

Ecosystem changes in large and shallow Võrtsjärv, a lake in Estonia — evidence from sediment pigments and phosphorus fractions

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Palaeopigments, organic matter dissolved in sediment porewater (pDOM) and phosphorus fractions were analysed in a sediment core from large shallow Võrtsjärv with the aim to assess whether the trends of climate-driven and anthropogenic changes in lake trophy within the 20th century are reflected in its sediment record. In the first half of the last century, the lake was naturally slightly eutrophic as the accumulation of palaeopigments was low and the load of nutrients stable; investigated variations in palaeoparameters were induced by the regular natural water level fluctuations. Since the mid-1950s eutrophication of Võrtsjärv has accelerated — content of fossil pigments, CaCO₃ and nutrients increased, while pDOM revealed high autochthonous matter input. The increase of palaeopigment's concentrations during the last decade may be consistent with regional climate warming. Investigated palaeoindicators and water level changes had a stronger relationship in the second half of the 20th century.

Introduction

Globally, the majority of lakes are classified as shallow waterbodies (Scheffer 1998). Large and shallow lakes are regionally highly important as they offer a wide spectrum of ecosystem services to mankind like sources of drinking water, fishery, recreation sites and waterway. Because of their intensive exploitation large shallow lakes are under multiple pressures via increased nutrient load and toxic pollution, exploitation

of bioresources, modification of hydrology and places for waste disposal (Nõges *et al.* 2008). Often the status of these lakes is impaired by exploitation, most commonly by nutrient enrichment causing eutrophication. In very shallow lakes, wind-induced resuspension increase the contact between sediment and water and frequently cause increased concentration of suspended solids in lake water (Ekholm *et al.* 1997, Hamilton and Mitchell 1997). Sondergaard *et al.* (2003) showed that in shallow-lake water sus-

pended solids and phosphorus can increase by a factor of 5–10 within a few windy days. The need to understand and resolve the problems arising from enhanced trophy has stimulated studies of shallow lakes; both their ecology and management have been receiving increased attention during the last decades (Gulati *et al.* 2007).

Large shallow lakes have large area/mean-depth ratio making them very sensitive to climate change, especially through changes in hydrological regime, causing large fluctuations of water level, change of lake volume and depth. In shallow lakes natural water-level fluctuation can be intra- or interannual, depending on regional climatic conditions (e.g. temperate, semi-arid) as well as on human activities (Coops *et al.* 2003). Fluctuations of water level in shallow lakes may alter the mean water-column irradiance and shift areas of sediment erosion, transportation, and accumulation (Bengtsson *et al.* 1990). Wind-induced resuspension and resulting processes, which frequently happen in large shallow lakes, are even more pronounced during low water-level periods. The dynamics of water level strongly affects lake biota. For instance, high water level during the growing season reduces light availability, while low water-level may damage plants via wave action or ice during winter and desiccation in summer (Coops and Hoesper 2002). Water-level fluctuation shifts shallow lakes between clear-water and turbid states, which are independent of nutrient enrichment and top-down effects. Such shifts can enhance species richness and diversity (Blindow 1992, Scheffer *et al.* 1993, Coops *et al.* 2003). As a result of water-level changes, phytoplankton in shallow lakes is exposed to high nutrient availability as well as to permanent mixing and variable light conditions. Climate, both directly and indirectly, affects lake physics (temperature, flushing), chemistry (DOC, pH, nutrients) and biology, therefore, a climate-driven change can potentially obscure or exaggerate the eutrophication process (Carvalho and Kirika 2003, Sondergaard *et al.* 2003). It has been noticed that climate change can significantly alter the functioning of shallow lakes and seasonal patterns in their water quality, but the responses to climate change are not easily predicted (Nõges *et al.* 2008). For instance, increasing water tempera-

tures are likely to increase winter phytoplankton biomass, but will similarly increase spring/autumn populations of grazing zooplankton; the net effect is uncertain (Carvalho and Kirika 2003).

Increasing water temperatures also enhance the potential of cyanobacteria to dominate the phytoplankton community (Elliott *et al.* 2006, Domis *et al.* 2007). Moreover, even moderate climate warming can enhance eutrophication problems as external loading is expected to increase due to shorter freezing time of watershed's soils and the increased precipitation (Moss *et al.* 2003, Nõges *et al.* 2005, Mooij *et al.* 2007).

Võrtsjärv is one of the largest lakes in eastern Europe by surface area but it is very shallow. About half of its catchment area is used for agriculture and cattle breeding. The modern lake is highly eutrophic and it has experienced anthropogenic pressure since the second half of the 20th century mainly due to accelerated urbanisation and intensive agricultural activity (Haberman *et al.* 1998, Nõges and Järvalt 2004). The lake underwent a rapid eutrophication during the 1970s and 1980s when practices in agriculture and wastewater treatments severely increased nutrient loads (Nõges *et al.* 2010a, 2011). Thereafter, despite a considerable decrease in nutrient loading, no significant decline in nutrient concentrations has been observed (Nõges and Kisand 1999, Nõges *et al.* 2010a). The apparent reason for this is the internal loading, which is affected by the climatically-induced cyclic water-level fluctuations. The long-term mean annual amplitude of water-level change in very shallow Võrtsjärv is 1.4 m and the absolute range is 3.2 m (Nõges *et al.* 2005), having strong influence on the ecosystem. Thus the water-level fluctuations are the leading force controlling light regime as well as nutrient cycles in this lake.

During the last decades a need to examine the water quality of lakes over long time-scales and to determine their current ecological status has become relevant. Sometimes, the palaeolimnological approach through the study of sediment profile is the only way to access past environmental changes (Bennion and Battarbee 2007, Heinsalu and Alliksaar 2009). The mixing of shallow lake surface sediments complicate an

interpretation of palaeolimnological information stored in sediments. However, within the last decade successful palaeolimnological investigations have been carried out also in shallow lakes (Eilers *et al.* 2006, Engstrom *et al.* 2006, Leeben *et al.* 2008).

