

Spatio-temporal variability of surface sediment phosphorus fractions and water phosphorus concentration in Lake Peipsi (Estonia/Russia)

Mihkel Kangur^a, Liisa Puusepp^a, Olga Buhvestova^b, Marina Haldna^b and Külli Kangur^b

^a Institute of Ecology, Tallinn University, Uus-Sadama 5, 10120 Tallinn, Estonia; mihkel.kangur@tlu.ee, liisa.puusepp@tlu.ee

^b Centre for Limnology, Institute of Agricultural and Environmental Sciences, Estonian University of Life Sciences, 61117 Rannu, Estonia; kylli.kangur@emu.ee, olga.buhvestova@emu.ee, marina.haldna@emu.ee

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Abstract. Spatial and temporal variations in the contents of total phosphorus and five P-fractions were investigated in the surface sediments of large and shallow Lake Peipsi (area 3555 km², mean depth 7.1 m) and compared with total phosphorus (TP), dissolved inorganic P (PO₄-P) and dissolved oxygen (O₂) concentration in the overlying water column. The aim of the study was to determine the relationships between the sediment P and water P concentration dynamics. Samples from the uppermost 10-cm layer of the sediment and water samples from surface and near-bottom layers were collected simultaneously at six monitoring stations twice a year (in March and August) from 2004 to 2009. The results indicated that the concentrations of different P-fractions in the studied sediments varied greatly. Total P in sediment ranged from 470 to 1400 mg kg⁻¹ dry mass (DM), while the loosely bound (labile) P (NH₄Cl-P) was the smallest and the most variable fraction (range from 3.6 to 43 mg kg⁻¹ DM). The metal oxide-bound P (NaOH-P) was also highly variable (range from 48 to 660 mg kg⁻¹ DM), whereas the concentration of calcium-bound P (HCl-P) was relatively even (range from 300 to 550 mg kg⁻¹ DM) in all the studied sediments. Redundancy analysis results revealed that different phosphorus fractions in sediment had statistically significant relationships with bottom-water variables like TP (in winter) and O₂ (in summer). Our results show that the oxygen conditions have deteriorated in the lake during the last decades, which may have enhanced the release of P from the sediments.

Key words: phosphorus in shallow lakes, phosphorus exchange, oxygen conditions, eutrophication.

INTRODUCTION

External load is the factor directly increasing the nutrient content of a lake (Niemistö et al. 2012). However, sediments may be temporally an important source of nutrients to a shallow lake ecosystem. Nutrients released from lake sediments can greatly influence water column nutrient concentrations and plankton productivity (Nürnberg 1991; Nowlin et al. 2005; Istvánovics 2008). Phosphorus (P) has been recognized as the most critical nutrient limiting lake productivity (Bradshaw et al. 2002; Carpenter 2005; Spears et al. 2006; Wang et al. 2006). Its supply to the euphotic zone depends on the external load and also on the tendency of sediments to retain or release phosphorus (Søndergaard et al. 1999; Kaiserli et al. 2002). Under certain environmental conditions, the sediments may become a potential P source that will support the elevated trophic status of the lake for extended periods of time (for centuries) after reduction of external loading (Carpenter 2005). Stratification and the intensity of water mixing play an important role in this process. Stratification may lead to anoxic conditions, lowered pH and accumulation of nutrients in the near-bottom layers of water and in surface sediments (Carpenter 2005) and

part of the sedimentary P may be resuspended several times before final burial (Niemistö et al. 2012). During the 1980s research on the role of internal P loading from lake sediments developed rapidly and new knowledge was gained about factors regulating this process in both shallow and deep lakes (Boström et al. 1982; Cullen & Forsberg 1988). A survey of long-term data from 35 lakes in Europe and North America concluded that internal release of P typically lasts for 10–15 years after the loading reduction (Jeppesen et al. 2005) but in some lakes internal release may last longer than for 20 years (Søndergaard et al. 2003).

The thickness of the sediment layer interacting with lake water is probably lake-specific and highly dependent on lake morphology, sediment characteristics and wind exposure (Søndergaard et al. 2003). Although some studies have shown that P is released from depths down to 20 cm (Søndergaard 2007), most often P in the uppermost layers (~10 cm) of lacustrine sediments is considered to take part in internal geo-biochemical matter cycling of shallow lakes (Boström et al. 1982; Kapanen 2012a). Phosphorus in both the water column and sediment is continuously being assimilated into the biomass and then released again by the decomposition

within a short time interval (Boström et al. 1988; Istvánovics 2008). The cycling of P across the sediment water interface is dependent on several biological and physico-chemical factors (Dillon & Rigler 1974; Boström et al. 1982). Parameters such as dry weight, organic matter content and content of iron, aluminium, calcium, clay and other elements with a capacity to bind and release P may all influence sediment–water interactions (Søndergaard et al. 1996, 2003). Total P (TP) concentration is a poor measure of the potential P release from sediments (Kaiserli et al. 2002). Chemical fractionation of sedimentary P has served as a tool to predict the P-binding capacity of sediments under different environmental conditions. In most cases, the potential internal load is the matter of interest. However, it has been difficult so far to establish general relationships between P forms and duration of internal loading (Søndergaard et al. 2003).

