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

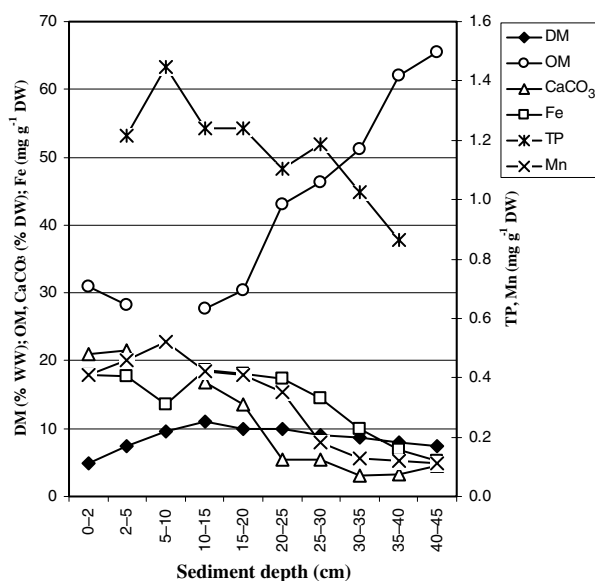Except of June 2001, NaOH-NRP was the largest phosphorus fraction in the surface sediment

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 $\mu g\ g^{-1}$ 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.

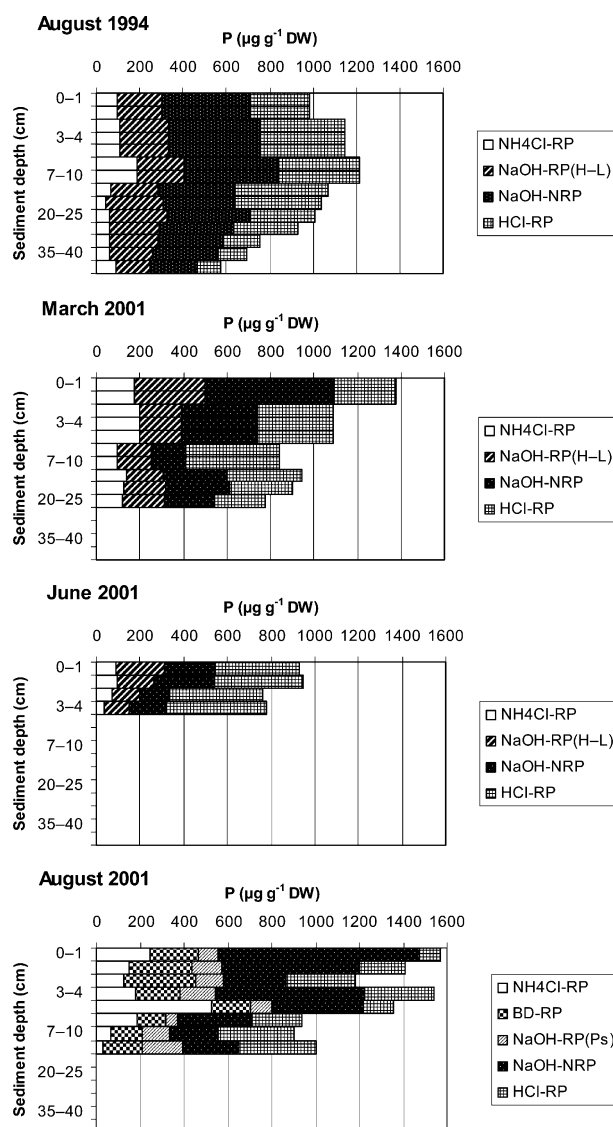The phosphorus content in upper 40 cm of the hypolimnetic bottom sediment was calculated on

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).

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.

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$_4$Cl-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

38

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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