Estonian Journal of Ecology, 2011, **60**, 1, 18–38 doi: 10.3176/eco.2011.1.03

Nitrogen and phosphorus in Estonian rivers discharging into Lake Peipsi: estimation of loads and seasonal and spatial distribution of concentrations

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Received 18 June 2010, revised 9 November 2010

Abstract. Our study aims to estimate the riverine loads of nutrients to Lake Peipsi *sensu stricto* and to assess their effect on the lake's water quality. The data of national monitoring of 1992–2007 were used for the determination of seasonal and spatial distribution of nitrogen and phosphorus in the rivers discharging into Lake Peipsi *s.s.* Statistical conclusions and tests were based on a multiparametric model. Our calculations revealed that the major Estonian rivers discharged approximately 5600 tonnes of nitrogen and 179 tonnes of phosphorus annually to Lake Peipsi *s.s.* Nitrogen export coefficients varied from 4 to 8 kg N ha^{-1} yr^{-1}, while the range of P losses was from 0.12 to 0.21 kg P ha^{-1} yr^{-1}. Seasonal variation in nitrogen concentrations had a sinusoidal pattern, with high concentrations during winter and spring and low values in summer, whereas phosphorus dynamics created a slightly different picture, with a much more irregular variation and a smaller amplitude over the year. Only a few rivers showed a pattern of notably higher phosphorus concentrations during summer low flows and more diluted concentrations during winter and spring. The differences in the concentration of phosphorus were mainly explained by variation in water discharge, while the availability of nitrogen in rivers was determined rather by seasonality. Nutrient concentrations in rivers discharging into Lake Peipsi are probably still influenced by nutrient stores from the period of intensive fertilization. Although a local effect of nitrogen loads on the lake's water quality was detected, the concentration of phosphorus in lake water remained insensitive to year-to-year changes in the riverine load of phosphorus.

Key words: Lake Peipsi, nutrient concentration, nutrient load, seasonal changes, water discharge, rivers.

INTRODUCTION

Intensification of human activities has led to widespread nutrient enrichment of surface waters causing a range of environmental, social, and economic problems encompassed under the term of eutrophication (Carpenter et al., 1998; Smith et al., 1999). The most common effects of eutrophication are enhanced vegetation growth and the imbalance of the aquatic ecosystems (Smith et al., 1999). However, the degradation of water resources by eutrophication has also more far-reaching effects such as fishing and boating recreation use losses, reduced biodiversity and conservation and amenity values, human health threat through the production of toxic cyanobacterial blooms (Carpenter et al., 1998; Smith et al., 1999; Moss et al., 2005; Dodds et al., 2009). Rivers are particularly vulnerable due to their proximity to population centres and sensitivity to land use changes (Withers & Jarvie, 2008). Nutrient concentrations in rivers are of great importance to the ecology of the river itself, but riverine transport of nutrients is also relevant to any further receiving medium (Salvia-Castellví et al., 2005).

Eutrophication is the most serious environmental problem in many shallow lakes in lowland areas (Moss et al., 2005), including Lake Peipsi. The limnological time-series data since the 1950s indicate deterioration of lake water quality and adverse changes in the whole ecosystem of Lake Peipsi. Eutrophication has led to an undesirable growth of algae, massive blooms of cyanobacteria accompanied by oxygen depletion during the night and fish kills, low water transparency, and siltation of the lake bottom (Kangur & Möls, 2008). Riverine transport is the most important pathway for input of nutrients from both point and nonpoint sources to Lake Peipsi (Loigu & Leisk, 1996; Blinova, 2001). Reduction of nutrient input into lakes should focus especially on decreasing the inputs by rivers, and requires knowledge of the sources and their contribution to the transport by the rivers (Behrendt & Opitz, 2000). Regional differences in weather and the hydrological regime in catchments together with local variations in nutrient emissions from various point and diffuse sources have a great impact on the accuracy of estimating the riverine loads (Kronvang et al., 2007).

The relative importance of the different nutrient sources varies greatly between different catchments depending on anthropogenic pressures and discharge (Räike et al., 2003; Stålnacke et al., 2004; Kronvang et al., 2005; Oenema et al., 2005; Withers & Jarvie, 2008). Therefore, qualitative and quantitative determinations of nutrients (i.e. concentrations and loads) are required to characterize and predict system responses. Although considerable research has been devoted to estimations of external nutrient loads to Lake Peipsi (Blinova, 2001; Stålnacke et al., 2002; Mourad et al., 2006; Loigu et al., 2008), much less attention has been paid to systematic evaluation of the seasonal and spatial distribution of nutrient dynamics in the catchment area of the lake. However, detailed knowledge of seasonal dynamics of nutrients in rivers is useful for the management and control of nutrient loadings to Lake Peipsi. In the present study we focused on nitrogen and phosphorus because enhanced availability of these nutrients is a worldwide cause for eutrophication of rivers, lakes, estuaries, and coastal oceans (Carpenter et al., 1998).

We aimed in our study at determining both the riverine nutrient loading to Lake Peipsi *sensu stricto* (*s.s.*) and the seasonal and spatial distribution of nitrogen and phosphorus in the rivers. The specific objectives of the study were (1) to estimate Estonian riverine loads of nutrients to Lake Peipsi *s.s.* and to compare nutrient export coefficients among basins; (2) to examine the seasonal dynamics of nutrients in the rivers discharging into the lake and the effect of seasonality, water temperature, and discharge on the dynamics of nutrients. Further we analysed the relationship between the nutrient concentration and water discharge in the specific catchments on a seasonal basis. Finally, we explored the dynamics of the catchment–lake system through following the long-term pattern of Estonian riverine load of nutrients to Lake Peipsi *s.s.* and the concentrations of nitrogen and phosphorus in the lake water.

MATERIAL AND METHODS

Site description

Peipsi is a shallow eutrophic lake on the border of Estonia and Russia (Fig. 1). The lake and its direct surroundings are considered an ecosystem of international importance. Lake Peipsi is significant for recreation and its amount of fresh water (25 km^3). Fish stocks of the lake have always been remarkably high, which makes it economically important for both commercial and recreational fishermen (Kangur et al., 2008).

