

DISTRIBUTION OF PHOSPHORUS IN THE SEDIMENT CORE OF HYPERTROPHIC LAKE RUUSMÄE AND SOME PALAEOECOLOGICAL CONCLUSIONS

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Abstract. The distribution of phosphorus fractions in the sediments that accumulated in Lake Ruusmäe during the last 4–5 decades was studied. The study focuses on the possible correlations between the vertical distribution of phosphorus fractions in the sediment core and the dynamics of the external load. The results suggest that sedimentation of organic material and its decomposition were the major mechanisms governing the distribution of phosphorus and its fractions in sediments at all depths except the interval of 29–20 cm, where a high phosphorus content was caused by redeposited matter. This general regularity is disturbed by variation in the aeration conditions, reflected in the changes in the content of phosphorus fractions. The fractional composition and increasing content of total phosphorus towards the surface indicate that although the external load decreased sharply in the 1990s, the actual phosphorus content in the lake has not yet been significantly reduced.

Key words: phosphorus, palaeolimnology, lake sediments, external load, trophic history.

INTRODUCTION

Intensive agricultural production, especially cattle breeding, since the 1970s has caused a high external load of nutrients on Lake Ruusmäe. As a result the lake has become hypertrophic (Punning et al., 1999). In the early 1990s the direct load was sharply reduced and the inflow of nutrients, especially phosphorus, decreased. To understand the impact of the external load of nutrients on the matter cycling in Lake Ruusmäe, the distribution of phosphorus fractions in the lake water and sediments was studied.

The cycling of phosphorus, the main nutrient controlling biogeochemical matter cycling in lakes, has been thoroughly studied during several decades (see Boström et al., 1982). It has been established that the sedimentation regime plays a fundamental role in the matter cycling, governing the energy flow through an aquatic ecosystem. The vertical distribution of phosphorus fractions in sediments and their interactions with water have been discussed in numerous papers (Istvanovics et al., 1989; Harry et al., 1992). Model experiments and calculations have shown that the contribution of phosphorus in the sediment to the external nutrient cycle of a lake is determined by the rate of organic sediment mineralization. The release of mineralized phosphorus into the water is controlled by many factors: diffusion from deeper layers to sediment surface; oxic conditions at the sediment–water interface; presence of Fe, Al, and Ca, which are the main elements that may under certain physicochemical conditions govern the sorption of orthophosphates and thus their returning to the sediments in the form of insoluble inorganic phosphorus (Jensen et al., 1992). Thus, phosphorus cycling in a lake is an extremely complicated process, which is closely related to the external load from the catchment and to matter cycling in the lake. The distribution of phosphorus compounds in sediments depends on the external load, physical and chemical processes and conditions (sedimentation, resuspension, mixing, sorption, oxygen content, etc.), and biological activity in the lake (Enell & Löfgren, 1988; Huttula & Nöges, 1998).

In the current study we attempt to interpret the distribution regularities of sedimentary P in Lake Ruusmäe in relation to the lake's trophic history (Punning et al., 1999). The study was focused on the possible relations between the vertical distribution of phosphorus compounds in the sediment core and data on the sedimentation and decomposition of organic matter.

THE STUDY AREA

The drainage basin of Lake Ruusmäe is situated in the Haanja Heights in southern Estonia. The landscape is rather variable, with a large number of lakes. Lake Ruusmäe, directed SE–NW, is situated in an upland catchment with altitude ranging from 228 to 270 m a.s.l. The lake is closed, being fed by precipitation and wells. Geomorphologically, the catchment represents a moraine plain where soddy-podzolic soils predominate. Also eroded and deluvial soils occur. The catchment vegetation consists of mixed and pine forest, meadow, and paludified pasture communities.