In the large and shallow Lake Peipsi eutrophication phenomena (algal blooms, oxygen deficit, cyanotoxins in water, fish kills, etc.) are persistent (Kangur et al. 2005; M. Kangur et al. 2007). For instance, main dominant diatom taxa in surface sediments have not changed during more than 25 years (between the 1970s and 2006), indicating continuous eutrophic conditions (Puusepp & Punning 2011). Causes of non-recovery from eutrophication of this lake may be multiple and not entirely understood. However, internal recycling of P from bottom sediments into water can contribute to lake eutrophication even when external load is decreasing. Data on the nutrient content of sediments and internal

loading are limited for Lake Peipsi. The present work is the first attempt to compare P concentration in the surface sediment and in the overlying water column in Lake Peipsi. We investigated the distribution of P forms in the uppermost 10 cm sediment layer of Lake Peipsi in order to examine the potential for sediment phosphorus release. For this purpose, sediment P was divided by a sequential extraction into different fractions. At the same time P and O₂ concentrations in the overlying water were determined.

The aims of this study were (1) to determine the distribution of P-fractions in the surficial sediments of the large shallow eutrophic Lake Peipsi, (2) to estimate the relationships between the P concentration dynamics in the sediment surface and in the overlying water, (3) to assess the influence of O₂ conditions in the near-bottom water layer to P mobility between water and sediment.

STUDY AREA

Lake Peipsi (57°51'–59°01'N; 26°57'–28°10'E), situated on the Estonian/Russian border (Fig. 1A), has a surface area of 3555 km² (at the mean water level of 30 m a.s.l.) and is the fourth largest lake in Europe. The lake is shallow, with a mean depth of 7.1 m, maximum depth of 15.3 m, lake volume of 25 km³ and hydraulic retention time of about 2 years. The catchment area is 47 800 km² (including the lake surface). The lake is submeridionally elongated and consists of three limnologically different

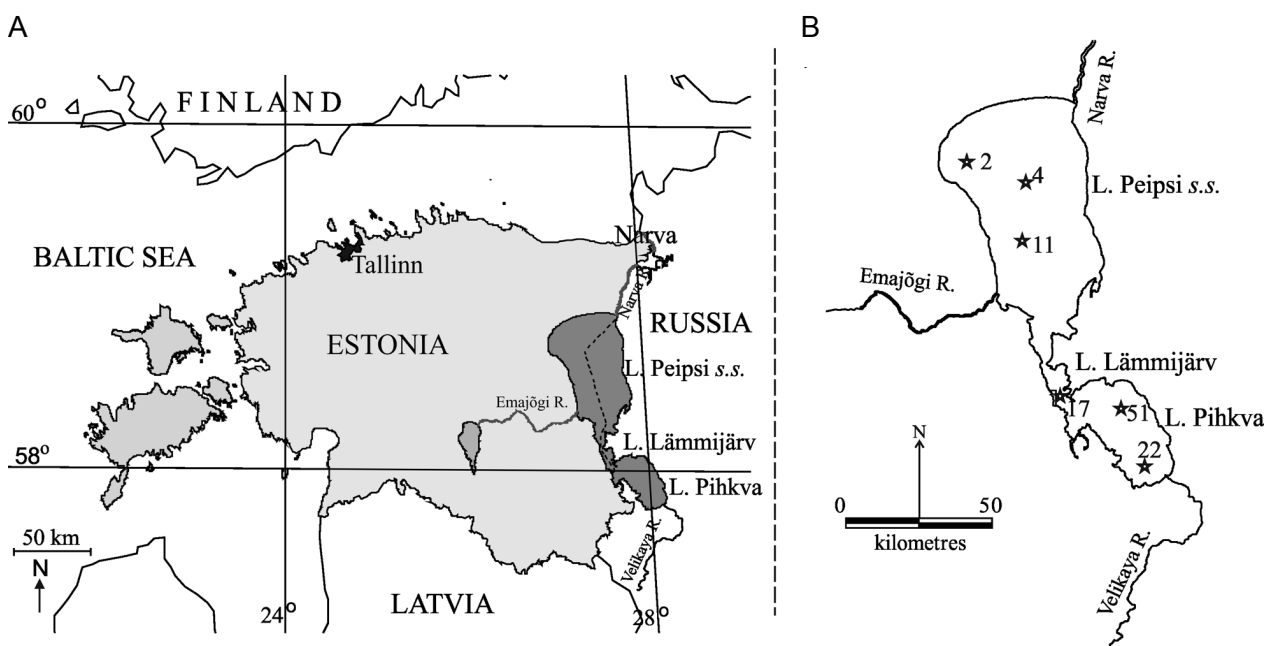


Fig. 1. Location of Lake Peipsi (A) and sampling stations (B).