Lake Peipsi consists of three parts. The northern part, Lake Peipsi *s.s.*, is the largest (2611 km^2) and has the greatest mean depth (8.3 m). The southern part, called Lake Pihkva, measures 708 km^2 and is 3.8 m deep on average. The strait between them is known as Lake Lämmijärv (236 km^2; mean depth 2.6 m). We concentrated in our study on Lake Peipsi *s.s.*, which constitutes 73% of the total surface area of the whole lake and of which 55% belongs to Estonia.

According to the OECD (1982) classification, the present-day conditions characterize Lake Peipsi *s.s.* as a eutrophic waterbody, while the trophic status of Lake Lämmijärv is close to hypertrophic and Lake Pihkva is a hypertrophic basin (Kangur & Möls, 2008). The average water retention time is about two years in

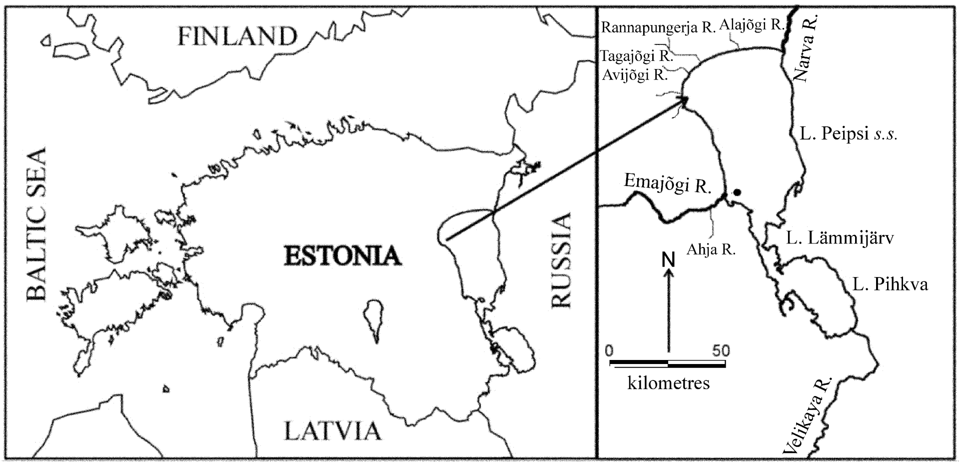

Fig. 1. Location of Lake Peipsi and the rivers discharging into the lake. The in-lake water sampling station close to the mouth of the Emajõgi River is shown by a filled dot.

the whole lake. Temperature stratification is unstable and the lake is usually rich in oxygen during the open-water period. The near-bottom water frequently suffers from oxygen deficiency when the lake is ice-covered (usually from December to April).

The drainage basin of Lake Peipsi measures 47 800 km^2 (including the lake surface). It is shared by Russia (58%), Estonia (34%) and, for a negligible part, by Latvia and Belarus (Jaani, 2008). The northern part of this drainage basin has a sedimentary cover consisting of Ordovician and Silurian limestones; the southern part is characterized by sandy–silty and clayey Devonian deposits, which are overlaid with Quaternary deposits. The topography of the catchment is relatively flat. The till-covered plain of the Estonian part of the catchment is higher in the south-west and north-west due to the presence of uplands (Pandivere, Haanja, Otepää, and Sakala) (Iital et al., 2005). The main land cover classes are forests (61%), which predominate in the north of the catchment, and agricultural land (28%); the latter is concentrated in Estonia and around the town of Pskov in Russia (Mourad, 2008). The rest of the land cover consists of peat bogs and built-up area. Major towns are Pskov in Russia (191 961 inhabitants) and Tartu in Estonia (102 455 inhabitants) (after World Gazetteer, 2010). Two main rivers in the drainage basin are the Velikaya (25 200 km^2) and the Emajõgi (9745 km^2). The Velikaya River drains the largest portion of the Russian and Latvian parts of the basin and discharges into Lake Pihkva. The Emajõgi River drains the majority of the Estonian part of the basin and discharges into Lake Peipsi *s.s.* The other major Estonian rivers flowing into Lake Peipsi *s.s.*, studied within the monitoring programme, are the Alajõgi, the Rannapungerja, and the Avijõgi (Fig. 1).

Surface water quality and water discharge data

We used the water quality data of the Estonian rivers discharging into Lake Peipsi *s.s.* (Emajõgi and its tributary the Ahja, Rannapungerja and its tributary the Tagajõgi, Avijõgi, and Alajõgi) gathered within Estonian national monitoring programme from 1992 to 2007. The sampling frequency was once a month in all rivers except in the Tagajõgi River, where samples were collected six times a year for most of the time period covered by our study. The river water was analysed in Tartu and Virumaa Environmental Researchers Ltd, Estonia.

Data on daily mean discharges in the studied rivers were obtained from the Estonian Institute of Meteorology and Hydrology (EMHI). The discharges were calculated in EMHI from monthly measurements of stream discharge with a portable propeller flowmeter using regression formulae. In the case of the Emajõgi and Ahja rivers, the water discharge station is located upstream of the water quality sampling sites (Table 1). Therefore the water discharge at these sites as well as at the river mouth was estimated by areal extrapolation.

Additionally, we used a hydrochemical data set for Lake Peipsi from 1985 to 1990 and from 1992 to 2007. The samples for nutrient analysis were collected from March to November. Most studies of lake water quality since 1992 have

Table 1. Total areas of the studied drainage basins and the areas upstream of gauging stations and water quality sampling sites in the catchment of Lake Peipsi

River	Drainage basin area, km^2	Area upstream of gauging station, km^2	Area upstream of water quality station, km^2
Alajõgi	150	140	140
Rannapungerja	601	313	313
Tagajõgi	252	252	252
Avijõgi	393	366	366
Emajõgi	9745	7840	8539
Ahja	930	896	930

been carried out on the Estonian part but several joint Estonian–Russian expeditions to the whole lake have also been conducted since 2001. Further background information on sampling in Lake Peipsi has been published by Haldna et al. (2008) and Kangur & Möls (2008). Chemical analyses were performed in the Institute of Zoology and Botany of the Estonian University of Life Sciences, and since 1992 in Tartu Environmental Researches Ltd, Estonia.

From water samples ammonium ion (NH4-N), nitrite ion (NO2-N), nitrate ion (NO3-N), total nitrogen (TN), orthophosphate ion (PO4-P), and total phosphorus (TP) were analysed according to international standards (APHA, 1981).