Lake Ruusmäe is a hypertrophic lake (Table 1). The water in the lake is strongly stratified in summer, and the seasonal and vertical differences in the oxygen content are very sharp. In summer the surface layers are supersaturated with oxygen (up to 160%) and by a depth of 3 m the oxygen content is almost zero. During the winter season anoxia occurs throughout the profile. Bioproduction

is very intensive in the lake and the Secchi disc measure of transparency is less than 1 m during the vegetation period. Since 1971, researchers of the Institute of Zoology and Botany have performed irregular hydrological and hydrochemical monitoring in Lake Ruusmäe (Pihu, 1990). According to the monitoring data, the content of HCO_3^- in water is 122–223 mg/L. The content of nutrients is very high: in summer 1990, P-tot was as high as 0.85 mg/L in the bottom layers and N-tot reached 5.45 mg/L in the upper layers. The pH values varied from 8.2 to 10.4 in the surface layers and from 6.4 to 9.2 in the near-bottom layers. The highest pH values (9.2 and 10.4 respectively) and the lowest transparency values (0.25 m) were recorded in 1990.

Table 1. General characteristics of Lake Ruusmäe

Parameter	Value
Area	4.7 ha
Maximum depth	11.0 m
Volume	160 000 m ³
Water turnover time	About 6 months
Trophic state	Hypertrophic
Stratification	Stratified from May to October
Oxygen content	Absent in the hypolimnion and bottom layers throughout the year
Total phosphorus	
Winter	720 mg/m ³
Summer, 1 m from the surface	95 mg/m ³
1 m from the bottom	540 mg/m ³
Soluble, reactive phosphorus	
Winter	320 mg/m ³
Summer, 1 m from the surface	32 mg/m ³
1 m from the bottom	425 mg/m ³
Biomass *	
Surface	3.8–7.8 g/m ³ (04.05.1995–17.10.1995)
Bottom	0.7–0.2 g/m ³ (04.05.1995–17.10.1995)
Transparency	0.6–1.2 m

* Data by Dr. Reet Laugaste (pers. comm.).

During summer about 30% of total phosphorus was soluble inorganic in the uppermost layer of the lake. In deeper layers the content of both soluble and total phosphorus increased. An especially sharp increase occurred below the thermocline, where the P content was in close correlation with the decreasing oxygen content (Fig. 1).

Human impact on Lake Ruusmäe was modest before World War II, growing from the 1950s onward. On the basis of the information collected, we divided the whole postwar history of human activities in the catchment of Lake Ruusmäe into

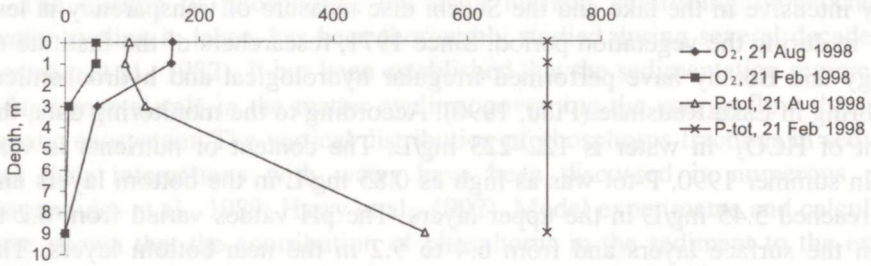


Fig. 1. Distribution of oxygen (%) and P-tot (mg/m³) in Lake Ruusmäe.

three periods. The distinction of the periods was mainly based on existing reliable maps, which were used to compile topographic and land-use maps for the years 1948, 1978, and 1996 (Punning et al., 1999).

1. The period before 1948. There were a number of simple farms around the lake. In 1948 the concentration of cattle breeding started and the village of Ruusmäe became the centre of a collective farm.

2. The period from 1949 to 1978 was the time of intensive development of the administrative and economic centre of the collective farm near the lake. In these years many apartment houses were built, as well as a sauna on the shore of the lake, a workshop and garages, an oil storage, and two cattle sheds (capacity of 104 head) were constructed. The building of a larger cattle shed (for 500) began at the end of the period.