basins (Fig. 1B). The northern part, Lake Peipsi *sensu stricto* (Peipsi *s.s.*) is the largest (2611 km²) and has the greatest mean depth (8.3 m). The southern part, called Lake Pihkva, measures 708 km², being 3.8 m deep on average. The strait between them is known as Lake Lämmijärv (236 km², mean depth 2.6 m). The water level of the entire Lake Peipsi is not regulated and its mean level is 30 m a.s.l. However, natural water level fluctuations are considerable and the levels have shown an overall range of 3.04 m over the last 80 years, with an average annual range of 1.15 m (Jaani 2001). The lake belongs to the polymictic type of lakes, where complete mixture of the water body takes place several times a year. Due to the large surface area and relative shallowness of the lake, thermal stratification is usually episodic and unstable, and can be disturbed already by a moderate wind or undulation. Lake Peipsi is situated in the northern region of the temperate zone with variable weather conditions. It is typically covered with ice from December until April; however, the ice-on and ice-off dates have varied markedly in recent years. Strong oxygen stratification and oxygen deficiency in the near-bottom water is observed during the ice-cover period (M. Kangur et al. 2007). During the open water period the lake is usually well aerated by waves and currents, whereas waves can be as high as 2.3–2.4 m (Jaani 2001), causing mixing and resuspension of accumulated sediments. The bottom of the lake consists mainly of till in deeper areas and sand in its coastal zone. According to most recent lithological studies, surface sediments of Peipsi *s.s.* comprise three main types: coarse-grained sediments (sands), fine-grained sediments (mainly silts) and silty sands (Punning et al. 2009). The first type occurs in the nearshore area and in the southern part of the lake, while the last two are found in its central deeper part; silty sediments are restricted mainly to the lake centre within the 8–11 m contour. The distribution of sediments reflects the impact of water currents in the lake.

Lake Peipsi belongs to the shallow unstratified polymictic type of lakes with a light water of medium hardness (average 2.3 mEq L⁻¹) located on mineral land (Kangur & Möls 2008). The lake is eutrophic, with mean total phosphorus (TP) and total nitrogen (TN) concentrations of 48 mg P m⁻³ and 784 mg N m⁻³, respectively, during the ice-free periods from 2006 to 2010 (Kangur et al. 2012). There is a clear south–north gradient in water quality – the nutrient concentrations are significantly lower in the northern, deepest part Lake Peipsi, than in the southern part, Lake Pihkva, which receives inflow from the Velikaya River (with a catchment area of 25 600 km²). The growing difference in P concentrations between the northern and southern parts has shown that the input of P from the south is increasing (Kangur & Möls 2008).

MATERIAL AND METHODS

Sampling

The water and sediment samples were taken simultaneously at six monitoring stations along a north–south transect over the whole Lake Peipsi (Fig. 1B) in eleven occasions: in March 2004–2009 and in August 2005–2009. Water samples for hydrochemical analysis were taken with a Ruttner sampler from the surface (from a depth of 0.5 m) and from the near-bottom layer of water (0.5 m from the bottom). Surface and near-bottom water temperature (WT) was measured simultaneously. A single exceptional sample was collected from the water surface at sampling site 4 in March 2005, when there was a two-layered ice cover. The sample was taken from water between the two ice layers but was excluded from further analysis. Sediment samples were taken with a modified Livingstone–Vallentyne piston corer from three parallel cores within the distance of 5 m. The uppermost 10 cm of the cores were separated immediately after sampling. The samples were kept in closed plastic bags in an icebox until they could be stored at 4 °C. The laboratory analyses began on the following day.

Laboratory analyses

In the water samples TP and PO₄-P were determined by the ammonium molybdate spectrometric method (see ECS 2000) and O₂ concentration was determined at the sampling site using an electrochemical method (ECS 1999). Chemical analyses were made by Tartu Environmental Research Ltd, Estonia.

In sediment samples the concentrations of dry matter (DM), organic matter, mineral (inorganic) matter, total P in sediment (TP_{sed}) and five P-fractions were analysed. The DM content of the sediment was determined by drying the samples at 105 °C up to constant weight. The organic matter concentration was determined by the loss of weight during ignition at 550 °C for 4 h (Heiri et al. 2001).

Sediment phosphorus fractionation was performed according to Williams' scheme (Ruban et al. 1999). The following P-fractions were gained: (1) NaOH-P – the P-fraction associated with metal (Fe, Al) oxides and hydroxides, (2) HCL-P – calcium-bound or apatite-P, (3) org-P – organic P, (4) inorg-P – inorganic P and (5) NH₄Cl-P – labile, loosely bound or exchangeable P (adsorbed P). Sediment was extracted in the following four steps: with 1 mol L⁻¹ NaOH (NaOH-P), 1 + 3.5 mol L⁻¹ HCl (HCL-P), HCl 3.5 mol L⁻¹ + calcinations (TP_{sed}) and HCl 1 mol L⁻¹ + calcinations (inorg-P and org-P) (Ruban et al. 1999). In addition, NH₄Cl-P was determined following the fractionation scheme of Hieltjes and Lijklema (Ruban et al. 1999). Concentrations of the TP_{sed} and P-fractions are expressed as mg kg⁻¹ DM.

