against OH^-, and phosphorus compounds soluble in bases.
3. NaOH-NRP (NRP = non-reactive phosphate) is calculated as the differences between total P in the NaOH extract, measured by peroxosulphate digestion, and NaOH-RP. It is assumed to represent the major part of organic and humic P.

4. HCl-RP represents phosphorus bound to carbonates, apatite-P and P released by the dissolution of oxides (not adsorbed to the surface).

In August 2001, the modified scheme of Psenner et al. (1988) was used for phosphorus fractionation. The advantage of the latter is the separation of iron-bound (BD-RP) and aluminium-bound phosphorus (NaOH-RP) by including an additional extraction step with reducing agent (buffered dithionite). The original scheme of Psenner et al. (1988) was modified by using 0.1 M NaOH instead of 1.0 M NaOH in the second extraction step for better comparison with the earlier results gained by the scheme of Hieltjes & Lijklema (1980). Results of phosphorus fractions are given as means of three or, in the case of two independent parallel cores, as six values.

Results

Dry and organic matter, carbonates

The content of dry matter (DM) of sediment samples varied from 2.8 to 30% of wet weight (WW). DM was lower at the sampling depth of 9 m and higher in shallower water (at 6–8 m). The maximum values of DM occurred around 2–10 cm below the sediment surface. In all cores, a gradual decrease was observed below peak values in the sediment depth between 7 and 15 cm. The lowest values always appeared in the surface layers of the cores differing up to 3.7 times between the cores (from 2.8 to 10.4% WW). The concentration of organic matter (OM) determined from the core of August 1994, showed increasing values towards the bottom of the core (Fig. 1), while the content of carbonates had the opposite vertical distribution.

Metals and total phosphorus

The concentration of Fe and Mn in the upper 40 cm of the sediment was 865–1448 and 110–520 mg g^{-1} DW, respectively, showing more than three-fold decrease from the surface layer towards the bottom of the core (Fig. 1). The concentration of total phosphorus reached the value of 1.5 mg g^{-1} DW in the sediment depth of 5–10 cm and declined more than 1.5 times by the depth of 40 cm. The Fe/P mass ratio was 7.9–18.1 in the core from August 1994 and remained below 10 in the layer of 5–10 cm and deeper than 30 cm.

Phosphorus fractions

Except of June 2001, NaOH-NRP was the largest phosphorus fraction in the surface sediment

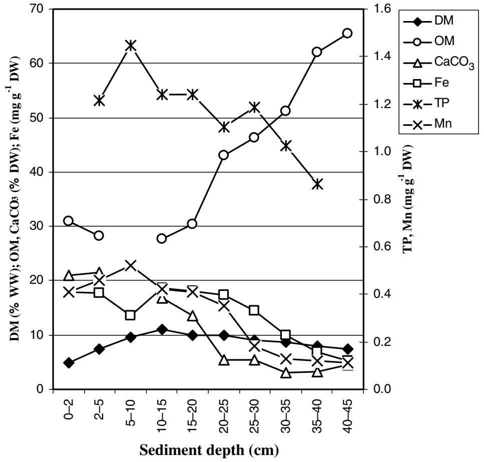

Figure 1. Vertical profiles of total phosphorus (TP), $CaCO_3$, dry weight (DW), organic matter (OM), total iron (Fe) and manganese (Mn) in the sediment of Lake Verevi in August 1994.

(Fig. 2). HCl-RP became dominant in some deeper (>7 cm) sediment layers. NaOH-RP, determined according to the fractionation scheme of Hieltjes & Lijklema, (1980) exceeded the concentration of NH_4Cl-RP. Analysed by the method of Psenner et al. (1988), NaOH-RP was the smallest fraction in upper 7 cm. Its concentration was 1.0–2.6 (average 1.9) times lower than that of BD-RP. Except of August 2001, NH_4Cl-RP was the smallest of all fractions. In August 2001, the extreme concentration of NH_4Cl-RP (526 μg g^{-1} DW) appeared in the depth of 4–5 cm constituting 39% of the sum of all phosphorus fractions in that sediment layer.