The present study aimed to address how climate and anthropogenic eutrophication interact as stressors to affect the Võrtsjärv ecosystem. This is an important question to answer in terms of lake management. For this purpose, a sediment core representing the last 100 years of the history of the lake was investigated for fossil phytoplankton pigments, sediment porewater dissolved organic matter (pDOM) and phosphorus (P) fractions. Changes in the distribution of these palaeoindicators of lake primary production, origin and sources of organic matter (OM) and eutrophication were compared with the measured climate-change-induced environmental variables, nutrient loadings and phytoplankton indices based on long-term monitoring data.

Study site

Võrtsjärv (Fig. 1) with a surface area of 270 km² is a very shallow, unstratified lake with a mean depth of 2.8 m and a maximum depth of 6.0 m. The lake has six main inflows and one outflow to Lake Peipsi via the Suur Emajõgi. Due to the complicated and restricted outflow conditions, water level in the lake fluctuates strongly (annual mean amplitude 1.4 m) depending on the amount of precipitation in the catchment area (3374 km²). Precipitation, on the other hand, is governed by variations in the North Atlantic Oscillation (NAO) that controls the strength of moisture transport by westerly winds and hence the water-level fluctuations in the lake, that exhibit a periodicity of about 30 years (Nõges and Nõges 1998, Jaani 2001). Because of its large area, shallowness and the predominating westerly winds, sediments of the lake are exposed to wave-induced resuspension making the water permanently highly turbid.

The lake is eutrophic, characterised by mean nutrient concentrations of about 2.0 mg l⁻¹ for total N and about 50 µg l⁻¹ for total P (P_{tot}). The lake water is weakly alkaline (193 mg HCO₃⁻ l⁻¹).



Fig. 1. Location of Võrtsjärv. Sediment coring point is marked with a star.

Diatoms and cyanobacteria dominate the phytoplankton biomass, recently the latter was shown to account for more than two-thirds of the biomass during the summer months (Nõges *et al.* 2010b). Regular limnological investigations of the lake started in the 1960s when the chemical and biological monitoring began; in the 1970s also nutrient loading measurements from four main inflows were initiated.

Material and methods

Sediment sampling and chronology

A freeze corer was used to take a 120 cm sediment core from the southern part of Võrtsjärv (58°09'42''N, 26°04'10''E, water depth 1.40 m) in March 2003 (Fig. 1). The *in situ* frozen sediment core was carefully cleaned and sliced into continuous 1-cm-thick sub-samples and stored at -20 °C in the dark prior to analyses.

For the chronology, the sediment samples were analysed for the activity of ²¹⁰Pb and ²²⁶Ra, and the artificial radionuclides of ¹³⁷Cs and ²⁴¹Am by gamma spectrometry using a low background germanium detector (Appleby *et al.* 1986). The ²¹⁰Pb radiometric ages were calculated applying the constant rate of supply model and corrected by ¹³⁷Cs and ²⁴¹Am measurements of the core. The obtained age scale was then validated by the

distribution in the sediment of microscopically enumerated spheroidal fly-ash particles — the products of high-temperature fossil-fuel combustion — whose concentration profile in sediments follow the characteristic features of fuel-burning history of the region (Nöges *et al.* 2006). All these dating analyses of the sediment core were undertaken by Heinsalu *et al.* (2008).

Standard methods were used for the determination of the basic sediment composition. The water content was measured by drying the samples to constant weight at 105 °C. Loss-on-ignition (550 °C for 4 h and at 950 °C for 2 h) was measured to evaluate sediment organic matter and carbonate contents (Heiri *et al.* 2001).

Fossil phytoplankton pigments

In Vörtsjärv, ca. 90% of the total phytoplankton biomass is formed by cyanobacteria (mainly filamentous forms) and diatoms (Nöges and Laugaste 1998, Nöges *et al.* 2004). Therefore, carotenoids like fucoxanthin and diadinoxanthin (Fuco and Diadino respectively) were chosen to track changes in sedimentary diatoms (Jeffrey *et al.* 1997, Bianchi *et al.* 2002, McGowan *et al.* 2005, Reuss *et al.* 2005). Lutein (Lute; indicating green algae) and zeaxanthin (Zea; indicating cyanobacteria) were taken together (Lute-Zea) as we failed to separate these pigments properly. According to Vörtsjärv phytoplankton composition where green algae are not the dominant group, Lute-Zea should mostly represent cyanobacteria. As all phytoplankton groups contain β -carotene, although in smaller concentrations, chlorophyll *a* (Chl *a*) together with β -carotene was chosen as a proxy for total phytoplankton biomass, although Chl *a* and β -carotene are also the major pigments in higher plants (Leavitt 1993, Jeffrey *et al.* 1997, Leavitt and Hodgson 2001, Patoine and Leavitt 2006). Pheophytin *a* (Pheo *a*) was used as a general Chl *a* derivative. To evaluate the preservation of palaeopigments the Chl *a*/Pheo *a* ratio was used.

The analysis of sediment pigments followed the recommendations of Leavitt and Hodgson (2001). The frozen sediment samples were freeze-dried and pigments were extracted with an acetone-methanol mixture (80:20 v:v) at –20 °C in

the dark for 24 h under N₂. Thereafter, the pigment extracts were clarified by filtration through a 0.45 μ m pore-size filter (Millex LCR, Millipore).

The reversed-phase high-pressure liquid chromatography (RP-HPLC) used for pigment separation consisted of a Cecil 1100 series instrument (Cecil Instrument, Cambridge, England) made up of binary pumps fitted with a dynamic gradient mixer (Cecil Instrument) with a system purge and a variable wavelength (200–800 nm) ultraviolet-visible detector (model CE1200, Cecil Instrument) with a 18 μ l flow cell. Injection was done using a Rheodyne model 7725 manual valve (Cotati, California, USA) fitted with a 50 μ l loop. Prior to the injection, 0.5 M ammonium acetate was added to each sample as an ion-pairing reagent (Wright *et al.* 1991).