Data analysis

Sediment phosphorus data were analysed using a detrended correspondence analysis (DCA) to assess the gradient length of the data (separately for the winter and summer database). This was then used to determine if linear or unimodal-based ordination methods were most appropriate for analysing the sediment phosphorus data. All gradient lengths were <2 standard deviation units, therefore, a linear ordination technique was used (Ter Braak & Prentice 1988; Ter Braak & Šmilauer 2002). Direct gradient ordination by redundancy analysis (RDA) with forward selection and Monte Carlo permutation tests with 999 permutations were carried out to determine the statistically significant ($p \leq 0.05$) relationship between three measured near-bottom water variables (O_2 , TP and PO_4 -P) and sediment total phosphorus (TP_{sed}) and phosphorus fractions (NaOH-P, HCL-P, org-P, inorg-P, NH_4Cl -P). The analyses were made separately on the sediment data sets for winter (March) and for summer (August). The RDA was performed using CANOCO for Windows, version 4.5 (Ter Braak & Šmilauer 2002). The ANOVA model for water and sediment variables was used to estimate differences between parameter values of two lake parts (Lake Peipsi *s.s.* and Lake Pihkva) and between the March and August data as well as their interactions. The procedure GLM of the SAS/STAT system (SAS 2008) and its ESTIMATE statement were used.

RESULTS

Sediment composition

The composition of sediment samples from Lake Peipsi exhibited a substantial spatial and seasonal heterogeneity (Table 1). The DM content of the investigated sediments was generally low, ranging between 7% and 19%. In northern and deeper Lake Peipsi *s.s.*, the DM content in summer was on average 2.5% higher than in winter ($p < 0.03$) but in shallower Lake Pihkva no significant difference was detected in parameter values between

summer and winter. Only the sediments in the southern part of the lake (sampling point 22) differed from the others by a higher DM content (25.3–50.5%), consisting mainly of mineral matter (88–95% DM). In the rest of samples the mineral matter content was usually lower (71–85% DM). The average concentration of organic matter in the investigated sediments varied from 9.5% to 27.0% DM.

Water variables

Oxygen concentration in water and near-bottom WT were seasonally variable (Fig. 2). The arithmetical average near-bottom WT was 1.67°C (0.4–3.9°C) in March and 19.2°C (17.2–21.7°C) in August. However, the near-bottom WT varied in different years during sampling in a relatively small range and did not show any correlation with sediment and near-bottom water variables. There was no substantial difference between the O_2 concentration in surface and near-bottom water in summer. The arithmetical average O_2 concentration was 10 mg L⁻¹ (8.8–11.2 mg L⁻¹) in surface water and 9 mg L⁻¹ (7.1–11.0 mg L⁻¹) in near-bottom water. In summer samples the difference between O_2 concentrations in surface and near-bottom water constituted on average 1 mg L⁻¹ (max 2.7 mg L⁻¹; min 0.2 mg L⁻¹).

On the contrary, a clear oxygen stratification occurred in winter, with a lower O_2 concentration in near-bottom water (average 2.9 mg L⁻¹, range 0.3–5.9 mg L⁻¹) compared to surface water (average 13.4 mg L⁻¹, range 7.2–15.3 mg L⁻¹). In winter samples the difference between O_2 concentrations in surface and near-bottom water constituted on average 10.5 mg L⁻¹ (range 3.8–14.1 mg L⁻¹).

A polarity appeared in the P concentration values of water between the northern and the southern part of the lake (Fig. 2B, C). In the northern part of the lake (stations 2, 4 and 11) TP concentration was relatively low both in surface (average 38 mg m⁻³, range 11–75 mg m⁻³) and near-bottom water (average 36 mg m⁻³, range 15–73 mg m⁻³). The PO_4 -P concentration was on average 10.5 mg m⁻³ (range 2–24 mg m⁻³) in surface water and 11.3 mg m⁻³ (4–18 mg m⁻³) in near-bottom water. The TP

Table 1. Water depth, the average and the range values of sediment characteristics at the sampling stations during 2004–2009

Station	Depth, m	Dry matter (DM), %	Mineral matter, % DM	Organic matter, % DM
2	8	9.2 (7.3–10.7)	78.0 (76.5–79.9)	22.0 (20.1–23.5)
4	10	7.2 (5.7–8.6)	73.0 (71.2–75.0)	27.0 (25.0–28.9)
11	11	8.4 (7.3–9.7)	76.0 (75.4–77.0)	24.0 (23.0–24.7)
17	6	15.5 (11.9–19.0)	81.3 (79.5–85.0)	18.7 (15.0–20.5)
51	4	10.6 (10.2–11.1)	75.3 (74.5–76.0)	24.7 (24.0–25.5)
22	3	33.6 (25.3–50.5)	90.5 (88.0–95.0)	9.5 (5.0–12.1)