The cores of June 2001, which were sampled from 6–8 m water depth, differed from other cores by comparatively high concentration of dry matter and low concentration of NaOH-NRP. In contrast to other cores, HCl-RP exceeded the NaOH-NRP concentration in surface layers.

The phosphorus content in upper 40 cm of the hypolimnetic bottom sediment was calculated on the basis of the data from August 1994 (Table 1). Due to poor sediment compaction, 5 cm thick surficial sediment layer contained only half of the phosphorus amount present in the 5–10 cm sediment layer. A gradual decrease of phosphorus amount appeared below 10 cm. Residual phosphorus, i.e. the calculated difference between the sum of measured phosphorus fractions and total phosphorus, constituted 0–10.7% (average 3.8%) of total phosphorus.

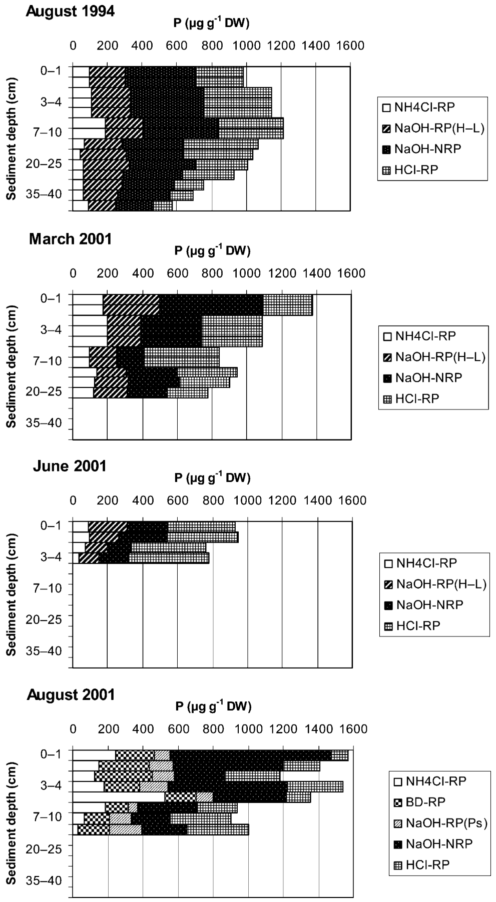

Figure 2. Distribution of phosphorus fractions in the sediment of Lake Verevi. H–L = determined according to Hieltjes & Lijklema (1980); Ps = determined according to modified scheme of Psenner et al. (1988). Intervals of the sediment slicing were different for different cores but fitted together with the smallest possible interval for comparison (see Materials and methods).

Discussion

Lake Verevi is highly eutrophic despite of the moderate external phosphorus load. The significant rise in phosphorus concentrations in hypolimnion during stagnation periods indicates that such a high content of that nutrient in the lake water is probably maintained by the phosphorus supply from the sediments (Nõges, 2005).

The total phosphorus content of the sediment of Lake Verevi was relatively low, compared to some other stratified and eutrophic Estonian lakes such as Lake Arbi (average for upper 35 cm 4.04 mg g^{-1}), Lake Martiska (average 2.6 mg g^{-1}) (unpublished data) and Lake Ruusmäe (average 5.2 mg g^{-1}) (Kruusement & Punning, 2000). Sediment phosphorus concentration of Lake Verevi was similar to shallow and eutrophic lakes such as Lake Võrtsjärv (average for upper 50 cm 0.78 mg g^{-1}) (Nõges & Kisand, 1999).

Total phosphorus content of lake sediment is not well correlated with the amount of released phosphorus, and the potentially mobile phosphorus in sediments is poorly defined. However, easily degradable organic phosphorus can be regarded as potentially mobile, and phosphorus adsorbed to iron surfaces is highly available during anaerobic conditions (Pettersson, 1998). In anoxic conditions, Fe^{3+} is reduced to Fe^{2+}. As a result, both iron and adsorbed phosphorus are transferred into soluble form (Boström et al., 1982). Using the fractionation scheme of Hieltjes & Lijklema (1980), phosphorus adsorbed to iron is included in NaOH-RP. The scheme of Psenner et al. (1988) separates this fraction into BD-RP (phosphorus adsorbed to iron) and NaOH-RP (Al-bound P). In the sediment of Lake Verevi BD-RP formed larger fraction than NaOH-RP.