3. The period from 1979 to 1990 was characterized by intensification of cattle breeding and related activity. The end of the 1980s was the economic heyday of the local state farm (reorganized from the collective farm). In the early 1990s, when the large-scale farm was completely reorganized, the economic production decreased very rapidly. The state of the lake, however, did not improve significantly, mainly due to a continuous inflow of nutrients from heavily contaminated soils around the lake.

MATERIALS AND METHODS

Water samples from various depths (1, 3, 5, 9, 10 m) in the lake and from the inlet were taken with a bathymeter during different seasons. The samples were stored in plastic bottles in a refrigerator. The water samples were analysed for total (P-tot) and soluble phosphorus. P-tot was measured after the digestion of the sample with a mixture of perchloric and nitric acid (APHA, 1971). Soluble phosphorus was measured after the filtration of water samples through a glass filter.

A sediment core, 64 cm in length, was taken from the deepest part of the lake (11.0 m). The core was obtained from ice in winter 1996 with a modified Livingstone-Vallentyne piston corer equipped with an extension rod. The lithology

of the sediments was recorded in the field. The sampling was continuous, at 1-cm intervals down to 40 cm and at 2-cm intervals deeper. The samples were put into plastic bags and stored in a refrigerator prior to analysis. The subsamples were analysed for dry weight, loss on ignition (LOI), and carbon, nitrogen, and phosphorus fractions.

The content of dry matter in sediment was determined by drying the samples at 105°C up to constant weight. Organic matter was measured as LOI upon heating at 500°C for 120 min. The contents of C and N were measured in the Institute of Chemistry at Tallinn Technical University with a Perken Elmer Elemental Analyser, type PE 2400/2. The results were expressed as percentage of dry weight at 105°C. On the basis of these data C/N ratios were calculated.

The P-tot content in the sediment samples was determined as P-PO₄ in the 0.5 M HCl digest of the combusted (550°C) sample. From parallel samples, extraction was performed successively with 1 M NH₄Cl (P-NH₄Cl), 0.1 M NaOH (P-NaOH), and 0.5 M HCl (P-HCl), following the stepwise fractionation scheme of Hieltjes & Lijklema (1980) (Fig. 2). The fraction of organic phosphorus

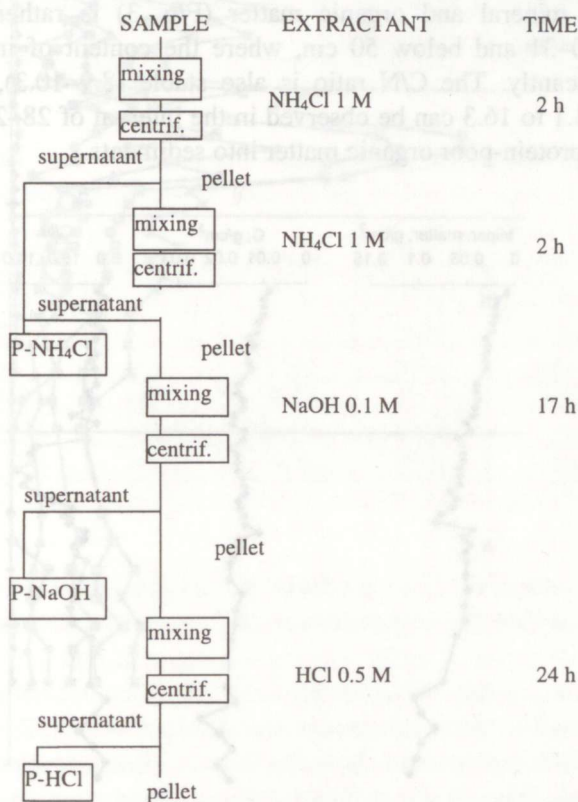


Fig. 2. Principal scheme of the determination of inorganic phosphorus fractions. P-NH₄Cl, interstitial plus loosely bound plus CaCO₃-absorbed phosphorus; P-NaOH, iron(III)- and aluminium(III)-bound phosphorus; P-HCl, calcium-bound phosphorus. All extractions were done with 5 mL extractant at 20°C.