Chromatographic separations were performed in the reversed-phase mode using a Waters (Milford, USA) Spherisorb ODS2 3 μ m column (150 mm \times 4.6 mm I.D.) in line with a pre-column containing the same phase. A binary gradient elution method, adapted from Zapata *et al.* (1987), was used with constant flow rate of 1.5 ml min⁻¹. The mobile phases and the elution program are shown in Table 1. After the analysis, the solvent composition was returned to the initial conditions for 10 min, which allowed the system equilibrium to be restored prior to the next sample injection. Before use, solvents were degassed under vacuum and bubbled with helium during chromatography. All solvents were HPLC gradient grade and chemicals were analytical grade. Analyses were carried out at room temperature (25 °C). The calculation of peak areas was made at 450 nm (Jeffrey *et al.* 1997). Identification and calibration of pigments was performed with commercially available standards from DHI Water and Environment (Denmark). A standard addition method was used to confirm peak identification.

Organic matter dissolved in sediment porewater

The molecular weight distribution of pDOM was evaluated using a high-performance size-exclusion chromatography (HPSEC) system which comprised a Dionex P680 HPLC Pump, Agilent 1200 Series (Agilent Technologies, UK)

diode array absorbance detector (DAD) and a Rheodyne injector valve with a 50 μ l sample loop. A BioSep-SEC-S 2000 PEEK analytical column (300 \times 7.50 mm, Phenomenex, USA) preceded by a suitable guard column (75 \times 7.50 mm, Phenomenex, USA) was used for separation. The applied flow rate was 1 ml min⁻¹. The column packing material was silica bonded with hydrophilic diol coating, with particle size of 5 μ m and pore size of 145Å. The mobile phase consisted of 0.10 M NH₄H₂PO₄–(NH₄)₂HPO₄ buffer (pH 6.8). The HPSEC system was calibrated using protein standards (Aqueous SEC 1 Std, Phenomenex, USA).

The frozen sediment samples were thawed at 4 °C, and the porewater was separated by centrifugation at 4500 rpm for 15 min. Samples were filtered through 0.45 μ m pore size filters (Millex LCR, Millipore) and analysed in triplicate on the same day. All solutions for the HPLC measurements were prepared using distilled water filtered through a MilliQ water system and degassed. Chromatograms were recorded and processed using an Agilent ChemStation software. Full details of the used method are described by Lepane *et al.* (2004).

Total peak areas of humic substances (HS; molecular size fraction 1.2–2.3 kDa, with shoulder 600–800 Da) were calculated from the chromatograms, representing the total UV-absorbing fraction of pDOM in the porewater sample. Weight-average molecular weight (M_w) of pDOM was calculated using the formula:

$$M_w = \Sigma(h_i M_i) / \Sigma h_i$$

where h_i is the detector output and M_i is the molecular weight, at the i th retention time (Mori and Barth 1999).

Sediment phosphorus fractions

Sediment P fractionation was performed in triplicates according to the modified method of Psenner *et al.* (1988). Prior analyses, the frozen sediment subsamples (–20 °C) were melted in darkness at 4 °C during 24 h; 120 mg of melted sediment was extracted in four consecutive steps with 10 ml of the following solution: ammonium chloride (1.0 M NH₄Cl, pH 7), bicarbonate-dithionite (BD; both NaHCO₃ and Na₂S₂O₄ 0.11 M), sodium hydroxide (0.1 M NaOH) and hydrochloric acid (0.5 M HCl). As the frequently used modification of the scheme of Psenner *et al.* (1988), 0.1 M NaOH was applied instead of the original 1.0 M NaOH. The extracts were centrifuged at 4000 rpm for 10 min. The soluble reactive P (SRP) in each fraction was determined spectrophotometrically with the molybdenum-blue method (Murphy and Riley 1962). This extraction procedure fractionates sedimentary P into loosely sorbed P (NH₄Cl-RP), reductant soluble P (BD-RP), metal-oxide bound P (NaOH-RP) and calcium bound P (HCl-RP). In addition to the obtained reactive P fractions, the amount of NaOH-non-reactive P (NaOH-NRP), representing organic P, was calculated as the difference between P_{tot} in the NaOH extract (NaOH-P_{tot}) and NaOH-RP. NaOH-P_{tot} was measured according to Murphy and Riley (1962) after persulphate digestion.

Statistical analysis of data

A Principal Component Analysis (PCA) was carried out for ordination and classification of the sub-samples of the sediment core in relation to sediment quality variables. PCA was applied to the whole data set, although in order to avoid

Table 1. Analytical gradient program and solvents used for RP-HPLC method.

Time (min)	0.5 M ammonium acetate (pH 7.2) and methanol (2:8 v:v) (%)	Methanol and acetone (8:2 v:v) (%)	Gradient system
0	50	50	Injection
2	50	50	Isocratic hold
15	0	100	Linear
23	0	100	Isocratic hold
25	50	50	Linear

redundancy and perform a more realistic ordination the variables with low percentage of contribution were eliminated. Kaiser's rule — suggesting that components with eigenvalues under 1.0 should be discarded — was applied to determine the number of components to be retained in PCA (Kaiser 1960). Sedimentary variables were analysed after centring and standardisation. PCA was performed with the Multivariate Statistical Package (MVSP) ver. 3.12 (Kovach 1999). Kruskal-Wallis ANOVA was used to check for differences among untreated palaeoparameters among PCA-separated periods. Spearman's rank order correlation (r_s) was used to find dependencies between untreated parameters. For both analyses STATISTICA (ver. 6.0) was used. The data on lake water-levels, annual mean air temperature (T_{air}) and precipitation for the city of Tartu (~50 km east from Võrtsjärv) were obtained from the Estonian Institute of Hydrology and Meteorology. Values of the NAO index for the period 1899–2001 were taken from <http://www.cru.uea.ac.uk/cru/data/nao/>. For the winter NAO index (NAO_w), four months starting with December of the previous year were selected.

Results

Chronology and lithostratigraphy

The results of the Võrtsjärv core-chronology study are presented in detail in Heinsalu *et al.* (2008). ^{210}Pb measurements of the recent sediments showed that the entire unsupported ^{210}Pb inventory was within the upper 94 cm, indicating an approximate age of 150 years. Peak concentrations of ^{137}Cs and ^{241}Am allowed locating the early 1960s (sediment depth of 35–40 cm) when the atmospheric nuclear tests were carried out. This chronology was confirmed by the sediment distribution of spheroidal fly-ash particle profile, documenting the characteristic changes in the fossil fuel-burning history of the region. According to the chronology, the 70-cm-long sediment core that was under study covered approximately 100 years, the period since about AD 1900.