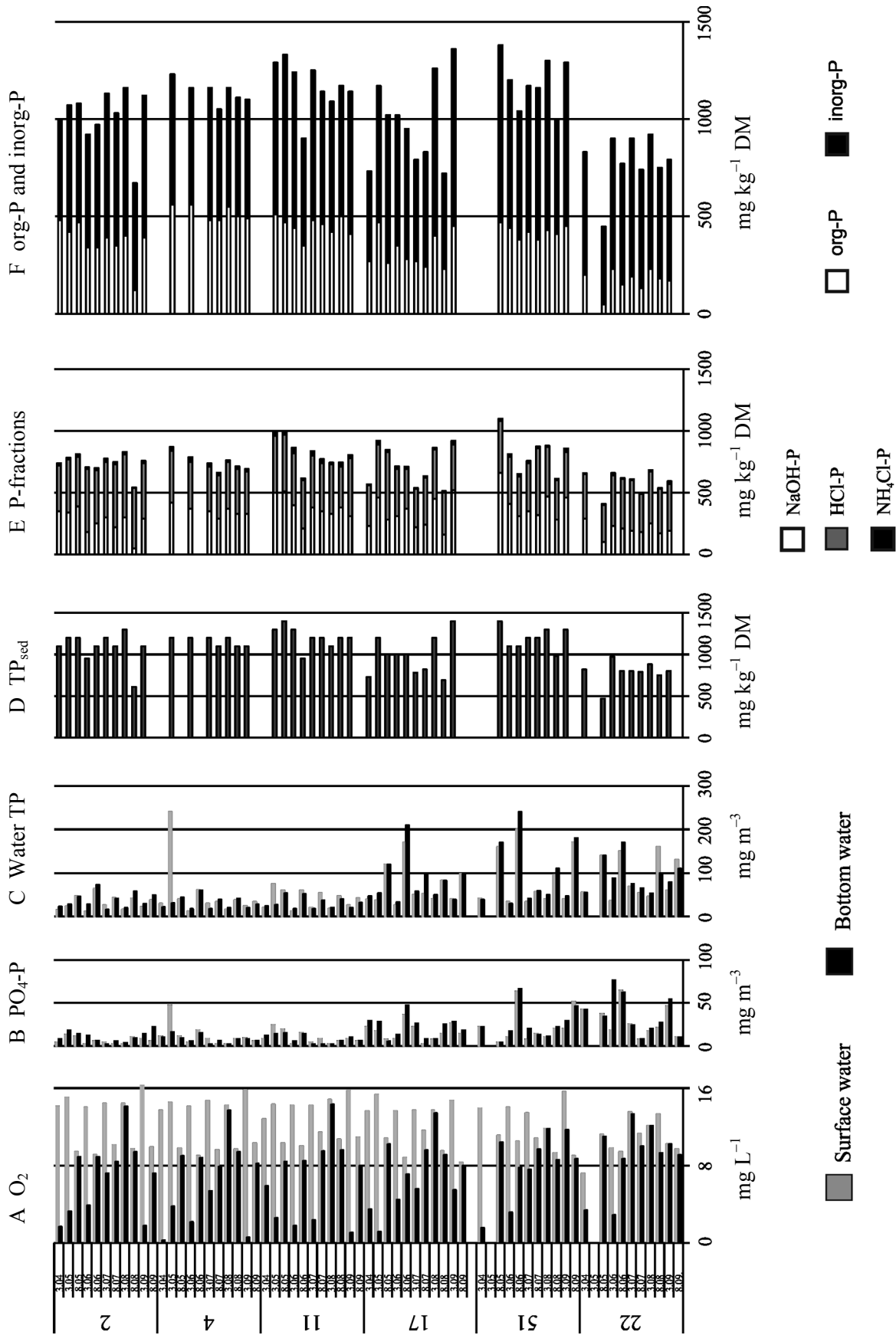


Fig. 2. Water dissolved oxygen (O_2), total phosphorus (TP) and dissolved inorganic P ($PO_4\text{-P}$) concentrations and sediment phosphorus (TP_{sed}) and five P-fractions concentrations at the six sampling stations during the sampling occasions: panels A–C water samples, panels D–F sediment samples.

concentrations were significantly higher than in August in winter, both in surface ($p = 0.0004$) and near-bottom water ($p < 0.0001$). Similarly, in summer the $\text{PO}_4\text{-P}$ concentrations were usually higher than in winter (Fig. 2B, C).

Both TP and $\text{PO}_4\text{-P}$ concentrations in water were generally higher ($p < 0.0001$) and more variable in the southernmost part of the lake (at sites 17, 51 and 22) than in the northern part of the lake (Fig. 2B, C). Significant differences ($p < 0.0001$) were observed between the summer and winter samples. In the southern part of the lake the TP concentration was on average 38 mg m^{-3} (range $26\text{--}56 \text{ mg m}^{-3}$) in surface water during winter and on average 157 mg m^{-3} ($120\text{--}200 \text{ mg m}^{-3}$) during summer (Fig. 2C). In near-bottom water the average TP concentration was 50 mg m^{-3} ($30\text{--}88 \text{ mg m}^{-3}$) in winter and 175 mg m^{-3} ($120\text{--}240 \text{ mg m}^{-3}$) in summer. Similar variation patterns were observed for $\text{PO}_4\text{-P}$ concentrations (Fig. 2B).

Phosphorus fractions in sediment samples

The most variable P-fraction in the sediment was $\text{NH}_4\text{Cl-P}$, but its concentration was the lowest ($3.6\text{--}43 \text{ mg kg}^{-1} \text{ DM}$) (Fig. 2E). The highest values of $\text{NH}_4\text{Cl-P}$ were observed in the deepest part of the lake (stations 4 and 11). The NaOH-P fraction was also highly variable ($48\text{--}660 \text{ mg kg}^{-1} \text{ DM}$). There appeared some temporal (inter-annual and within-a-year) variations in the NaOH-P concentration (Fig. 2E), whereas parameter values were mostly higher in winter samples ($p = 0.045$). The concentration of HCl-P was relatively stable ($300\text{--}550 \text{ mg kg}^{-1} \text{ DM}$) at all sampling sites (Fig. 2E). The inorg-P concentration ($400\text{--}910 \text{ mg kg}^{-1} \text{ DM}$) may vary spatially and temporally over a twofold range (Fig. 2F).