(P-org) was calculated as the difference between P-tot and the sum of inorganic phosphorus fractions (P-inorg). Sometimes not all extractable phosphorus goes into the solution at extraction. It may remain in insoluble particles and so the extractant cannot dissolve it. On ignition, however, the particulate organic carbon is transformed into carbon dioxide and all phosphorus becomes available to the extractor. Therefore, overestimation of organic phosphorus and underestimation of inorganic phosphorus is possible.

Vertical profiles of temperature, oxygen content, and pH values were established. Measurements were carried out in August and February at depths 0.5, 1.0, 3.0, and 9.0 m.

RESULTS

The upper part (up to 60 cm) of the sediments is typical blackish-grey homogeneous gyttja without major visual macroremnants. The water content in the surface sediments is about 95–97%, decreasing to 86% at a depth of 64 cm. The content of mineral and organic matter (Fig. 3) is rather stable except for depths of 20–31 and below 50 cm, where the content of inorganic matter increases significantly. The C/N ratio is also stable (8.9–10.3), but a marked increase from 13.1 to 16.3 can be observed in the interval of 28–21 cm, which is due to influx of protein-poor organic matter into sediments.

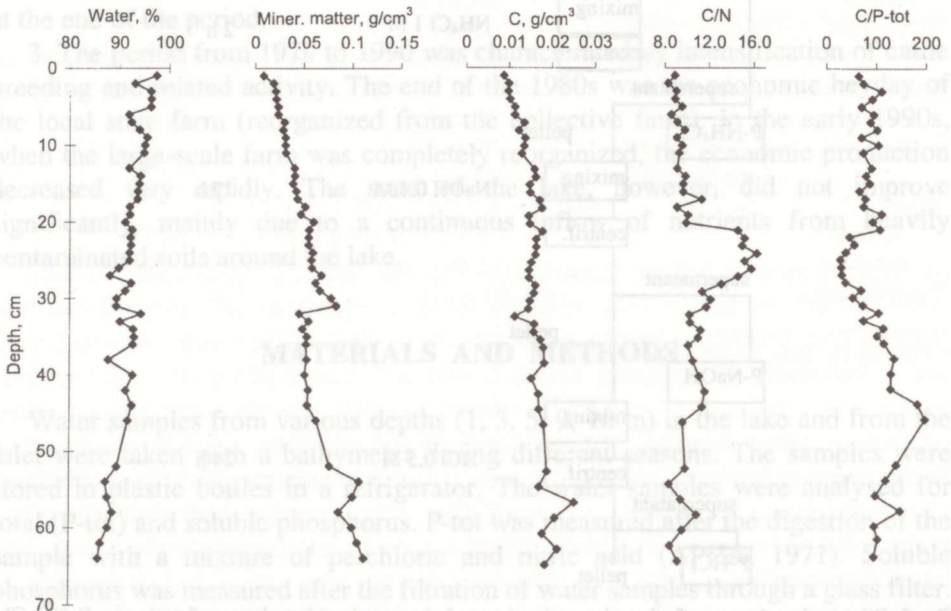


Fig. 3. Sediment characterization of a core from Lake Ruusmäe.

The concentration of P-tot increases almost continuously from the bottom of the analysed core up to the surface layers (Fig. 4). The total increase from a depth of 64 cm to the surface is more than twofold, with the exception of the layers at depths from 29 to 22 cm, where a remarkable rise in total as well as inorganic phosphorus fractions is observed.