The anoxic conditions and presence of H_2S in the hypolimnion of Lake Verevi suggest iron to occur in reduced form since sulphate reduction takes place at lower redox potential than the reduction of iron (Boström et al., 1982). In addition, in a reaction between Fe^{2+} and S^{2-} FeS can be formed which is highly a insoluble compound in natural conditions and hence inactivates iron. The mass ratio between active iron and phosphorus may be critical for phosphorus release if the sediment is oxidized or shifts from reduced conditions to oxidized status. This can be important for the sediment with changing oxidized or reduced conditions at the border of the hypolimnetic bottom area. Jensen et al. (1992) suggested, that a Fe/P ratio by weight of 15 in oxidized sediment would be able to control release of SRP (soluble reactive phosphorus) to the overlying water column if the pH of the sediment surface is less than 8.0. In the sediment core sampled from

Table 1. The contents of total phosphorus and phosphorus fractions (kg) in different sediment layers of the hypolimnetic bottom (40% of the lake bottom area)

	NH_4Cl-RP	NaOH-RP	NaOH-NRP	HCl-RP	TP	TP, cumulative
0–2 cm	5	10	20	14	49	49
2–5 cm	12	26	49	45	140	189
5–10 cm	46	55	109	93	362	551
10–15 cm	20	63	103	124	361	912
15–20 cm	12	69	87	105	327	1239
20–25 cm	15	68	99	79	285	1524
25–30 cm	14	54	80	68	277	1802
30–35 cm	14	50	67	38	228	2030
35–40 cm	12	41	63	27	178	2207

hypolimnetic bottom of Lake Verevi in August 1994 most Fe/P values remained below 15.

NaOH-NRP has been shown to be a potentially mobile phosphorus fraction (Rydin, 2000). This fraction is traditionally considered to consist of mainly organically bound phosphorus. Hupfer & Rübe (2004) showed in their study with many different lake sediments that up to 46% of the NaOH-NRP consisted of intracellular inorganic polyphosphates of microorganisms. The transformation of organic phosphorus compounds and polyphosphates can contribute significantly to the release of phosphorus during early diagenesis.

NH_4Cl-RP includes dissolved phosphates of sediment pore water. This phosphorus pool is maintained by the dissolution of particulate sediment phosphorus while diffusion into lake water takes place simultaneously to compensate the concentration gradient. High concentrations of NH_4Cl-RP at the depth of 4–5 cm in cores of August 2001 could refer to the extensive phosphorus saturation of the sediment. This stage could be favoured by seasonal changes such as enhanced sedimentation of organic matter and its intensive degradation due to high summer temperatures. However, somewhat higher concentration variations of all phosphorus fractions could probably be detected in previous sampling cases, too, if a more detailed depth resolution was used in surficial sediment layers.

NH_4Cl-RP, NaOH-NRP and BD-RP can be considered potentially available phosphorus fractions in Lake Verevi, i.e. a part of these fractions can be released into lake water under appropriate conditions. Referring to Table 1 and considering, that approximately two third of NaOH-RP (measured according to Hieltjes & Lijklema) consists of BD-RP, potentially mobile fractions form 301 kg in upper 10 cm thick sediment layer of hypolimnetic bottom sediment (40% of lake bottom area). The actual share of phosphorus to be released cannot be determined on the basis of phosphorus fractions.