The magnitude of variations in org-P concentration exceeded a tenfold range ($47\text{--}560 \text{ mg kg}^{-1} \text{ DM}$) (Fig. 2F), in both temporal and spatial scales. In winter, the org-P concentration was on average $45 \text{ mg kg}^{-1} \text{ DM}$ higher than in summer ($p = 0.015$). Variations in the TP_{sed} concentration ranged from 470 to $1400 \text{ mg kg}^{-1} \text{ DM}$ (Fig. 2D). However, the TP_{sed} concentration was on average $116 \text{ mg kg}^{-1} \text{ DM}$ higher in winter than in summer ($p < 0.005$).

Relationships between water variables and concentrations of sediment P-fractions

To assess the relationship between measured near-bottom water characteristics and the concentration of phosphorus and its fractions in surface sediment, RDA was carried out separately for winter and summer data. The eigenvalues of the RDA axes 1 and 2 were 0.286 and 0.039 for winter data and 0.297 and 0.022 for summer data, respectively. All measured bottom-water variables together (O_2 , TP and $\text{PO}_4\text{-P}$) explained a statistically significant part of variances of sediment phosphorus concentration ($p < 0.01$) in both databases (winter and summer). However, the RDA with forward selection identified that the only independently significant variables in explaining different phosphorus fractions in sediment were the bottom-water TP during winter time and O_2 concentrations during summer (Fig. 3A, B). In winter, the concentration of TP was strongly and negatively correlated with the sediment org-P and TP_{sed} concentration (Fig. 3A) and in summer, O_2 concentrations in near-bottom water were negatively correlated with sediment org-P and TP_{sed} concentrations (Fig. 3B).

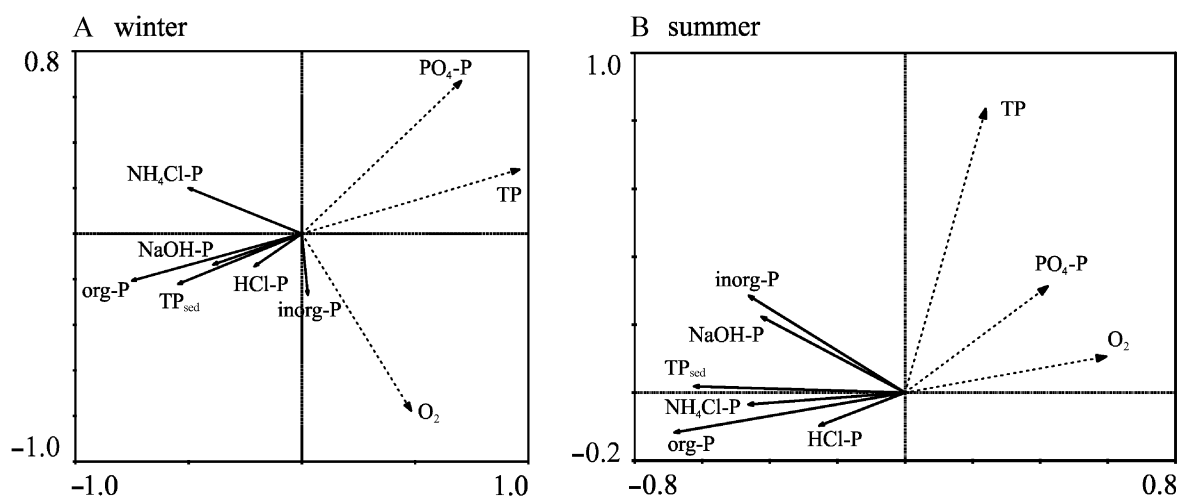


Fig. 3. Redundancy analysis (RDA) biplot constrained to the three measured bottom-water variables (O_2 , $\text{PO}_4\text{-P}$, TP) that explained variances of sediment phosphorus fractions. Biplot A presents winter and B summer data.