The uppermost part of the sediment core was poorly compacted (water content was > 90%). The carbonate content started to increase in the

mid-1950s and peaked sharply during the 1990s (Fig. 2). The OM content also rose during the past 15 years (Fig. 2).

Pigment stratigraphy

After an increase in the 1930s, the content of Lute-Zea, as well as Fuco decreased in the 1940s (Fig. 2). The content of Chl *a*, β -carotene and Lute-Zea increased since the 1950s while Fuco and Diadino increased since the 1980s. The dynamics of Pheo *a* showed no obvious trend. From the mid-1990s onward, investigated sediment pigments contents distinctly increased. The Chl *a*/Pheo *a* ratio showed an increasing trend since the mid-1990s (Fig. 2).

Changes in pDOM quantity and structure

The dominating UV-absorbing organic fraction in Võrtsjärv sediment porewater was the HS fraction (Lepane *et al.* 2010). The HS fraction content showed no trend until the 1970s, thereafter HS was decreasing (Fig. 2). The temporal distributions of molecular weight of pDOM showed mainly scattered values with no obvious trends (Fig. 2). However, a slight decrease of pDOM molecular weight was observed since the 1970s, thus indicating that the amount of organic compounds of autochthonous origin increased. M_w varied from 1.2 to 2.3 kDa, being close to aquatic fulvic compounds.

Changes in the dynamics of sediment phosphorus fractions

The average content of P fractions sum (ΣFR) was $730 \mu\text{g g}^{-1}$ DW, ranging from 460 to $1360 \mu\text{g g}^{-1}$ DW (Fig. 2). The dominating P fraction, BD-RP, accounted for 24%–49% of ΣFR and was strongly positively correlated with ΣFR ($r_s = 0.94$, $n = 31$, $p < 0.05$). The most labile P fraction ($\text{NH}_4\text{Cl-RP}$) contributed 0.7%–4% to ΣFR . The distinct rise in ΣFR began in the 1950s followed by the decrease in the 1970s on account of BD-RP and NaOH-RP. Another rise in ΣFR occurred in the mid-1990s. Although the con-

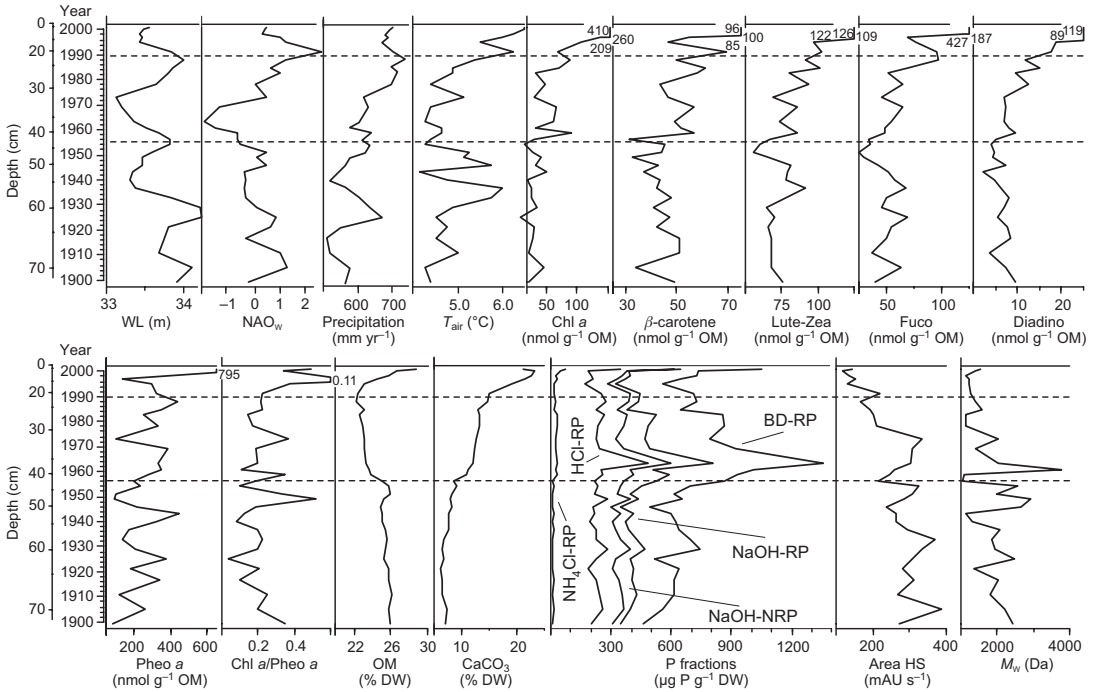


Fig. 2. The dynamics of palaeoparameters in sediments and water level oscillation (WL) in Vörtsjärv together with the fluctuation of annual mean air temperature (T_{air}), North Atlantic Oscillation winter index (NAO_w) and amount of precipitation for the period 1900–2001. Chl a = chlorophyll a ; Lute-Zea = lutein and zeaxanthin; Fuco = fucoxanthin; Diadino = diadinoxanthin; Pheo a = pheophytin a ; BD-RP = reductant soluble sedimentary phosphorus (P) fraction; NH_4Cl -RP = loosely sorbed P; HCl-RP = calcium bound P; NaOH-NRP = organic P; NaOH-RP = metal oxide bound P; Area HS = total peak areas of humic substances in the organic matter dissolved in sediment porewater (pDOM) ($mAU s^{-1}$ = milli arbitrary units by seconds); M_w = weight-average molecular weight of pDOM; DW = dry weight; OM = organic matter; Da = dalton.

tents of HCl-RP and NaOH-NRP increased in the early 1960s and in the mid-1990s, respectively, their dynamics showed no obvious trend throughout the 20th century (Fig. 2).

Periods distinguished by PCA

The PCA over the 100-year period was based on all analysed variables except pDOM characteristics as the percentage of contribution of these parameters was low. The first two axes of PCA described 83.4% of the total variance in the data set. The first factor explained most of the variability (58.2%) and had positive loadings for $CaCO_3$ content, NH_4Cl -RP and sediment pigments. The second factor, accounting for 25.2% of the total variance, was correlated primarily with ΣFR , BD-RP and NaOH-RP.