Lake Verevi is stratified during most of the year. Phosphorus, released from sediments, accumulates in hypolimnion, often resulting in more than ten-fold concentration of this nutrient compared to that in epilimnion (Ott et al., 2005a). Since water mixing by wave action does not play an important role in Lake Verevi, phosphorus can spread into upper water column only during water circulation in spring and autumn. These events are followed by algal blooms (Kõiv & Kangro, 2005). Some of the phosphorus is likely to be removed from water column by macrophytes as Lake Verevi is relatively small by area, and, therefore, relatively significant phosphorus uptake by littoral zone vegetation could be suspected. After decaying of planktonic organisms, phosphorus is released both in water column and in sediments. Pettersson (1998) studied the phosphorus content in suspended matter, settling particles and sediment of stratified eutrophic Lake Erken, and showed that phosphorus rich material in the water releases phosphorus on its way down to the sediment, and that a further release takes place from the sediment. Probably it was the case for Lake Verevi too, the most part of organic material trapped into epi-, meta- and hypolimnion and was degraded before it ever reached to the sediments (Ott et al., 2005b). The remaining material reaches sediments and partially returns to the water column again.

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IV

Kisand, A. & P. Nõges (2003). SEDIMENT PHOSPHORUS RELEASE IN
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SHALLOW LAKES: IMPORTANCE OF OXYGEN CONDITIONS.
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Sediment phosphorus release in phytoplankton dominated *versus* macrophyte dominated shallow lakes: importance of oxygen conditions

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Key words: lake sediments, phosphorus release, phosphorus fractionation, redox conditions

Abstract

We studied the potential release of phosphorus from the surface sediments of two shallow eutrophic lakes, plankton-dominated Lake Kaiavere and calcareous macrophyte-dominated Lake Prossa, in relation to phosphorus forms and anoxic-oxic conditions. The distribution of phosphorus forms was determined before and after six-week-long incubation of the sediments in oxic and anoxic (H_2S enriched) conditions. The phosphorus fractionation scheme of Psenner et al. (1988) was basically followed. Summarising the release from all considered fractions, the L. Kaiavere sediment lost two times more phosphorus in anoxic than in oxic conditions while no significant difference between these oxygen conditions was found in the L. Prossa sediment. NH_4Cl-RP and NaOH-RP showed similar release patterns in both sediments. In NaOH-NRP (the dominant fraction in both sediments), BD-RP and HCl-RP differences between lakes occurred. About half of the HCl-RP pool in L. Prossa sediment was released during the incubation whereas the phosphorus content in this fraction remained comparatively stable in L. Kaiavere sediments. Calcium-bound phosphorus compounds measured in this fraction seem to have a variable potential mobility. The results of this study indicate that the potential phosphorus release from a single sediment phosphorus fraction may differ between lakes despite similar oxygen conditions.

Introduction

Phosphorus is the key element of eutrophication processes in many lakes. Attempts to improve the trophic status of many lakes has led to a knowledge of the complex nature of the phosphorus cycle in sediments; Heidenreich & Kleeberg, 2003; Hupfer & Dollan, 2003; Søndergaard et al., 2003. Sediments can both accumulate and release phosphorus.

Phosphorus release from sediments is a function of the quantity and distribution of phosphorus compounds within the sediment, the degree of saturation of exchangeable phosphorus, the intensity of biological processes in sediment and lake water, and of hydrological conditions (Jansson et al., 1988). One approach to understanding the complex nature of phosphorus mobilisation is to look for relationships between the distribution of the various forms of phosphorus in sediment and the effect of certain environmental conditions (Gunatilaka et al., 1988).

We performed a laboratory release experiment on surface sediments of two shallow eutrophic lakes. Our aim was (1) to compare the potential sediment phosphorus release in oxic and anoxic conditions and (2) to estimate whether the same phosphorus fractions from different lake sediments have the same capacity to retain or release phosphorus in certain oxygen conditions.

Study site

Lake Prossa and Lake Kaiavere are situated in Central Estonia. Both lakes are shallow, non-stratifying and eutrophic. The surface area of Lake Prossa is 33 ha, mean depth 2.2 m, maximum depth 4.2 m (Mäemets, 1977). The lake bottom is largely covered by macrophytes, mainly *Chara* species, but *Potamogeton* species are also abundant. Oxygen depletion has occurred in the water column of L. Prossa during the ice-covered period. A sapropel layer (thickness 1.5 m) covers the bottom of the lake (Mäemets, 1977). Vertical compaction results in a dry weight content that changes from 7% of wet weight in the one cm thick surface layer to 23% at a depth of 7 cm .