Load and area-specific load calculations

To achieve a less biased estimate of load at this (monthly) sampling frequency we used the method described by Järvet (2001) and Johnes (2007):

$$\text{Load} = \frac{K\sum_{i=1}^{n}(C_i Q_i)}{\sum_{i=1}^{n} Q_i}\overline{Q_r},$$

where K is conversion factor to take into account the period of record, C_i is instantaneous concentration associated with individual samples (mg L^{-1}), Q_i is instantaneous discharge at the time of sampling (m^3 s^{-1}), n is number of samples, $\overline{Q_r}$ is mean discharge for the period of record (m^3 s^{-1}), and $(K\sum_{i=1}^{n}(C_i Q_i))\big/(\sum_{i=1}^{n} Q_i)$ is nutrient flow-weighted concentration.

In cases the site of collecting samples for estimating water quality did not coincide with the flow measurement station, the water discharge for the sampling site was calculated on the basis of the proportions of the catchment areas, as previously described by Sileika et al. (2006). We interpolated the loads calculated for the water quality sampling sites to the mouths of the studied rivers. Two of the water quality sampling sites (in the Emajõgi and Rannapungerja rivers) were located close to the river mouth, but still excluded nutrient contributions from their tributaries (the Ahja and Tagajõgi rivers, respectively) located downstream from the sampling sites. To obtain the loads to Lake Peipsi, the inputs from the tributaries were added to the values obtained for the main rivers.

To compare nutrient export among basins, annual export coefficients were calculated by dividing the annual load value with the size of the catchment area of the river concerned.

Statistical tests

We used boxplot diagrams for describing the sample statistics of the observed water parameters in rivers discharging into Lake Peipsi *s.s.* in different seasons. Prior to investigating the seasonal effect on nutrient concentrations in different rivers we divided the whole observation period into four fixed seasons: spring (Sp: March, April, May), summer (S: June, July, August), autumn (A: September, October, November), and winter (W: December, January, February).

Before modelling all nutrient concentrations were log-transformed to make the distribution closer to the normal one. Statistical conclusions and tests were made on the basis of a multiparametric model, specifying how nutrient concentration depends on water discharge and temperature of different seasons in the observed rivers. Seasonal time was represented in the model through a linear combination of three β-distribution functions calculated from the number of the day within the year (Möls, 2005). First we found the best-fitted model (the largest R^2) for exploring whether there was a time lag between water discharge and its effect on nutrient concentration. We used the GLM procedure of the SAS/STAT system (SAS Institute Inc., 1999) and its CONTRAST statement to test the effect of water discharge in different seasons on nutrient concentrations in a specific river. We examined the effect of Estonian riverine loads on the nutrient concentration in lake water on the basis of loads calculated for the largest inflow into Lake Peipsi *s.s.*, the Emajõgi River, and nutrient concentrations measured in the sampling station in the lake close to the river mouth (Fig. 1). Before finding the effect of load on concentration we included in the linear model (sequential type 1 model, incremental improvement in the error SS as each effect is added to the model) the effects of season, year, and their interactions.

RESULTS

Nutrient fluxes from the Estonian part of the catchment to Lake Peipsi *s.s.* and annual export coefficients

The annual inflow of water to Lake Peipsi *s.s.*, calculated as the mean value for 1992–2007, was estimated at 80 $m^3 s^{-1}$ (Table 2). The average annual load of nutrients discharged into Lake Peipsi *s.s.* by major Estonian rivers during the

Table 2. Total annual discharge and riverine loads of nutrients to Lake Peipsi *s.s.* from the Estonian side of the catchment in 1992–2007

River	Discharge, $m^3 s^{-1}$	TN, tonnes yr^{-1}	TP, tonnes yr^{-1}
Alajõgi	1.56	113	2.5
Rannapungerja[a]	5.39	351	8.3
Tagajõgi	2.09	132	3.6
Avijõgi	3.30	314	4.9
Emajõgi[b]	69.93	4822	163.4
Ahja	6.83	369	20.0
Total	80.00	5600	179.1

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[a] The loads include the input from the Tagajõgi River.
[b] The loads include the input from the Ahja River.

same period comprised 5600 tonnes of N and 179 tonnes of P according to our estimates. Quantitative estimates of pollution load as well as water discharge values varied between different rivers in the study area depending on the size of the river basin. The Emajõgi River contributed approximately 86% (4820 t yr^{-1}) of the nitrogen and 91% (163 t yr^{-1}) of the total Estonian riverine phosphorus load.

Normalized loads allow comparison of nutrient exports among basins, avoiding most of the hydrology-related annual variations. Nitrogen export coefficients varied from 4 to 8 kg N ha^{-1} yr^{-1}. The highest annual export coefficient (area-specific load) of nitrogen was calculated for the Avijõgi River (Table 3). As a rule, the rivers discharging into the northern part of Lake Peipsi *s.s.* had higher values of area-specific load of nitrogen than the Emajõgi River. The range of phosphorus losses was from 0.12 to 0.21 kg P ha^{-1} yr^{-1}. The highest losses of TP in the study area were calculated for the catchment of the Emajõgi River.

Table 3. Time-averaged specific runoff and area-specific riverine export of nutrients from Estonian river basins in the catchment of Lake Peipsi *s.s.* in 1992–2007

River basin	Specific runoff, L s^{-1} km^{-2}	TN, kg ha yr^{-1}	TP, kg ha yr^{-1}
Alajõgi	10.40	7.5	0.17
Rannapungerja	8.96	5.8	0.14
Tagajõgi	8.28	5.2	0.14
Avijõgi	8.41	8.0	0.12
Emajõgi	7.18	4.9	0.17
Ahja	7.35	4.0	0.21
Mean	7.36	5.1	0.16

Seasonal variations in nutrient concentrations in rivers

The Avijõgi River exhibited higher levels of nitrogen round the year (Fig. 2): annual flow-weighted concentrations of TN and NO3-N were 3040 and 1874 mg N m^{-3}, respectively. The concentrations of TN and NO3-N displayed a very similar seasonal dynamics in the studied rivers (Fig. 2), presenting a typical sinusoidal pattern with low concentrations in summer and high values during winter and spring with no significant differences between winter and spring. However, large differences existed between nitrogen concentrations measured during spring and summer, especially in the Emajõgi and Rannapungerja rivers.