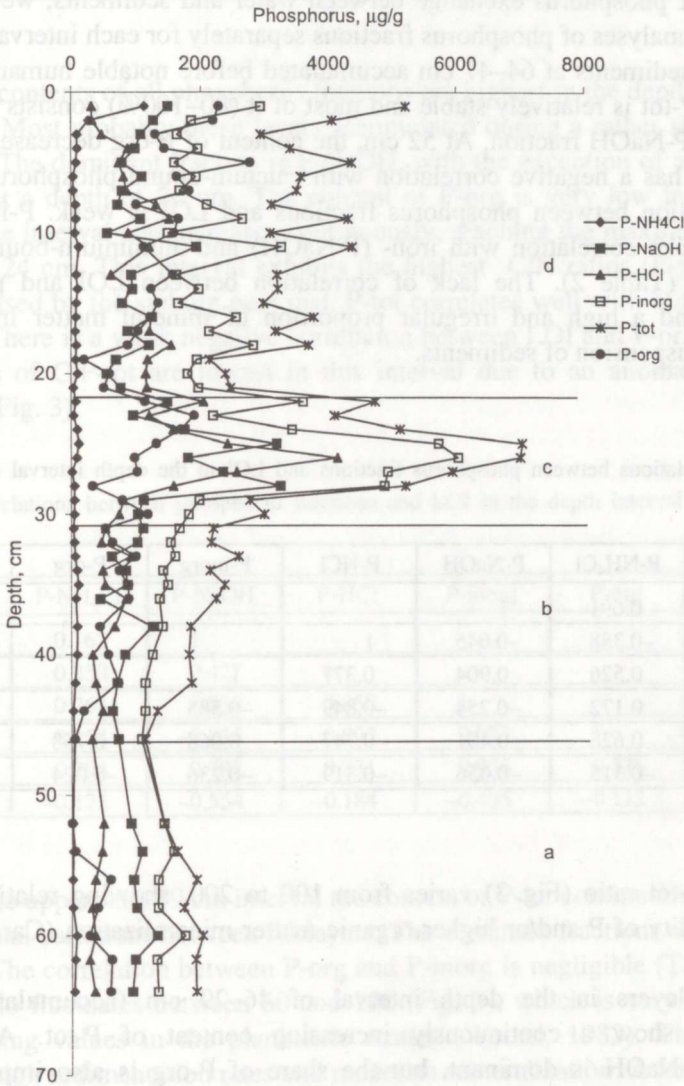


Fig. 4. Phosphorus fractions in the sediment profile in intervals distinguished (a, b, c, and d) for correlation analysis (see text).

Below this elevated phosphorus concentration level, at a depth of 29 cm, the main compound is P-inorg, mostly P-NaOH. Above the 22 cm level, the proportion of the P-org pool in P-tot is comparable with the inorganic phosphorus pool. The content of loosely bound phosphorus (P-NH₄Cl) is high only in the upper layers (3–0 cm).

On the basis of P-tot values and the share of its different fractions, four intervals could be distinguished in the phosphorus records (Fig. 4). To study the dynamics of phosphorus exchange between water and sediments, we performed correlation analyses of phosphorus fractions separately for each interval.

(a) The sediments at 64–47 cm accumulated before notable human load. The content of P-tot is relatively stable and most of it (80–100%) consists of P-inorg, mainly the P-NaOH fraction. At 52 cm, the content of P-org decreases to almost zero. P-org has a negative correlation with calcium-bound phosphorus (P-HCl). The correlation between phosphorus fractions and LOI is weak. P-inorg has a strong positive correlation with iron- (P-NaOH) and aluminium-bound (P-HCl) phosphorus (Table 2). The lack of correlation between LOI and phosphorus fractions, and a high and irregular proportion of mineral matter in sublayers indicate resuspension of sediments.

Table 2. Correlations between phosphorus fractions and LOI in the depth interval of 64–47 cm ($p < 0.05$)

Parameter	P-NH ₄ Cl	P-NaOH	P-HCl	P-inorg	P-org	P-tot
P-NaOH	0.691	1				
P-HCl	-0.388	-0.045	1			
P-inorg	0.526	0.904	0.377	1		
P-org	0.172	-0.254	-0.849	-0.585	1	
P-tot	0.628	0.401	-0.747	0.068	0.768	1
LOI	-0.315	-0.056	-0.319	-0.236	-0.024	-0.216

The C/P-tot ratio (Fig. 3) varies from 100 to 200, showing relatively small sorption ability of P and/or higher organic matter mineralization (Caracao et al., 1991).