Lake Kaiavere is a plankton-dominated lake with a surface area of 250 ha, mean depth 2.8 m and maximum depth 5 m. Sapropel covers 150 ha of the lake bottom (Mäemets, 1977). The lake is exposed to winds and the turbidity of lake water can be high due to sediment resuspension. The sediment is mixed up frequently and is very homogenous. The dry weight content increases from 5% of wet weight in the sediment surface to 12% at 20 cm depth. The lake has received sewage water from a poultry farm.

Materials and methods

Field work

One sediment core was collected by Willner sampler from the deepest parts of each lake on 8 Nov. 2001. Immediately after sampling, a three cm thick sediment surface layer was separated and kept in cooling boxes (ca one hour) until storing in refrigerator at 4 °C. The laboratory analyses started on the following day.

Release experiment

The fractional composition of sediment phosphorus was determined before and after a 6-weeks-long release experiment. Samples of the wet sediment (about 400 mg) were weighed and added, along with 10 ml distilled water, into bags formed of dialysis membrane tubing (SPECTRA/POR 4, cut-off 12 000–14 000 D, Spectrum Medical Industries Inc.). The bags were put into 250 ml Erlenmeyer flasks filled up with either oxic or anoxic water, and covered with caps. Three parallel samples were included for both lake sediments in both oxygen conditions. Distilled water was intensively aerated during 20 min to create the oxic conditions. The anoxic conditions were created by storing distilled water with gaseous H_2S in a closed system. The resulting anoxic solution was neutralised with 0.1 m NaOH to avoid effects of low pH on phosphorus release processes. The water in the flasks was replaced once a week to maintain sharp concentration gradients and to support diffusion of phosphorus through the dialysis membrane. The experiment was run at room temperature to accelerate the release of phosphorus, and in darkness. At the end of the incubation the contents of the dialysis bags were filtered (25 mm GF-F, 0.45 μm) and sequential extraction performed on the sediments together with the filter. For further calculations the dry weight of filtered material was considered to be equal to the dry weight of sediment initially included in dialysis bags.

Laboratory analyses

The water content of the sediment was calculated from weight differences before and after drying of triplicate sediment samples at 105 °C to constant weight.

Phosphorus forms in the sediment were determined from three parallel samples using the modified fractionation scheme of Psenner et al. (1988). For the sodium hydroxide extraction step 0.1 M NaOH was used instead of 1 m NaOH as in the original scheme (Rydin, 1999). Five phosphorus fractions were determined: NH_4Cl-RP (RP = reactive phosphorus), BD (buffered dithionite)-RP, NaOH-RP, NaOH-NRP (NRP = non-reactive phosphorus) and HCl-RP. NH_4Cl represents loosely sorbed P including calcite P; BD-RP extracts Fe-P and Mn-P; NaOH-RP includes Al-P; NaOH-NRP consists of P bound to organic compounds; HCl-RP represents Ca-bound P. Total phosphorus measurements, and hence the calculation of a residual phosphorus fraction, were omitted due to technical reasons. Reactive phosphorus was measured spectrophotometrically according to Murphy & Riley (1962). Non-reactive phosphorus in the NaOH extract was calculated from the difference between reactive phosphorus and total phosphorus measured after oxidation of NaOH extract by $K_2S_2O_8$ at 120 °C during 1 h.

Results

The dominant phosphorus fraction in the sediments of both lakes was NaOH-NRP (on an average 330 μg P/g DW in L. Prossa and 315 μg P/g DW in L. Kaiavere). In L. Prossa it was followed by HCl-RP (206 μg P/g DW) and smaller fractions of BD-RP, NaOH-RP and NH_4Cl-RP with concentration of each between 60 and 75 μg P/g DW. In L. Kaiavere NaOH-NRP was followed by a large portion of NH_4Cl-RP (163 μg P/g DW) and smaller fractions of NaOH-RP, HCl-RP and BD-RP with concentrations of each ranging from 63 to 80 μg P/g DW.