On the basis of the PCA, three periods were distinguished (Fig. 3): 1900–mid-1950s, mid-1950s–mid-1990s and mid-1990s–early 2000s. According to Kruskal-Wallis ANOVA, the investigated variables differed significantly between the first two periods ($CaCO_3$, organic matter, Chl a , ΣFR , NH_4Cl -RP, BD-RP), and between the first and the last period ($CaCO_3$, organic matter, Chl a , β -carotene, Lute-Zea, Fuco, Diadino, HS, NH_4Cl -RP, BD-RP, NaOH-NRP).

Water-level changes correlated strongly and positively with NAO_w , T_{air} and precipitation in the second half of the 20th century (Table 2). Correlations of water level and climate parameters with selected palaeodata in different investigated periods are given in Table 3. During the investigated period, palaeopigments (except Pheo a) correlated positively with $CaCO_3$ and NH_4Cl -RP and negatively with HS (Table 4).

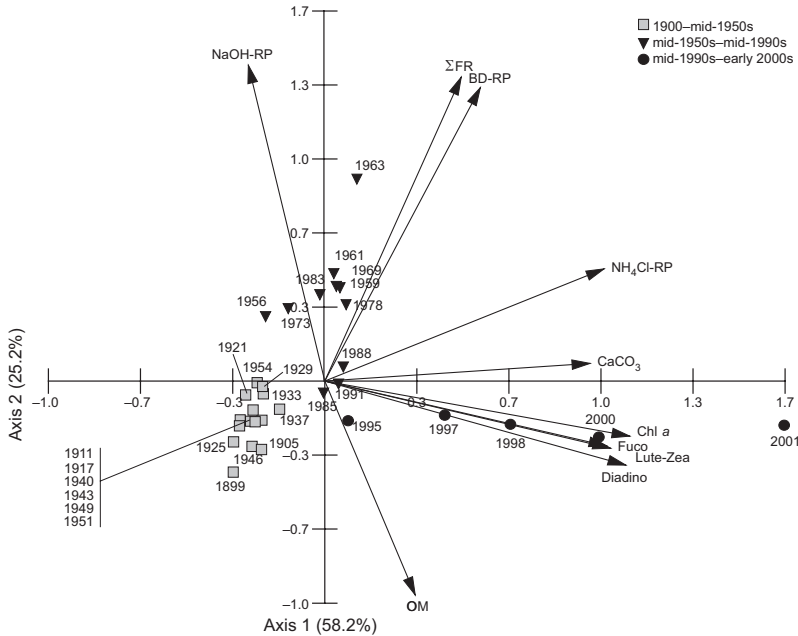


Fig. 3. Principal Component Analysis (PCA) biplot indicating three periods distinguished using selected palaeoparameters (arrows) from the 1900–2001 Vörtsjärv sediment core. For abbreviations *see* Fig. 2. Σ FR = sum of sedimentary phosphorus fractions.

Discussion

The palaeopigment composition in Vörtsjärv sediments indicates that cyanobacteria and diatoms were the dominant phytoplankton groups in the lake during the first half of the 20th century (Fig. 2), the first period clearly distinguishable in the PCA plot (Fig. 3). During this period, no significant increase in P input from the lake catchment occurred as the content and variability of studied P fractions was rather low (Fig. 2). Sediment resuspension was probably the most important P source for Vörtsjärv phytoplankton at that time. The large catchment area ensures naturally higher nutrient inflow to Vörtsjärv while the shallowness of the lake causing strong resuspension favors nutrient release from sediments into water. Therefore, slightly eutrophic conditions prevailed in the lake already from 1900 to the mid-1950s. Earlier Heinsalu *et al.* (2008) also showed that the sedimentary diatom flora since

about 1840 indicated moderately eutrophic, shallow-water conditions in Vörtsjärv. The reasons for that were likely natural — the lake's large catchment area, its shallowness resulting in high resuspension of sediments, hence sediments being a source of nutrients.

The regular oscillation of the water level has a strong impact on the Vörtsjärv ecosystem controlling its light climate as well as nutrient cycles, and through that also bioproduction and OM decomposition. The water level itself is determined mainly by the winter climatic conditions. In Estonia, the western airflow from the Atlantic during positive NAO remarkably increases air temperature and the amount of precipitation in winter. Warmer winters cause higher water level in Vörtsjärv in spring and also during the following summer and autumn. With higher water level, algal density is determined by light availability rather than by nutrients which results in lower phytoplankton biomass. When water

Table 2. Spearman rank order correlations of Vörtsjärv water level with climate parameters in different periods in the 20th century. Correlation coefficients set in boldface are significant at $p < 0.05$.

Water level in different periods	Winter NAO _w	Annual mean air temperature (T_{air})	Precipitation
1900 to mid-1950s; $n = 15$	0.352	-0.279	0.580
Mid-1950s to mid-1990s; $n = 11$	0.654	0.483	0.636

level is lower, more light is available and nutrient limitation takes over the control of phytoplankton. The shallower lake means higher phytoplankton biomass per unit volume and also per unit area (Nöges *et al.* 2003, Nöges *et al.* 2010a). In Vörtsjärv, the estimated euphotic-zone depth is 1.6–3.2 m, being generally smaller than the mean (2.8 m) or maximum (6.0 m) water depth (Haberman *et al.* 1998). Thus, euphotic zone penetration to the lake bottom is limited and the benthic algal community development is depressed. Moreover in deeper areas of Vörtsjärv the sediment surface consists of very fine floating material which is not the best substrate for phyto-benthos. Phytoplankton investigations in Vörtsjärv indicate that during the low-water-level period, algae from the sediment surface increase the phytoplankton species number in the water column, but do not contribute remarkably to biomass (Nöges *et al.* 2004). Thus the proportion of pigments derived from phyto-benthos is negligible in the pigment content accumulated in the Vörtsjärv sediment.