The P dynamics had a slightly different pattern, with much more irregular variation and smaller amplitude over the year. The annual flow-weighted concentration of TP in the Emajõgi River was 74 mg P m^{-3}, i.e. markedly higher than in the other rivers; PO4-P comprised only 30% of TP. However, phosphate was clearly the principal form of TP (60%) present in the Alajõgi River, where the most elevated concentrations of PO4-P (annual flow-weighted concentration was 49 mg P m^{-3}) were observed. Most of the studied rivers exhibited no considerable changes in the seasonal dynamics of TP and PO4-P (Fig. 3). The Alajõgi and

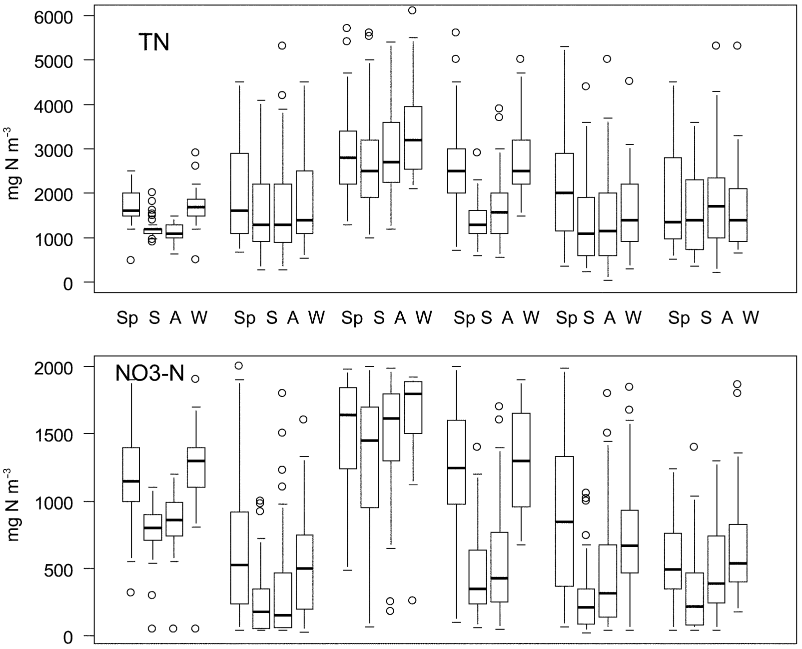

Fig. 2. Seasonal variation of the total nitrogen (TN) and nitrate (NO3-N) concentration measured in Estonian rivers discharging into Lake Peipsi *s.s.* in 1992–2007. Spring (Sp), summer (S), autumn (A), and winter (W) concentrations are represented. The circles document outliers. Boxplots indicate medians and interquartile ranges, and whiskers show 5% and 95% quantiles.

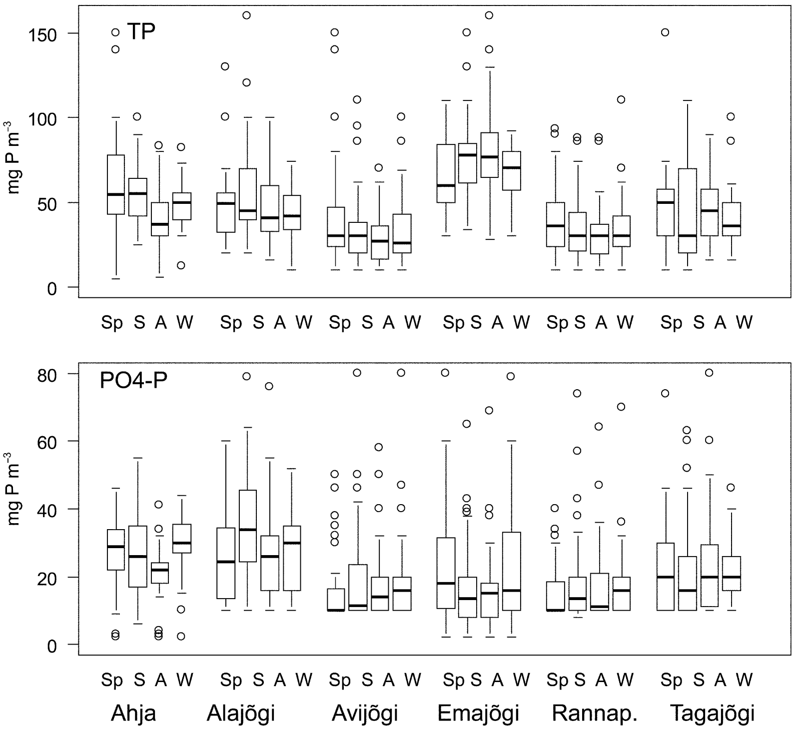

Fig. 3. Seasonal variation of the total phosphorus (TP) and phosphate (PO4-P) concentration measured in Estonian rivers discharging into Lake Peipsi *s.s.* in 1992–2007. Spring (Sp), summer (S), autumn (A), and winter (W) concentrations are represented. The circles document outliers. Boxplots indicate medians and interquartile ranges, and whiskers show 5% and 95% quantiles. The detection limit of PO4-P (2 mgP m^{-3}) is reached in some cases.

Emajõgi rivers showed notably higher P concentrations during summer low flows and more diluted concentrations during winter and spring. In the Alajõgi River, the median value of both PO4-P and TP concentration in summer was approximately 1.3 times higher than in winter ($p = 0.011$ and $p = 0.015$, respectively). In the Emajõgi River, the median value of TP concentration was 78 mg P m^{-3} in summer, while it was about 1.2 times lower in spring ($p = 0.012$).

The effect of seasonality, water temperature, and discharge on nutrient concentrations in the studied rivers

Natural factors such as seasonality, temperature, and discharge are extremely important for determining the dynamics of nutrients in Estonian rivers discharging into Lake Peipsi (Table 4). The results of the statistical analysis with the general linear model showed that seasonality was responsible for the variation in NO2-N, NO3-N, PO4-P, TN, and TP concentrations. The most pronounced effect of

Table 4. Significance probabilities (*p*-values) of the effect of water temperature (*t*), water discharge (*Q*), and seasonality on the nutrient concentration in all major rivers discharging into Lake Peipsi *s.s.* from the Estonian side in 1992–2007

Parameter	*t*	*Q*	Seasonality
NH4-N	0.030	0.035	0.767
NO2-N	0.026	<0.001	0.001
NO3-N	0.0002	0.693	<0.001
TN	0.369	0.225	0.004
PO4-P	0.813	0.053	0.020
TP	0.857	<0.001	0.006

seasonality was detected in the case of NO3-N ($p < 0.001$). Temperature appeared to have been an important factor for changes in dissolved inorganic nitrogen forms.