(b) The layers in the depth interval of 46–29 cm (accumulated in the 1950s–60s) show a continuously increasing content of P-tot. Among the fractions, P-NaOH is dominant, but the share of P-org is also important and increases upwards (Fig. 4). P-tot shows quite a strong positive correlation with P-org, but with LOI the correlation is weak and negative (Table 3). In this interval the C/P-tot ratio decreases from ca 180 to 40 (Fig. 3).

Table 3. Correlations between phosphorus fractions and LOI in the depth interval of 46–29 cm ($p < 0.05$)

Parameter	P-NH ₄ Cl	P-NaOH	P-HCl	P-inorg	P-org	P-tot
P-NaOH	0.147	1				
P-HCl	0.073	-0.135	1			
P-inorg	0.068	0.482	0.590	1		
P-org	0.351	-0.031	0.631	0.699	1	
P-tot	0.253	0.197	0.664	0.892	0.947	1
LOI	0.471	-0.354	-0.232	-0.695	-0.288	-0.495

(c) The contents of all phosphorus fractions are highest in the depth interval of 29–20 cm. Most probably these layers accumulated during a rather short time in the 1970s. The dominant fraction is P-NaOH, with the exception of a sharp peak of P-HCl at a depth of 26 cm. The content of P-org is very low in the deeper layers of the interval and increases continuously, reaching the maximum value at a depth of 24 cm. This interval exhibits the highest C/N ratios (Fig. 3), which may be caused by the sinking peat mat. P-tot correlates well with both inorganic fractions. There is a weak negative correlation between LOI and P-org (Table 4). The values of C/P-tot are lowest in this interval due to an anomalously high P content (Fig. 3).

Table 4. Correlations between phosphorus fractions and LOI in the depth interval of 29–20 cm ($p < 0.05$)

Parameter	P-NH ₄ Cl	P-NaOH	P-HCl	P-inorg	P-org	P-tot
P-NaOH	0.162	1				
P-HCl	0.250	0.427	1			
P-inorg	0.263	0.838	0.850	1		
P-org	0.154	-0.036	0.092	0.037	1	
P-tot	0.294	0.782	0.831	0.956	0.326	1
LOI	-0.173	-0.554	-0.184	-0.435	-0.112	-0.444

(d) In the uppermost 19 cm interval the content of P-tot continuously increases with essential variations between sublayers. The dominant fractions are P-org and P-NaOH. The correlation between P-org and P-inorg is negligible (Table 5). The C/P-tot ratio fluctuates between 60 and 100 (Fig. 3), which is very close to the corresponding values in the planktonic matter (Wetzel, 1983). This indicates relatively high sedimentation rates and moderate mineralization. A large variation in the P-inorg content occurs indicating changes in the oxygen supply.

Table 5. Correlations between phosphorus fractions and LOI in the depth interval of 19 cm up to the surface ($p < 0.05$)

Parameter	P-NH ₄ Cl	P-NaOH	P-HCl	P-inorg	P-org	P-tot
P-NaOH	0.428	1				
P-HCl	-0.487	-0.053	1			
P-inorg	0.403	0.795	0.437	1		
P-org	0.392	0.095	-0.609	-0.182	1	
P-tot	0.619	0.665	-0.177	0.589	0.686	1
LOI	0.306	0.289	-0.372	0.065	0.538	0.491

DISCUSSION

The anoxic conditions existing in the bottom waters throughout almost the whole year and the low redox potential in the surface sediment layers suggest a stimulated phosphorus release from the sediments (Mortimer, 1941). High P-tot (especially soluble reactive phosphorus) concentrations in the water of Lake Ruusmäe in winter and in bottom layers during the summer season support the classical scheme of phosphorus behaviour at the water-sediment interface. Oxygen distribution data in the lake over the period 1996-98, as well as the data from 1971, 1973, 1981, 1990, and 1995 (Pihu, 1990), show that in recent decades there was permanent oxygen saturation in the epilimnion, and marked oxygen deficiency in the hypolimnion. The sorption and binding of released phosphorus were possible only during short periods around the spring and autumn overturns.