Table 1. Comparison of the P fractions under oxic and anoxic conditions in L. Kaiaver and L. Prossa

Fractions	Difference between Lakes	 Initial/oxic/anoxic	Coeffect Lake*initial/oxic/anoxic
NH_4Cl-RP	***	***	n.s
BD-RP	n.s.	***	*
NaOH-RP	**	***	n.s.
NaOH-NRP	n.s.	***	**
HCl-RP	***	***	***

Statistical differences in ANOVA between grouping variables - different lakes and different oxic conditions compared to initial status. *** $p < 0.001$. ** $p < 0.01$. * $p < 0.05$. n.s. - not significant.

The sum of phosphorus measured from all of the five fractions before incubation, was 697 (S.D.±36) μg P/g DW in the sediment of L. Kaiavere. Twenty six percent of that amount (182±67 μg P/g DW) was lost during incubation in oxic conditions and 49% (344±45 μg P/g DW) in anoxic conditions. In the sediment of L. Prossa the original phosphorus content in all fractions was 737 μg P/g DW, with 42% of it (312±58 μg P/g DW) released under oxic conditions and 38% (281±59 μg P/g DW) under anoxic conditions. According to the ANOVA Post-hoc Bonferroni/Donn test these two treatments did not differ significantly in L. Prossa unlike in L. Kaiavere (for L. Kaiavere $p < 0.01$).

In the sediment of L. Kaiavere the average phosphorus release from each fraction was generally higher in reduced than in oxidised conditions (see Fig. 1). In the sediment of L. Prossa the average concentrations of P in NaOH-RP, NaOH-NRP and HCl-RP were slightly higher in the anoxic environment than in the oxic. However, the differences between anoxic and oxic treatments were statistically significant only for NH_4Cl-RP, NaOH-NRP and HCl-RP of the sediment of L.Kaiavere, and for NH_4Cl-RP and NaOH-RP of the sediment of L. Prossa. Differences between the original status and oxic treatment, and between original status and anoxic treatment, of the L. Prossa sediment, and between the original status and anoxic treatment of L. Kaiavere sediment, were significant. On the other hand, the differences between the original status and oxic treatment of the L. Kaiavere sediment were significant only for NH_4Cl-RP and NaOH-NRP. As a result of variance in redox behaviour, BD-RP, the largest fraction NaOH-NRP, and HCl-RP showed different phosphorus release/retention patterns in the two lakes (Table 1).

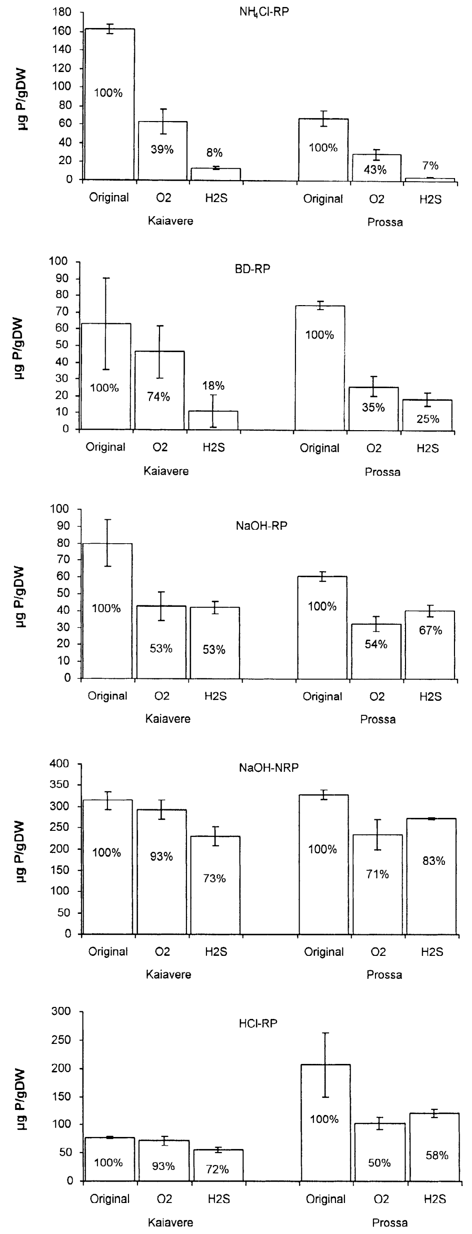

Figure 1. Sediment phosphorus fractions (± S.D.) before and after incubation in oxic (O_2) and anoxic (H_2S) conditions in Lake Prossa and Lake Kaiavere.