The differences in the concentrations of NO2-N and TP were mainly explained by variations in water discharge. However, the effect of discharge on nutrient concentration in a specific river discharging into Lake Peipsi was different depending on season (Figs 4–6). The differences in the relationship between water discharge and river water nutrient concentration were the most evident between spring and summer. In the Emajõgi River, the established relationship between discharge and TP concentration showed a decrease in TP concentration with increasing discharge during spring (Fig. 4). In the Alajõgi River, a comparable effect of water discharge on the PO4-P concentration in spring was observed (Fig. 5). However, the relationship reversed entirely in summer. In the Emajõgi River, the concentration of TP remained stable during summer despite changes in water discharge. The above-mentioned relationships between TP and PO4-P concentrations and water discharge observed in the Emajõgi and Alajõgi rivers were statistically significant ($R^2 = 0.32$; $p < 0.05$ and $R^2 = 0.19$; $p < 0.001$, respectively) (Fig. 4).

The results of our model proved that the effect of water discharge was the most prominent in defining the dynamics of dissolved inorganic nitrogen. The Ranna-

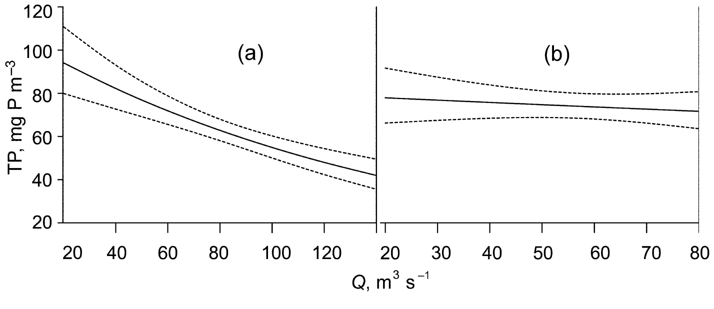

Fig. 4. Relationship between the total phosphorus (TP) concentration and water discharge (*Q*) in spring (a) and summer (b) in the Emajõgi River; trend-line and confidence limits are represented.

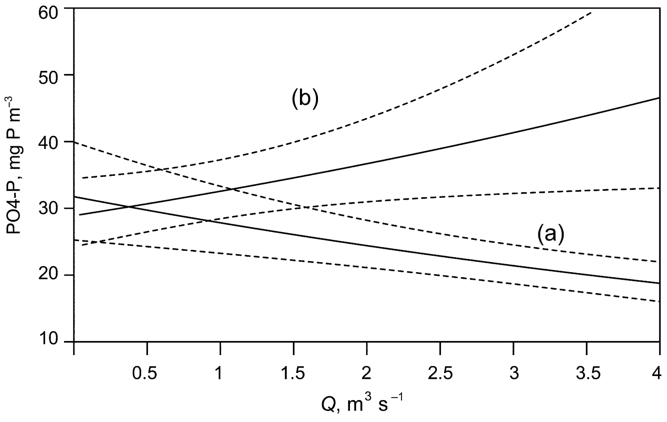

Fig. 5. Relationship between the phosphate (PO4-P) concentration and water discharge (*Q*) in spring (a) and summer (b) in the Alajõgi River; trend-line and confidence limits are represented.

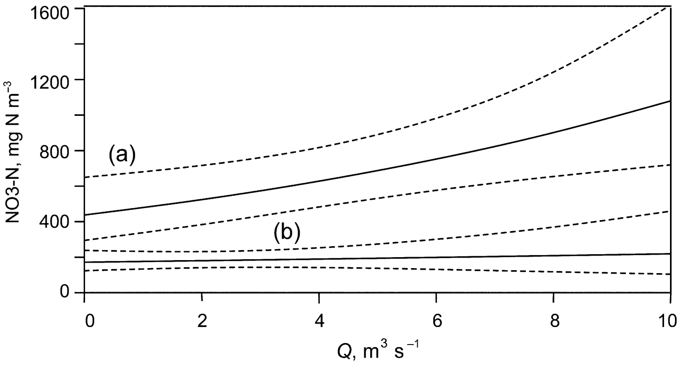

Fig. 6. Relationship between the nitrate (NO3-N) concentration and water discharge (*Q*) in spring (a) and summer (b) in the Rannapungerja River; trend-line and confidence limits are represented.

pungerja (Fig. 6) and the Alajõgi rivers experienced similar changes in NO3-N concentrations: an increase in the concentration with increasing discharge during autumn, winter, and spring was revealed, while in summer there were no changes. The established relationships in these rivers were statistically significant ($R^2 = 0.48$; $p = 0.007$ and $R^2 = 0.36$; $p < 0.001$, respectively).

Nitrogen and phosphorus concentrations in the water of Lake Peipsi during periods with different nutrient fluxes

We compared average values of nutrient concentrations in lake water in two periods, 1985–1990 and 1992–2007, characterized by different loading. From 1992 to 2007 the mean annual in-lake concentration of TN (630 mg N m^{-3}) was significantly lower ($p = 0.006$) than in 1985–1990, when the value amounted to 687 mg N m^{-3}. The concentration of TP also differed significantly ($p < 0.001$) between the two periods: 39 mg P m^{-3} in 1992–2007 as opposed to 30 mg P m^{-3} in 1985–1990.

A local impact of N loads on the lake water quality was detected. The TN concentration in the lake water close to the mouth of the Emajõgi River was significantly influenced ($p = 0.002$) by the N input from the river (Fig. 7). The concentration of TP in lake water was not so sensitive to year-by-year changes in the riverine P load (Fig. 8), and the effect of the load on the concentration was not

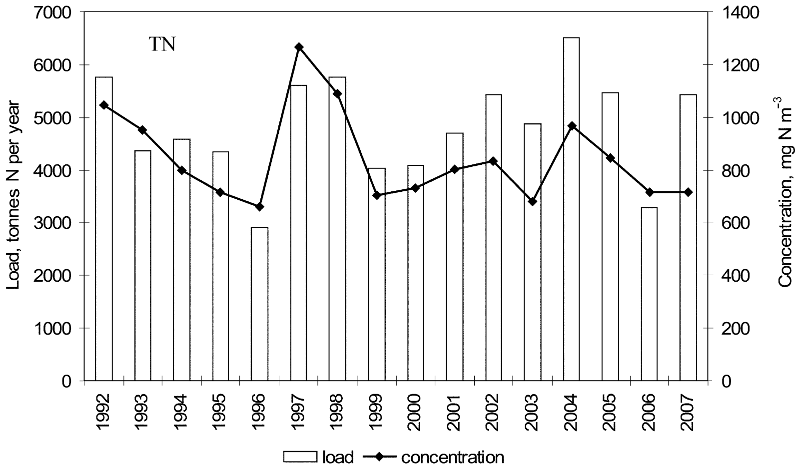

Fig. 7. Total nitrogen (TN) load discharged by the Emajõgi River and in-lake concentration close to the river mouth in 1992–2007.