In the first half of the 20th century, water level correlated positively with precipitation (Table 2). Of the fossil pigments, only diadinoxanthin correlated significantly and positively with water level. Also the water level fluctuations and the amount of precipitation significantly affected pDOM characteristics like HS quantity (expressed as area of HS) and M_w (Table 3). A positive relationship suggests higher transport of land-derived organic particles and substances into the lake during increased water level. According to Toming *et al.* (2009), in Vörtsjärv water level and yellow substance (constituting up to 90% of DOM in boreal region) correlate positively. Concentration of yellow substance reaches maximum in spring and generally decreases towards autumn. The reason why the relationship between water level and phytoplankton biomass in the water column (Nöges *et al.* 2003, Nöges *et al.* 2010b) was not found for the total phytoplankton biomass (Chl *a* and β -carotene) and the fossil phytoplankton pigments in the sediment record can be a result of wind-induced waves constantly mixing surface sediment layers in this shallow lake causing decay of settled algae and their pigments. Other arguments for the lack of this relationship can be

Table 3. Spearman rank order correlations of selected palaeodata from Vörtsjärv dated sediment core with climate parameters and water-level in different time periods within the 20th century. Correlation coefficients set in boldface are significant at $p < 0.05$. Area HS = total peak areas of humic substances in the organic matter dissolved in sediment porewater (pDOM); M_w = weight-average molecular weight of pDOM; ΣFR = sum of sedimentary phosphorus (P) fractions; BD-RP = reductant soluble P; NaOH-RP = metal oxide bound P.

Palaeodata	1900–mid-1950s; $n = 15$				mid-1950s–mid-1990s; $n = 11$			
	NAO _w	Annual mean air temperature (T_{air})	Precipitation	Water level	NAO _w	Annual mean air temperature (T_{air})	Precipitation	Water level
Chlorophyll <i>a</i>	0.137	-0.017	-0.139	-0.196	0.391	0.399	0.384	0.237
β -carotene	-0.078	-0.001	-0.188	0.246	0.300	0.349	0.363	0.363
Lutein and zeaxanthin	-0.237	0.161	-0.353	-0.321	0.608	0.526	0.601	0.433
Fucoxanthin	0.034	-0.177	-0.15	0.096	0.629	0.498	0.671	0.405
Diadinoxanthin	0.078	0.095	-0.037	0.478	0.720	0.621	0.692	0.433
Area HS	-0.034	-0.082	0.559	0.646	-0.643	-0.438	-0.664	-0.664
M_w	0.076	0.087	0.491	0.260	-0.230	0.067	-0.377	-0.377
ΣFR	-0.434	0.310	0.224	-0.032	-0.888	-0.816	-0.650	-0.398
BD-RP	-0.479	0.385	0.127	-0.167	-0.888	-0.869	-0.615	-0.447
NaOH-RP	-0.148	0.143	0.168	0.185	-0.671	-0.703	-0.489	-0.356

quite weak correlation between NAO_w and water level found for the first half of the 20th century (Table 2), and the relatively high standard error of dates for deeper sediment horizons (*see* fig. 1c in Heinsalu *et al.* 2008), which is the common feature for calculated ^{210}Pb radiometric ages and what can complicate temporal comparison of datasets.

Besides water-level changes, also air-temperature fluctuation may influence the entire water column of shallow, non-stratified lakes and therefore these lakes are likely to respond more directly to short-term weather variations (Arvola *et al.* 2010). Higher water temperature in summer favour cyanobacterial blooms (Blenckner *et al.* 2010) and therefore the short-term increase in Lute-Zea in the 1930s could be induced by the rise of T_{air} in that decade (Fig. 2).

The PCA analysis revealed changes in Vörtsjärv ecological conditions since the 1950s (Fig. 3). Increase in palaeopigments (except Pheo *a*), elevated contents of P fractions (except NaOH-NRP and HCl-RP) and CaCO_3 as well as decline in HS and M_w are distinctive for the period from the mid-1950s to the mid-1990s (Fig. 2). Earlier investigations indicated that since the 1960s, urbanisation and agricultural activities in the Vörtsjärv drainage area intensified. A long-term monitoring dataset revealed that due to higher nutrient loading to the lake phytoplankton biomass increased in the 1960s reaching its maximum in the 1970s (Nöges and Laugaste 1998, Nöges and Nöges 2006). Moreover, the analysis of phytoplankton taxonomic

indices showed a continuous deterioration of Vörtsjärv ecological status during the 44-year period of limnological investigations (1964–2007; Nöges *et al.* 2010a). Increase in the content of palaeopigments and P fractions from the mid-1950s onwards confirm increased nutrient loading to the lake and a rise in bioproduction. Positive correlations of palaeopigments (except Pheo *a*) with $\text{NH}_4\text{Cl-RP}$ and CaCO_3 indicate accelerated eutrophication of the lake (Table 4). $\text{NH}_4\text{Cl-RP}$ includes phosphates dissolved in sediment porewater and loosely sorbed on sediment particles. Higher concentration of $\text{NH}_4\text{Cl-RP}$ facilitates P diffusion from the sediment to the lake water, since diffusion is driven by concentration gradients. If no other processes precipitate phosphates again, diffusion from sediments can constantly provide P supply for lake primary producers. The increase in CaCO_3 content in the sediments from the mid-1950s onwards has been considered an indicator of lake eutrophication, as intensive primary production rises water pH which results in accelerated CaCO_3 precipitation (Hodell *et al.* 1998, Dean 1999). The decline in the HS and M_w values since the 1960s–1970s coincided with the phytoplankton maximum values in the 1970s, as well as with an increase in palaeopigments since the mid-1950s (Fig. 2). The lower HS values and lower molecular weight of pDOM in sediments indicate autochthonous rather than allochthonous origin of OM (Bergström and Jansson 2000, Jansson *et al.* 2000), and hence increased in-lake bioproduction. Negative relationship of HS with palaeopigments supports the above assumption. However, lower M_w might indicate that microbial mineralization of OM is an important degradation process in the Vörtsjärv sediments (Münster and Chróst 1990).

Between the mid-1950s and the mid-1990s, the correlations between all used climate parameters (NAO_w , T_{air} , the amount of precipitation) and water level were much stronger (Table 2). In Vörtsjärv, the NAO_w index is positively correlated with biomass of cyanobacteria and diatoms as well as with total biomass of phytoplankton in spring (Nöges and Järvalt 2004, Nöges *et al.* 2010b). Our results show that between the mid-1950s and the mid-1990s, NAO_w , precipitation and T_{air} correlated positively with palaeopig-

Table 4. Spearman rank order correlations between selected palaeoparameters ($n = 31$) of Vörtsjärv for the period 1900–2001. All correlation coefficients are significant at $p < 0.05$. Area HS = total peak areas of humic substances in the organic matter dissolved in sediment porewater; $\text{NH}_4\text{Cl-RP}$ = loosely sorbed sedimentary phosphorus fraction.