Discussion

Anoxia is likely to occur not only in the sediments of stratified lakes with anoxic hypolimnion, but also in the sediments overlaid with oxic water. In the latter case the decomposition of organic matter can create anoxic microlayers under the oxic surface layer of sediments. The oxygen conditions used in the present study simulate redox status above and below the redoxcline in sediments. In addition, oxygen depletion during winter has been reported in L. Prossa (Mäemets, 1977), indicating anoxia at the sediment-water interface as well.

The sediments of L. Kaiavere and L. Prossa have different sensitivity to oxygen conditions. The pool of potentially mobile phosphorus in the L. Kaiavere sediment was two times higher in anoxic than in oxic conditions. The phosphorus amounts released from L. Prossa sediments did not differ significantly. As a rough estimate, about half of the phosphorus included in all studied fractions could be released from these sediments under appropriate oxygen conditions. The different release pattern from sediments with similar total phosphorus concentration once again supports the fact that the total phosphorus content in particulate matter does not reflect the role of sediment in phosphorus cycling between sediment and water (Boström et al., 1982). The sediment's different sensitivity to redox conditions derived not only from the different distribution of phosphorus forms, but also from the varied responses of individual fractions to altered oxygen conditions. The proportion released from BD-RP in oxidised conditions was much higher in the sediment of L. Prossa than that of L. Kaiavere. However, similar proportions of phosphorus were released from BD-RP in reduced conditions. A different redox behaviour was found in the dominating fraction of NaOH-NRP. Rydin (1999) found that a 1 cm thick L. Erken surface sediment released five times more phosphorus in reduced than oxidised conditions, the maximum loss being about half of the original NaOH-NRP pool.

A potentially mobile portion of calcium-bound P was included in the HCl-RP fraction in the sediment of L. Prossa but not in L. Kaiavere. This fraction released about half of its phosphorus in the sediment of the calcareous macrophyte-dominated lake, while it remained comparatively stable in the sediment of the plankton-dominated lake. The differences derived from oxygen conditions were of minor importance. HCl-RP is generally considered to consist primarily of apatite. However, Pettersson et al. (1988) stress that in calcareous sediments phosphorus can be bound to calcium without having to be in apatite form. Phosphorus can be adsorbed on the surface of calcium carbonate. L. Prossa has a large proportion of HCl-RP in its sediments. This pool can be supported by phosphorus adsorbed on the calcite crusts that can be seen on *Chara* stems in L. Prossa. The formation of such a crust is a well-known process (Graneli & Solander, 1988). Ammonium chloride used in the first steps of sequential extractions dissolves calcium carbonate and releases phosphorus adsorbed to calcite (Pettersson et al., 1988). Pettersson & Istvanovics (1988) demonstrated that up to three times more phosphorus was extracted from calcareous L. Balaton sediment when the ammonium chloride extraction step was repeated eleven times instead of the two times normally used. In the calcareous L. Prossa sediment the second NH_4Cl extraction yielded as much reactive phosphorus as the first extraction. In the L. Kaiavere sediment the extracted phosphorus amounts declined three times along these two steps. We suggest that during the first fractionation of the sediment of L. Prossa the NH_4Cl extraction left a lot of easily desorbed calcium-bound phosphorus in place due to too few repetitions and that this P was extracted in the last extraction step by HCl.

The impact of sulfide content was not considered in this study, although addition of H_2S could enhance the mobilisation of phosphates during anoxic incubation (Roden & Edmonds, 1997). Nevertheless, the treatment was consistent for both sediments, allowing for comparision of the results from the two lakes.