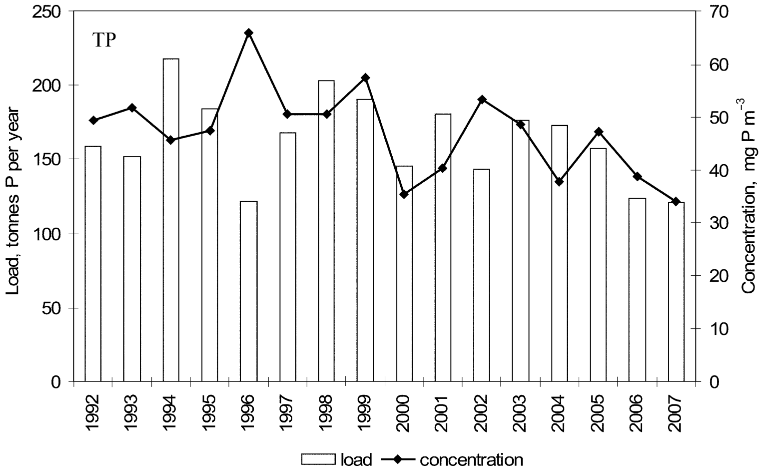

Fig. 8. Total phosphorus (TP) load discharged by the Emajõgi River and in-lake concentration close to the river mouth in 1992–2007.

statistically significant. However, a marginal decline in both P load of the Emajõgi River and in-lake TP concentration can be followed since 1998 when Tartu wastewater treatment plant was reconstructed.

DISCUSSION

Our estimations of riverine nutrient fluxes to Lake Peipsi *s.s.* for the period from 1992 to 2007 are generally within the range of the other analogous studies (Table 5). Deviations can arise from different factors. According to Quilbé et al. (2006), the accuracy of the methods of load estimation depends on the frequency of sampling, the length of the estimation period, the size of the catchment, the behaviour of contaminants, as well as human activities. The routine monitoring programmes with infrequent sampling often result in biased estimates of the nutrient transport (Kronvang et al., 2007). According to Johnes (2007), river sampling at monthly frequency (as was the case in this study) gives highly uncertain load estimates. To achieve a less biased estimate of load at the monthly sampling frequency we used the method recommended by Johnes (2007).

The loading of N into Lake Peipsi *s.s.* from the Estonian catchment decreased substantially from the period of intensive agricultural activity (the periods 1985–1989 and 1980–1991 have been used by different authors) to the present time (1992–2004, 1995–1999, 1992–2007, 2001–2005), whereas the loading of P decreased much less (Table 5). Mourad et al. (2006) explained the difference in response between N and P by greater susceptibility of P for retention along the hydrological pathways between the soil surface and the lake. The importance of accumulation of phosphorus in soils and the influence of this on long-term P losses has been stressed by many authors (Räike et al., 2003; Stålnacke et al., 2003; Iital et al., 2005). Leaching of nutrients can continue for a long time after reduced fertilization because of the soil's capacity to retain nutrients.

Table 5. Estimates of the total riverine loads of nutrients to Lake Peipsi *s.s.* from various studies

Study period	TN, t yr^{-1}	TP, t yr^{-1}	Source
1985–1989[a]	16 696	288	Mourad et al., 2006
1980–1991[b]	11 770	294	Nõges et al., 2007
1995–1999[a]	7 706	187	Mourad et al., 2006
1992–2004[b]	7 124	256	Nõges et al., 2007
2001–2005[c]	6 328	195	Loigu et al., 2008
1992–2007	5 600	179	This study

[a] Composed of Estonian and Russian rivers discharging into Lake Peipsi *s.s.*

[b] Composed of Estonian riverine loads to Lake Peipsi.

[c] Composed of nutrient loads from the Emajõgi, Kääpa, Rannapungerja, Avijõgi, and Alajõgi rivers.

The area-specific load of TP to Lake Peipsi was 0.16 kg P ha^{-1} yr^{-1} (Table 3), which can be compared with the mean of 0.15 kg P ha^{-1} yr^{-1} for the Gulf of Riga (Laznik et al., 1999). Elevated loads of TP were observed in the Emajõgi and Alajõgi river basins, which can be explained by high point-source emissions (e.g. Tartu in the Emajõgi River basin and households in the Alajõgi River basin). According to Loigu et al. (2008), the point-source emissions of phosphorus to the Emajõgi River alone accounted for about 81% of the total point-source loading in the Estonian part of the Lake Peipsi drainage basin in 2005. The high loss of TP in the Alajõgi River can also be associated with the relatively high specific runoff (Table 3). Still our values were lower than the TP export of 0.3–6.0 kg ha^{-1} yr^{-1} reported by Ulén et al. (2007) for small agricultural streams of north-west European countries, where surface erosion can contribute 40–88% to the TP transfer. Kronvang et al. (2007) also confirmed the large variation (0.1–6.0 kg ha^{-1} yr^{-1}) in the average annual TP loss from agricultural land in the 17 European macro-catchments, with the greatest values in the basins characterized by soil erosion. Kronvang et al. (2007) noted the importance of catchment hydrology (total run-off), population density, and the area of surface waters in the catchment in governing the resulting TP export at the macro-catchment scale (250–11 000 km^2).