DISCUSSION

The trophic status and water quality of lakes are mostly determined by P concentration in water as P is conventionally thought to limit production in fresh water (Håkanson et al. 2003; Moss et al. 2013). High P content is thought to be the main reason for degradation also in the shallow lowland Lake Peipsi (M. Kangur et al. 2007; Kangur & Möls 2008). Strong influence of sediments on P concentration in lake water is a typical phenomenon in nutrient-rich shallow waters, which are usually highly mixed and warmed to the bottom in the summer months (Maassen et al. 2005). Furthermore, due to the absence of a stable stratification, the nutrients are transported rapidly into the euphotic zone. In some lakes, sediment nutrient release may represent an ecologically more important process than inputs from external nutrient sources because P released from sediments often contains a larger portion of immediately bioavailable P (Nowlin et al. 2005). The intensity and duration of internal load may have a very significant impact on lake water P concentration and subsequently on lake water quality (Søndergaard et al. 1999; Kelderman et al. 2005). According to Punning & Kapanen (2009), there is a big storage of P in the sediments of Lake Peipsi *s.s.* As much of 13–60% of TP_{sed} contained in the surface sediment for over 100 years has been remobilized during accumulation and could be exported to the overlying water (Kapanen 2012b). The recycling of phosphorus from sediments enriched by years of high nutrient inputs can cause slow recovery, or nonrecovery of lakes from eutrophication (Carpenter 2005). This process (internal loading) can also probably be observed in Lake Peipsi where eutrophication phenomena are persistent. This is confirmed by our results, according to which TP and PO₄-P concentrations in the lake water were significantly higher in August than in March. Similarly, TP concentrations in 15 shallow eutrophic Danish lakes were two to three times higher during summer than during winter (Søndergaard et al. 2002). Increasing P concentrations in summer appear to be a general phenomenon in shallow eutrophic lakes (Søndergaard et al. 2002) and in most cases this increase can only be the result of increased sediment loading, implying that summer P concentrations are largely controlled by internal processes (Søndergaard et al. 2003). Moreover, our results revealed that the increase in P concentrations (three to four times) both in surface and near-bottom water during summer was more pronounced in smaller and shallower Lake Pihkva than in larger and deeper Lake Peipsi *s.s.* (Fig. 1). Lake Pihkva is more eutrophic (P concentrations are significantly higher), warmer and the cycling of P between sediment

and water is there probably more intense than in Lake Peipsi *s.s.* in summer. Apart from direct sediment–water interactions, changes in lake biological processes also influence nutrient concentrations (Jeppesen et al. 1997; Søndergaard et al. 2002; Istvánovics 2008). Increased temperatures strengthen microbial processes and diffusion from the sediments resulting in elevated P concentration in the overlying water column (Boström et al. 1982; Maassen et al. 2005). Internal loading may be intensified also by active transport of nutrients from the bottom to the water column by algae. Håkanson et al. (2003) and Istvánovics (2008) stressed the significance of bio-uptake and retention of P in biota for phosphorus fluxes in lakes. Bio-uptake and active transport of P in the cells of cyanobacteria from bottom to surface water seems to be the main reason for the observed water TP contents an order of magnitude greater during algal blooms than usual in Lake Peipsi (Kangur et al. 2003).

The TP_{sed} concentrations in the investigated surficial sediments from Lake Peipsi (470–1400 mg kg⁻¹ DM) were similar to values measured by Nöges & Kisand (1999) in the surface sediments of Lake Võrtsjärv (900–1400 mg kg⁻¹ DM). Similarly, in a 44-cm sediment core from the central part of Lake Peipsi *s.s.* the average TP_{sed} was 1036 mg kg⁻¹ DM (Kapanen 2012b). However, TP_{sed} concentrations in sediments are not sufficient to predict the potential ecological danger (Kaiserli et al. 2002). The behaviour of sediment P in promoting eutrophication of fresh water can be more efficiently assessed on the basis of different P-fractions instead of TP concentration (Kaiserli et al. 2002; Spears et al. 2006; Wang et al. 2006). Similarly to previous assessments, different P-containing fractions within sediments varied with the spatial heterogeneity of sediment characteristics within Lake Peipsi, potentially affecting the P-binding capacity of sediments (Nowlin et al. 2005).

Our analysis shows strong relationships between the sediment P concentrations and near-bottom water P concentrations in winter. Generally, the PO₄-P and TP concentrations in near-bottom water had strong negative correlation with the TP_{sed} and org-P concentrations in sediment in March. The negative correlation probably shows that in winter (when the lake is ice-covered and the near-bottom WT is low) the bulk of potentially mobile P is located in the sediment and P concentrations in the water column are low in comparison with summer values. The organic matter in the profundal sediment of the lake originates mainly from plankton which is settled during winter. Decomposition of this material and release of org-P may constitute an important source of P to the overlying water column during the growing season. According to Søndergaard et al. (2003, 2005), onset of the increasing biological activity in spring in

the most eutrophic lakes triggered the release of some of the P retained during winter. Phosphorus release from the sediment into lake water depends on the sediment surface–water column ratio, leading to a higher intensity of P release in large and shallow lakes (Søndergaard et al. 2003) like Lake Peipsi. Our results in Lake Peipsi indicated that O₂ concentration in water in summer had significant relationships with different phosphorus fractions in sediment, supporting the conclusion of Nowlin et al. (2005) that variation in O₂ concentration in waters above sediment is affecting nutrient release rates. The release of P from sediments into overlying water during summer hypolimnetic anoxia is a result of complex interaction between biotic and abiotic processes in the water column and sediment (Nowlin et al. 2005).

We observed that in winter TP_{sed} concentration was significantly higher than in summer in Lake Peipsi. Concentrations of loosely bound P-fractions, such as NH₄Cl-P, NaOH-P and org-P in the sediment varied most greatly and release of these P-fractions may have a significant impact on the P concentration in the water column. Both NaOH-P and org-P concentrations were mostly higher in winter than in summer. These P-fractions are easily releasable under appropriate conditions and can influence nutrient concentrations in the water column (Ruban et al. 1999).