Palaeopigments	CaCO_3 content	Area HS	$\text{NH}_4\text{Cl-RP}$
Chlorophyll <i>a</i>	0.747	−0.640	0.696
β -carotene	0.590	−0.477	0.592
Lutein and zeaxanthin	0.745	−0.751	0.606
Fucoxanthin	0.577	−0.556	0.473
Diadinoxanthin	0.664	−0.647	0.563

ments (Lute-Zea, Fuco and Diadino) and negatively with P fractions (Σ FR, BD-RP and NaOH-RP). Accelerated eutrophication and better preservation conditions of palaeopigments during higher water level can be the cause of the overall rise in fossil pigments content and their positive relationship with the NAO_w index.

Higher floods follow usually colder winters because due to frozen soils most of the meltwater reaches rivers as surface runoff, carrying large quantities of nutrients to the lake (Nöges and Järvalt 2004). This could be one possible explanation for negative correlation of NAO_w and T_{air} with Σ FR, BD-RP and NaOH-RP. Eutrophication will increase because of climate warming as it is expected to lead to increased external nutrient loading. However, the effects of climate change on shallow temperate lakes will mimic the effects of human-induced eutrophication and to ascertain its magnitude is complicated (Mooij *et al.* 2007, Nöges *et al.* 2008). In case of Vörtsjärv, the effects of climate change include change in temperature, but even more hydrological changes that are likely to be much more important. Water level oscillations in Vörtsjärv induce changes in the composition of dominant phytoplankton species: during high-water period shadow-tolerant species are favoured and vice versa (Nöges *et al.* 2003, Nöges *et al.* 2010b). Unfortunately, palaeopigments are only bioindicators of phytoplankton groups not species (Leavitt and Hodgson 2001). In our opinion this is the reason why photosynthetic pigments are poor water-level-fluctuation indicators in Vörtsjärv.

Together with the collapse of extensive agriculture in the early 1990s, the external load of nutrients to Vörtsjärv declined remarkably (Järvet 2004). Along with weakening anthropogenic pressure on the lake ecosystem P fractions (except NaOH-RP), fossil pigments, sediment OM and $CaCO_3$ content in the sediment core sharply increased since the mid-1990s (Fig. 2). The most likely explanation would be that the upper 0–13 cm sediment layers (period from mid 1990s to early 2000s) are unconsolidated and therefore clearly differ from other horizons. Microbial activity and thus degradation processes of settled material in upper sediment layers are much more intensive than in deeper sediments (Wetzel 2001). Due to resuspension,

surface sediment layers are involved in the lake's P cycle and a part of settled P is released back to the water column. The peak of the Chl *a*/Pheo *a* ratio in the 1990s reveals that degradation of fossil pigments was in progress (Fig. 2). However, the sharp increase in palaeopigments coincided with the rise of monthly chlorophyll *a* concentration in the water column since the 1990s: from about 20 mg m^{-3} to 50 mg m^{-3} (Fig. 7; Nöges *et al.* 2011). According to the monitoring data, the biomass of the filamentous cyanobacteria *Limnothrix planctonica* has increased in Vörtsjärv since the 1990s. This cyanobacteria build up a considerable standing stock by autumn. High biomass in autumn is characterized by a high Chl *a* content (Nöges *et al.* 2011). Together with the palaeopigments the T_{air} increased since the 1980s (Fig. 2). Generally phytoplankton is the first to benefit from higher water temperatures (Mooij *et al.* 2007). Thus, the rise in palaeopigments since the mid-1990s could also result from increasing T_{air} .

Conclusions

Our palaeolimnological investigation revealed that distinct changes in the Vörtsjärv ecosystem occurred in the last century. In the first half of the 20th century the lake was naturally slightly eutrophic and the changes in palaeoindices reflect natural variations induced by the regular oscillation of the water level. Accumulation of palaeopigments was low and the load of nutrients was stable. As water level did not correlate strongly with the climate parameters, the relationship between palaeoparameters and water level was also generally weak.

The deterioration of the Vörtsjärv ecosystem from the mid-1950s onwards was caused by increased eutrophication. The increase in $CaCO_3$ content, palaeopigments and nutrients, and low molecular weight of OM in sediments reflect high autochthonous matter input. The situation as compared with that during the pre-eutrophication period — when lake water contained substances with various molecular weights (from in-lake production and catchment-derived) the share of which depended on water-level fluctuations — changed and substances of autoch-

thonous origin with smaller molecular weights started to predominate. Group-specific fossil pigments are poor water-level-fluctuation indicators in Võrtsjärv, as water-level oscillations induce changes in the composition of dominant phytoplankton species.

From the mid-1990s to the early 2000s the increase in palaeopigment concentrations could be caused by risen air and water temperatures. However, degradation of fossil pigments is also in progress in upper sediment layers.