Mourad et al. (2006) showed that 31% to 45% of diffuse N emissions between 1985 and 1989 reached the river network, largely via the groundwater pathway, while this was only 3% to 10% of the total diffuse P emissions, mainly via the surface pathway. Changes in agricultural management do not automatically lead to changes in nutrient loading. It may take decades in some drainage basins to record reductions in nutrient loading because of high groundwater nitrate concentrations from previous heavy use of fertilizers (Kronvang et al., 2005). Thus, it can be supposed that losses of N are still influenced by the N storage from the period of intensive fertilization. In our study the highest TN area-specific loads were calculated for the Avijõgi River basin. In this basin, agricultural land occupies about 26.1% of the total area (Iital et al., 2005). The average annual TN specific load was 8.3 kg ha^{-1} for the Gulf of Riga (Laznik et al., 1999), while the value was 5.1 kg ha^{-1} for Lake Peipsi according to our study. Laznik et al. (1999) stated that all nitrogen loads calculated for the Gulf of Riga were relatively modest (thus also for the Estonian rivers in the drainage basin of Lake Peipsi *s.s.*) in a Baltic Sea perspective.

Nutrient dynamics in rivers discharging into Lake Peipsi *s.s.*

The seasonal dynamics of nitrate concentration in Estonian rivers discharging into Lake Peipsi *s.s.* was similar to that in Laznik et al. (1999), who attributed lower nitrogen levels during summer to the consumption of NO3-N by phytoplankton, uptake by crops and other biota, and denitrification processes in soil and groundwater. Later, in autumn and early winter, the concentrations rose again, most likely due to remineralization and increased losses from soils and lower biological activity in the rivers. The highest nitrogen concentrations, which can be associated with the high flow period, were observed in winter and spring (Fig. 2).

The results of our study confirm the previous statement of Salvia-Castellví et al. (2005) that the mean values and the amplitude of the waves of nitrate concentrations can clearly be accounted for by agricultural pressure. Higher nitrate concentrations were found in the Avijõgi River throughout the year. This river draws its water from the Pandivere Upland. Groundwater is the most important nitrogen source (mainly nitrates) in streams that have their headwaters near the Pandivere Upland (Pall & Viik, 2001). The high nitrate content of the water in these rivers may be connected with intensive agriculture in Soviet times in the region (Pall & Viik, 2001). Because of the thin layer of Quaternary deposits on well-jointed karstic limestone the region is very sensitive to nitrate pollution, and overfertilization has seriously affected the groundwater. The release of nitrogen to many European rivers was found to be controlled by slow mineralization of large pools of organically bound nitrogen (Grimvall et al., 2000; Räike et al., 2003; Stålnacke et al., 2003, 2004; Oenema et al., 2005). Therefore, NO3-N remained the principal form of nitrogen in the Avijõgi River, fluctuating around a more or less constant level irrespective of season.

The Emajõgi and Rannapungerja rivers exhibited large variation in nitrogen concentration between spring and summer. Losses from agricultural soils probably represent the major source of nitrate in the drainage area of the Emajõgi River, where the proportion of agricultural areas is high (43.6%) (Iital et al., 2005). For the Rannapungerja River, the respective number is twice lower. The elevated concentrations of nitrogen in the rivers of the northern drainage basin of Lake Peipsi are commonly attributed to large wetland areas in the basin (Leisk & Loigu, 2001). In a case study from rural catchments in Luxemburg it was demonstrated that about 60% of the total nitrate load occurs in less than 20% of the year, due to the higher concentrations and higher discharges during the wet period (Salvia-Castellví et al., 2005). A positive effect of water discharge on the NO3-N concentration in autumn, winter, and spring was detected in the Alajõgi and Rannapungerja rivers. Nevertheless, with respect to NO3-N, no significant effect of discharge was found on its dynamics (Table 4). Mineral forms of N are mobile ions. Their transport depends on the availability in soil solution rather than on flow conditions (Quilbé et al., 2006).

Phosphorus is delivered to the rivers from point and diffuse sources. Phosphate phosphorus originates mainly from point sources. Depending on the pressure of the households in the basins, point source loads coming with sewage water appear to be relevant during the dry season (Salvia-Castellví et al., 2005; Edwards & Withers, 2007; Withers & Jarvie, 2008). In our study, this situation was demonstrated as an inverse relationship between the flow and the concentration of PO4-P in summer for the Alajõgi River (Fig. 5). As PO4-P comprises a large fraction of TP, TP also showed the same seasonal pattern. The Alajõgi River exhibited a pronounced seasonal pattern controlled by the river dilution capacity of point sources. In the other rivers, for which point sources play a smaller role, PO4-P summer concentrations were smaller and thus, seasonality was less marked. In the northern part of the Lake Peipsi drainage basin, where the population densities are less than 3 inhabitants per km^2 (Iital et al., 2005), a smaller human impact can be expected. Surprisingly, the seasonal pattern of phosphorus in the Alajõgi River was different from that observed in the other northern rivers. In the Emajõgi River, a significant seasonal variability in TP rather than in PO4-P concentrations was observed. This was most likely due to the concomitant influence of diffuse sources on TP inputs (agriculture is mostly concentrated in the southern part of the drainage basin of Lake Peipsi). Withers & Jarvie (2008) emphasized that whereas wastewater inputs are relatively continuous, diffuse P inputs occur more often intermittently and mostly as a particulate form. Thus, obviously, in the Emajõgi River the effect of water discharge on the TP concentration in summer was different from that on the PO4-P concentration in the Alajõgi River (Figs 4 and 5). The Emajõgi River has the largest basin (Table 1) of the studied rivers, and the dynamics of TP seems to be controlled by a series of factors.

The effect of Estonian riverine loads of nutrients on the water quality of Lake Peipsi *s.s.*

The nutrient content has always been different between the three parts of Lake Peipsi: the northern part of the lake is significantly poorer in nutrients than the southern part (Kangur & Möls, 2008). However, long-term patterns of the spatial distribution of TN and TP (the polarity) are not similar. The TN concentration in lake water remained relatively stable over the years and can be related to differences in natural conditions between the different parts of the lake. Moreover, it refers to the resilience of the lake to year-to-year changes in riverine loads of nutrients. This might be due to in-lake processes: N_2 fixation and denitrification. In contrast, the increasing difference in P concentrations between the northern and southern parts of the lake clearly shows that the input of P from the south is increasing. Also Nõges et al. (2007) supposed the growth of phosphorus loading from the Russian subcatchment in the period 1992–2002 in comparison with the loading of the 1980s. The major part of the loading from the south reaches Lake Peipsi *s.s.* through Lake Lämmijärv. Thus, the increased loading of phosphorus from the south can have affected the water quality in Lake Peipsi *s.s.* According to calculations by Rumyantsev et al. (2005), the average annual load of P to Lake Peipsi *s.s.* comprised 280 tonnes both through the rivers of the Russian part of the catchment and the water flow from Lake Pihkva during 1992–2003. The value exceeded our calculated average annual Estonian riverine load for the period 1992–2007 (179 tonnes of P). Thus, we identified a small decrease of the mean annual in-lake TN concentration and an increase of TP concentration by the period the Estonian riverine loading fell. This might have been caused by the increased load of P from the south as the increasing gradient between the southern and northern parts of the lake shows. Moreover, the natural processes may have influenced the lake water quality. Lower water level in combination with higher summer temperatures may have enhanced the internal nutrient loading as indicated by an increase in the TP concentration in lake water in 1992–2007 (Haldna et al., 2008). Previous investigations showed that in-lake concentrations of nutrients may vary over the years depending on variations in natural conditions. Interannual variation in the concentration of TP was substantial, with a twofold difference between the cool and wet 2004 and the warm and dry 2005. This variation cannot be explained by steep changes of nutrient loading (Kangur et al., 2006).