This suggests that the content of deposited organic matter and the degree of its mineralization are the main factors governing the transport of phosphorus back to the lake. These factors are also determined by the intensity of external phosphorus load, primary production, and its intensity gradient in the water column. Higher concentrations of loosely bound phosphorus in the upper sediment layers and its practical disappearance at depths 3-4 cm from the surface indicate weak destruction of organic matter in the already deposited and buried material, as well as inhibited diffusion of the reactive phosphorus in the vertical profile of sediments. As redox potential had high negative values throughout the core, the anaerobic destruction of organic matter was low. Therefore, the presence of oxygen in near-bottom layers and the rate of sedimentation seem to be important factors determining the dynamics of phosphorus release. As demonstrated by Anderson et al. (1993), a direct correlation of the increased phosphorus inputs with sedimentary phosphorus profiles might be very complicated and therefore only comprehensive study of the lake's history could reveal the changes in the matter cycling in the lake.

Our results on phosphorus distribution in the Lake Ruusmäe sediment core were compared with organic compound data, especially fossil pigments, and with the historical records of human load to the lake (Punning et al., 1999) in order to

differentiate periods of impact and to determine a chronology for the sediment core. The rapid increase in the content of fossil pigments at a depth of 32 cm refers to principal changes in the lake ecosystem. From historical data it is known that one of the most important milestones in the dynamics of the pollution load was the construction of a large cattle shed near to the lake and a rapid increase in domestic waste discharge from homes, a sauna, and storehouses at the beginning of the 1970s. Consequently the ecological state of the lake deteriorated and remediation measures were taken, including the mechanical mixing of bottom sediments. A major accident happened in 1969 (1970?) when 3 t of fertilizer (ammonium nitrate) was washed from the shore into the lake by precipitation. This notably accelerated the rate of biogeochemical cycling. According to local inhabitants, the peat mat in the littoral NW part of the lake was cut by musk rats in the late 1970s and peat pieces were seen floating on the lake, partly sinking to the bottom. This could explain the rapid increase in the C/N ratio in zone (c) and might therefore serve as a time marker for dating the core. Furthermore, the high content of P-org at a depth of 23–26 cm may have been due to the sinking peat mat. The fossil pigment data support our findings as concentrations start to decrease from these layers upwards (Punning et al., 1999). This might be a combined result of increased biomass production and hindered degradation of pigments due to the decrease in the transparency and oxygen content in the hypolimnion and an increased sedimentation rate.

We compared the important events with the formation of layers in the interval from 26 to 23 cm. Most probably, the mixing and resuspension caused an abrupt increase in sedimentation in the studied site. At the beginning of the period when the sediments of this depth interval accumulated, mineralization was intensive (especially high values of P-HCl) and the P-org content low. Due to mixing and aeration, the sorption of phosphorus increased and its release back into the lake might have been hindered.

The most rapid changes in the phosphorus fraction contents were observed in the samples from depths 29–20 cm. The increase in the calcium-bound phosphorus is related to an increase in secondary mineral matter, carried into the lake by erosion or heavy redeposition, possibly as a result of the attempt to improve the ecological state of the lake.

At a depth of 19 cm, a slight increase in average values of P-tot begins, with a relatively large pool of P-org. Thus, the distribution regularities of phosphorus fractions in the studied core, reflecting temporal changes in the biogeochemical cycling during the last decades, show clear periods in the lake's history. The relatively low values of P-tot in the upper part of sediments and the predomination of P-NaOH provide evidence of improved aeration and a relatively low external phosphorus load. From a depth of 40 cm upwards a permanent increase in P-tot in the sediments was observed and there is a strong positive correlation between P-tot and P-org, and a negative correlation between LOI and P-inorg. The increase in P-org suggests that the deposited organic matter was only partially decomposed.