In many sediment studies connected to water management or lake restoration, researchers need to estimate the maximum (or potential) release of sediment phosphorus in oxic and anoxic conditions. However, we face uncertainties when predicting potential phosphorus release based only on the distribution of phosphorus forms because we do not know what proportion could be liberated from a given fraction in the case of a given sediment.

Conclusions

The two lake sediments studied, had different sensitivities to oxygen conditions. In calcareous macrophyte-dominated Lake Prossa the amounts of phosphorus released in oxic and anoxic conditions were equal, whereas in the plankton dominated L. Kaiavere two times more phosphorus was released in anoxic than in oxic conditions.

Comparing the oxic/anoxic phosphorus release pattern of each phosphorus fraction, significant differences between the two studied sediments appeared in the case of BD-RP, NaOH-NRP and HCl-RP.

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Projects:

2008-2013, Target financed project SF0170011s08 "Will climate change alter the relative importance of catchment and in-lake processes in the carbon balance of shallow lakes?", principal performer

2008-2013, Estonian Science Foundation grant 7600 "Is Lake Võrtsjärv an autotrophic or heterotrophic system? The role of autochthonous and allochthonous organic matter in the budget of a large shallow lake", principal performer

2006-2008, Estonian Science Foundation grant 6741 "Organic matter and photosynthetic pigments in sediments of lakes Peipsi and Võrtsjärv as markers to follow ecosystem changes in large shallow lakes", PhD student

2005-2007, Estonian Science Foundation grant 6080 "Microbial diversity and activity in the sediments and water column of shallow lakes", PhD student

2003-2007, Estonian Science Foundation grant 5738 "Impact of climate change on ecosystems of large shallow lakes, mediated by the altered inflow of substances", PhD student.

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2000-2003, Estonian Science Foundation grant 4080 "Ecosystem functioning in phytoplankton-dominated vs.macrophyte-dominated shallow lakes", MSc student.

1999-2001, EVK1-CT-1999-39 "Ecological quality and functioning of shallow lake ecosystems with respect to the needs of the European Water Framework Directive" (ECOFRAME), MSc student.

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Projektid:

2008-2013, Sihtfinantseeritav teema SF0362480s03 “Kas kliimamuutus muudab valgala- ja järvesiseste protsesside osakaalu madala järve süsinikubilansis?”, põhitäitja

2008-2013, Eesti Teadusfondi grant 7600 “Kas Võrtsjärv on valdavalt auto- või heterotroofne süsteem? Autohtoonse ja allohtoonse orgaanilise aine vahekord suure madala järve ainebilansis”, põhitäitja

2006-2008, Eesti Teadusfondi grant 6741 “Orgaaniline aine ja fotosünteesipigmendid Peipsi ning Võrtsjärve settes kui markerid ökosüsteemi muutuste jälgimiseks suurtes madalates järvedes”, doktorant

2005-2007, Eesti Teadusfondi grant 6080 “Mikroobne mitmekesisus ja aktiivsus madalate järved setetes ning vees”, doktorant

2004-2007, Eesti Teadusfondi grant 5738 “Kliimamuutuste mõju suure madala järve ökosüsteemile ainete sissekande muutuste kaudu”, doktorant

2003-2007, Sihtfinantseeritav teema SF0362480s03 “Kliimamuutuste mõju madalate järvede ökosüsteemile, doktorant

2000-2003, Eesti Teadusfondi grant 4080 “Ökosüsteemi talitluse erinevused fütoplanktoni- ja makrofüüdienamusega madalates järvedes”, magistrant

1999-2001, EVK1-CT-1999-39 “Ecological quality and functioning of shallow lake ecosystems with respect to the needs of the European Water Framework Directive” (ECOFRAME), magistrant.

1998-2000, Eesti Teadusfondi grant 3579 “Suvise temperatuurikihistuse mõju aineringele järve ökosüsteemis”, magistrant

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3.2. Papers published in books by Estonian or foreign publishers not listed in the ISI Web of Proceeding

Ott, I. & A. Kisand, 2002. Neitsijärve noorendamisprobleemidest: ökosüsteemi seisund ja sette osatähtsus. A. Maastik (Ed.), Jäätmed ja loodushoid. Waste and nature protection: 69-85.

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