An evident local effect in the proximity to the mouth of the Emajõgi River confirmed the temporal response of TN concentrations in the lake to changes in the nitrogen loading. However, no similar effect was detected in the case of TP, which refers to its non-conservative nature and susceptibility to more complicated modes during transfer. Consequently, the in-lake TP concentration may be more sensitive to natural changes in water level and temperature than to year-to-year changes in phosphorus loading.

The nutrient concentrations in Lake Peipsi and especially in its northern part, Lake Peipsi *s.s.*, are not sensitive to year-to-year changes in riverine nutrient loads due to relatively long water residence time (on average 2 years). It is also confirmed by the conclusions of Jeppesen et al. (2005), who examined 35 long-term lake re-oligotrophication case studies. In lakes where the TN loading was reduced, the annual mean in-lake concentration responded in general rapidly (in less than 5 years). Reduction of the external TP loading resulted in a lower in-lake TP concentration typically after 10–15 years, because internal loading delayed the recovery (Jeppesen et., 2005). Improvement in lake water quality is governed by equilibrium conditions that exist between sediment and water column, which in turn is influenced by water residence time (Spears et al., 2007). There is a big storage of phosphorus in the sediments of Lake Peipsi *s.s.* (Punning & Kapanen, 2009). In addition, the water residence time is relatively long. Thus, the reduction of the P loading may be delayed. The responses of the southern part, Lake Pihkva, and the larger, deeper northern part, Lake Peipsi *s.s.*, most likely differ. The water quality of the former is characterized by greater temporal variation while the latter is more resilient to changes in nutrient loading. Longer water residence times provide greater opportunities for sediment–water contact, thereby promoting retention processes such as denitrification and sedimentation and preventing nitrogen accumulating to sediments (Saunders & Kalff, 2001). As a result, aspects other than just Estonian riverine loads of nutrients should be taken into consideration in the management of Lake Peipsi.

CONCLUSIONS

Many circumstances, such as multiple combinations of land use, household impacts, and physical–geographical factors may be responsible for variation in nutrient export in the study area. The point-source impact, expressed as a pronounced seasonal pattern of PO4-P controlled by the dilution capacity of point sources by rivers, was observed in a smaller basin, characterized by a relative homogeneity inside the unit. The large variation in nitrogen concentrations between spring and summer in rivers discharging into Lake Peipsi can be attributed to the agricultural pressure. The availability of nitrogen in rivers was determined to a large extent by seasonality rather than by water discharge and temperature.

The in-lake concentrations of phosphorus were not sensitive to year-to-year changes in riverine nutrient loads, while in the case of nitrogen the effect of riverine load on the in-lake water concentration was apparent. Other aspects than only Estonian riverine loads of nutrients should be taken into consideration in the management of Lake Peipsi.

We suppose that reduction of point sources may help to minimize the magnitude of the nutrient fluxes at the catchment scale, while reduction of diffuse sources may help to restore a good water quality at the scale of individual tributaries.

ACKNOWLEDGEMENTS

This study was funded by the target-financed project SF 0170006s08 of the Estonian Ministry of Education and Research and by the Estonian Science Foundation under grants 7392 and 7643.

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Lämmastik ja fosfor Peipsisse suubuvates Eesti-poolsetes jõgedes: ajalis-ruumiline varieeruvus

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On hinnatud Peipsi *sensu stricto* Eesti-poolsete jõgede toiteelementide (lämmastiku ja fosfori) reostuskoormust, uuritud toiteelementide kontsentratsioonide ajalis-ruumilist muutlikkust neis jõgedes ning seda mõjutavaid faktoreid ja käsitletud

reostuskoormuste ning järve vee kvaliteedi vahelisi seoseid. Töös on kasutatud riikliku seire 1992–2007 andmeid. Tehtud hinnangute järgi kanti jõgede kaudu Peipsisse *sensu stricto* aastatel 1992–2007 keskmiselt 5600 tonni lämmastikku (N) ja 179 tonni fosforit (P) aastas. Olenevalt valgla pindalast varieerusid nii uuritavate jõgede vooluhulgad kui ka toiteelementide reostuskoormused suurtes piirides. Seepärast leidsime toiteelementide koormused valgla pindalaühiku kohta (erireostuskoormused), mis N-i puhul varieerusid vahemikus 4 kuni 8 kg N ha^{-1} aastas; P kadu oli 0,12 kuni 0,21 kg ha^{-1} aastas. N ja P käitusid Peipsisse suubuvates jõgedes sesooniti erinevalt. N-i puhul oli iseloomulik kontsentratsioonide suurenemine talvel ja kevadel ning vähenemine suvel. Samas ei kõikunud P kontsentratsioonid suurel määral. Mõnes jões täheldati P kontsentratsiooni vähenemist kõrgvooluperioodil (talvel, kevadel) ja suurenemist suvel. Statistiline analüüs näitas, et P kontsentratsiooni varieeruvus oli määratud valdavalt vooluhulga muutustega; N-i kontsentratsiooni varieerumise peamiseks faktoriks oli aga sesoonsus. Tänapäevast jõgede vee kvaliteeti mõjutab olulisel määral intensiivse põllumajandustegevuse ja väetiste kasutamise perioodist säilinud toitainete varu pinnases. Me täheldasime jõe lämmastikukoormuse kohalikku mõju järve vee lämmastiku kontsentratsioonile. Muutused jõe fosforikoormuses ei kajastunud järve vee fosfori kontsentratsioonides.