A direct correlation of the increased P inputs with sedimentary phosphorus profiles might be very complicated and in the absence of historical water chemistry data and P loading data it is not possible to assess how accurately the geochemical P profile tracks the trophic history of Lake Ruusmäe. A number of studies have demonstrated potential problems in relating P loading history to sedimentary P profiles owing to factors such as phosphorus mobilization and diagenesis (e.g., Engstrom & Wright, 1984; Anderson et al., 1993). The results of our comprehensive study, however, indicate that fundamental changes took place in the cycling of matter in Lake Ruusmäe.

CONCLUSIONS

The continuous increase in the phosphorus content from bottom to surface (excluding the interval of 29–20 cm) gives evidence of an increasing external phosphorus load to the lake. The obtained results suggest that at all depths, except the interval of 29–20 cm where the high phosphorus content was caused by redeposited matter, the major mechanism governing the distribution of phosphorus and its fractions in sediments was bioproduction and decomposition of organic matter.

This general regularity is disturbed by the changes in the aeration conditions, which are reflected in the changes in the content of phosphorus fractions. The fractional composition of the surface layers indicates that although there was a sharp decrease in the external load in the 1990s, the actual phosphorus content in the lake has not yet decreased significantly. The tendency of P-NaOH to increase upwards indicates an improvement in oxygen conditions in the near-bottom layers.

The smallest fraction of phosphorus in the Lake Ruusmäe sediment core was loosely-bound phosphorus (P-NH₄Cl), with the exception of the uppermost 2–3 cm. This is most likely due to active decomposition of organic material occurring only in the surface layers, which are periodically supplied with oxygen. The transport of oxygen to the near-bottom layers takes place at seasonally different intensities. Therefore the share of P-inorg varies greatly. Oxygen diffusion reaches a depth of only a few centimetres and is the most important mechanism for regulating the exchange between dissolved phosphorus in sediments and water.

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FOSFORI JAGUNEMINE HÜPERTROOFSE RUUSMÄE JÄRVE PÕHJASETETES JA SELLE PALEOÖKOLOOGILINE PÕHJENDUS

Kristjan KRUUSEMENT ja Jaan-Mati PUNNING

On analüüsitud fosfori erinevate esinemisvormide sisaldust Ruusmäe järve viimastel aastakümnetel akumuleerunud põhjasetetes eesmärgiga leida ajalisi seoseid järve valgalalt tulnud fosforivoogudega. Selgus, et fosforivahetus vee

ja sette piirpinnal on olulisel määral reguleeritud orgaanilise aine lagunemiskiirusega ja reaktiivse fosfori difusiooniga lahusesse. Fosfori kontsentratsiooni muutusele setetes on omane mõningane tsüklilisus, mis on ajaliselt korreleeritav järve valgatal toimunud majandustegevusega. Üldtendents on fosfori kontsentratsiooni pidev suurenemine uuritud setetes, mis on akumulbeerunud alates 1950. aastatest kuni käesoleva ajani.

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PÕHJASETTES JA SELLE PALEOÖKOLOOGILISE PÕHENDUS

AKTINNIMÄÄRITUS
Kristjan KRÜSEMANN ja Jaan-Mati PUNNING

On analüüsitud fosfori, ränikvanti, orgaanilise süsiniku ja ränikvanti suhteid Ruusmäe järve põhiosa sedimendis. Sedimendis on leitud fosfori ja ränikvanti suhteid, mis on ajaliselt korreleeritavad järve valgatal toimunud majandustegevusega. Üldtendents on fosfori kontsentratsiooni pidev suurenemine uuritud setetes, mis on akumulbeerunud alates 1950. aastatest kuni käesoleva ajani.