On the contrary, calcium-bound P (HCl-P) and inorg-P were the most stable sediment P-fractions in Lake Peipsi in the spatial and temporal scales and probably are more resistant to resuspension. According to Kaiserli et al. (2002), calcium-bound P is a relatively stable fraction of sedimentary P and contributes to a permanent burial of P in sediments.

The influence of oxygen conditions on the mobility of P from the sediment to the overlying water has been demonstrated in a number of studies (Andersen & Ring 1999; Kaiserli et al. 2002). Data from the long-term monitoring of Lake Peipsi indicate that oxygen conditions have deteriorated during last decades and since the 1990s anoxic conditions have occurred in the near-bottom waters during winter (M. Kangur et al. 2007). Increased concentrations of sediment organic matter, leading to a higher sediment O₂ consumption, and the eventual depletion of O₂ in the bottom water are a common consequence of eutrophication (Lehtoranta 2003). The results of the present study demonstrate strong oxygen stratification and low O₂ content of the bottom water in Lake Peipsi during winter. Our research proved that release of NaOH-P from the sediment might occur in areas where anoxic conditions prevail in the near-bottom layer of water during a long ice-covered period. The NaOH-P fraction can be used for the

estimation of both short-term and long-term available P in sediments and as a measure of algal-available P (Kaiserli et al. 2002). According to Ting & Appan (1996), NaOH-P could be released for the growth of phytoplankton when anoxic conditions prevail at the sediment–water interface. Similarly, Andersen & Ring (1999) found that under anoxic conditions, iron-bound P was the most important fraction for the loss of P from the sediments.

The deterioration of oxygen conditions in bottom layers water of Lake Peipsi indicates that internal loading of P could increasingly contribute to the degradation of the lake ecosystem. We can assume that internal processes may delay lake recovery for decades even when external phosphorus input would significantly decrease.

CONCLUSIONS

The results of the current study indicated that the distribution of P-fractions in surface (10 cm) lacustrine sediments of the large shallow eutrophic Lake Peipsi was variable, both on temporal and spatial scales. The most variable fractions were NH₄Cl-P, NaOH-P and org-P, while the HCl-P concentrations in sediments were more stable.

To identify the measured bottom-water variables that were important in controlling P concentrations in sediment, a RDA was conducted. The most significant variables were TP in winter and O₂ in summer. The RDA analysis indicated negative correlation between TP concentrations in the bottom water and org-P concentrations in the sediments in winter. Near-bottom oxygen conditions correlated negatively with TP_{sed} and org-P concentrations in summer. The results showed a relationship between the P content dynamics in the water and the sediment, which indicates that internal processes may determine eutrophic conditions in Lake Peipsi for many years. The information should improve our understanding of how lake systems and sediment P content may respond to water oxygen and phosphorus change in the future. Further studies, including in situ experiments, are needed for quantifying sediment P contribution to the bio-geochemical matter cycle of Lake Peipsi.

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Peipsi järve pindmiste setete fosfori fraktsioonide ja vee fosfori kontsentratsioonide ajalis-ruumiline varieerumine

Mihkel Kangur, Liisa Puusepp, Olga Buhvestova, Marina Haldna ja Külli Kangur

On käsitletud üldfosfori (TP_{sed}) ja viie fosfori fraktsiooni kontsentratsioonide ajalis-ruumilist varieeruvust Peipsi järve pindmistes settekihtides ning võrreldud üldfosfori- (TP), lahustunud anorgaanilise fosfori (PO₄-P) ja hapnikusisaldustega veesambas. Artikli eesmärgiks on selgitada sette pindmiste kihtide ja järvevee fosforisisalduse omavahelisi seoseid ning dünaamikat, mis aitaksid hinnata settest lähtuva fosfori osatähtsust järvevee fosforisisalduse kujunemisel. Setteproovid tüsedusega 10 cm ja veeproovid põhja- ning pinnalähedasest veekihi koguti samaaegselt kuuest seirepunktist kaks korda aastas (märtsis ja augustis) aastatel 2004 kuni 2009. Uuringu tulemused näitavad, et fosfori erinevate fraktsioonide kontsentratsioonid varieeruvad nii ajaliselt kui ka ruumiliselt küllalt olulisel määral. Liiasusanalüüsi (RDA) tulemused näitavad, et erinevate fosfori fraktsioonide varieeruvus korreleerub olulisel määral veesamba põhjalähedaste üldfosfori- (talvel) ja hapnikusisaldustega (suvel). Talvel oli setetes rohkem üldfosforit ja orgaanilist fosforit, mis on tõenäoliselt seotud suvel produtseeritud orgaanilise aine sadenemisega veekogu põhja. Suvel oli veesambas kolm kuni neli korda rohkem fosforit kui talvel. Fosfori kontsentratsiooni suurenemine järvevees suvekuudel settest lähtuva fosfori sisekoormuse ja järvesiseste protsesside tulemusel on tüüpiline madalates ning eutroofsetes järvedes. Käesoleva uuringu tulemused kinnitavad, et viimaste aastakümnete jooksul toimunud hapnikutingimuste muutused Peipsi järves võivad viia settest lähtuva fosfori sisekoormuse suurenemiseni.