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References

- Appleby P.G., Nolan P.J., Gifford D.W., Godfrey M.J., Oldfield F., Anderson N.J. & Battarbee R.W. 1986. ^{210}Pb dating by low background gamma counting. *Hydrobiologia* 141: 21–27.
- Arvola L., George G., Livingstone D.M., Järvinen M., Blenckner T., Dokulil M.T., Jennings E., Aonghusa C.N., Nõges P., Nõges T. & Weyhenmeyer G.A. 2010. The impact of the changing climate on the thermal characteristics of lakes. *Aquatic Ecology Series* 4: 85–101.
- Bengtsson L., Hellström T. & Rakoczi L. 1990. Redistribution of sediments in three Swedish lakes. *Hydrobiologia* 192: 167–181.
- Bennion H. & Battarbee R. 2007. The European Union Water Framework Directive: opportunities for palaeolimnology. *Journal of Paleolimnology* 38: 285–295.
- Bergström A.K. & Jansson M. 2000. Bacterioplankton production in humic Lake Öträsken in relation to input of bacterial cells and input of allochthonous organic carbon. *Microbial Ecology* 39: 101–115.
- Bianchi T.S., Rolff C., Widbom B. & Elmgren R. 2002. Phytoplankton pigments in Baltic Sea seston and sediments: seasonal variability, fluxes, and transformations. *Estuarine, Coastal and Shelf Science* 55: 369–383.
- Blenckner T., Adrian R., Arvola L., Järvinen M., Nõges P., Nõges T., Petterson K. & Weyhenmeyer G.A. 2010. The impact of climate change on lakes in northern Europe. *Aquatic Ecology Series* 4: 339–358.
- Blindow, I. 1992. Long- and short-term dynamics of submerged macrophytes in two shallow eutrophic lakes. *Freshwater Biology* 28: 15–27.
- Carvalho L. & Kirika A. 2003. Changes in shallow lake functioning: response to climate change and nutrient reduction. *Hydrobiologia* 506–509: 789–796.
- Coops H., Beklioglu M. & Crisman T.L. 2003. The role of water-level fluctuations in shallow lake ecosystems — workshop conclusions. *Hydrobiologia* 506–509: 23–27.
- Coops H. & Hoper S.H. 2002. Water-level management as a tool for the restoration of shallow lakes in the Netherlands. *Lake and Reservoir Management* 18: 292–297.
- Dean W.E. 1999. The carbon cycle and biogeochemical dynamics in lake sediments. *Journal of Paleolimnology* 21: 375–393.
- Domis L.N.S., Mooij W.M. & Huisman J. 2007. Climate-induced shifts in an experimental phytoplankton community: a mechanistic approach. *Hydrobiologia* 584: 403–413.
- Eilers J.M., Kann J., Cornett J., Moser K. & St. Amand A. 2006. Paleolimnological evidence of change in a shallow, hypereutrophic lake: Upper Klamath Lake, Oregon, USA. *Hydrobiologia* 520: 7–18.
- Ekhölm P., Malve O. & Kirkkala T. 1997. Internal and external loading as regulators of nutrient concentrations in the agriculturally loaded Lake Pyhäjärvi, southwest Finland. *Hydrobiologia* 345: 3–14.
- Elliott J.A., Jones I.D. & Thackeray S.J. 2006. Testing the sensitivity of phytoplankton communities to changes in water temperature and nutrient load, in a temperate lake. *Hydrobiologia* 559: 401–411.
- Engstrom D.R., Schottler S.P., Leavitt P.R. & Havens K.E. 2006. A reevaluation of the cultural eutrophication of Lake Okeechobee using multiproxy sediment records. *Ecological Applications* 16: 1194–1206.
- Gulati R.D., Lammens E., De Pauw N. & Van Donk E. (eds.) 2007. *Shallow Lakes in a Changing World: Proceedings of the 5th International Symposium on Shallow Lakes, Held at Dalfsen, The Netherlands, 5–9 June 2005*. Springer, The Netherlands.
- Haberman J., Nõges P., Nõges T., Pihu E., Kangur K., Kangur A. & Kisand V. 1998. Characterization of Võrtsjärv. *Limnologia* 28: 3–11.
- Hamilton D.P. & Mitchell S.F. 1997. Wave-induced shear stresses, plant nutrients and chlorophyll in seven shallow lakes. *Freshwater Biology* 38: 159–168.
- Heinsalu A. & Alliksaar T. 2009. Palaeolimnological assessment of the reference conditions and ecological status of lakes in Estonia — implications for the European Union Water Framework Directive. *Estonian Journal of Earth Sciences* 58: 334–341.
- Heinsalu A., Luup H., Alliksaar T., Nõges P. & Nõges T. 2008. Water level changes in a large shallow lake as reflected by the plankton:periphyton ratio of sedimentary diatoms. *Hydrobiologia* 599: 23–30.
- Heiri O., Lotter A.F. & Lemcke G. 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. *Journal of Paleolimnology* 25: 101–110.
- Hodell D.A., Schelske C.L., Fahnenstiel G.L. & Robbins L.L. 1998. Biologically induced calcite and its isotopic composition in Lake Ontario. *Limnology and Oceanography* 43: 187–199.

- Jaani A. 2001. Hydrological regime and water balance. In: Nõges T. (ed.), *Lake Peipsi: meteorology, hydrology, hydrochemistry*, Sulemees Publishers, Tartu, pp. 10–17.
- Jansson M., Bergström A.K., Blomqvist P. & Drakare S. 2000. Allochthonous organic carbon and phytoplankton/bacterioplankton production relationships in lakes. *Ecology* 81: 3250–3255.
- Järvet A. 2004. Pollution load to Võrtsjärv. In: Haberman J., Pihu E. & Raukas A. (eds.), *Võrtsjärv*, Estonian Encyclopaedia Publishers, Tallinn, pp. 151–171.
- Jeffrey S.W., Mantoura R.F.C. & Bjørnland T. 1997. Data for the identification of 47 key phytoplankton pigments. In: Jeffrey S.W., Mantoura R.F.C. & Wright S.W. (eds.), *Phytoplankton pigments in oceanography: guidelines to modern methods*, UNESCO Publishing, Paris, pp. 449–559.
- Kaiser H.F. 1960. The application of electronic computers to factor analysis. *Educational and Psychological Measurement* 20: 141–151.
- Kovach W.L. 1999. *MVSP — a multivariate statistical package for Windows, ver. 3.1*. Kovach Computing Services, Pentraeth, Wales, UK.
- Leavitt P.R. & Hodgson D.A. 2001. Sedimentary pigments. In: Smol J.P., Birks H.J.B. & Last W.M. (eds.), *Tracking environmental change using lake sediments, vol. 3: Terrestrial, algal, and siliceous indicators*, Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 295–325.
- Leavitt P.R. 1993. A review of factors that regulate carotenoid and chlorophyll deposition and fossil pigment abundance. *Journal of Paleolimnology* 9: 109–127.
- Leeben A., Tönno I., Freiberg R., Lepane V., Bonningues N., Makarõtševa N., Heinsalu A. & Alliksaar T. 2008. History of anthropogenically mediated eutrophication of Lake Peipsi as revealed by the stratigraphy of fossil pigments and molecular size fractions of pore-water dissolved organic matter. *Hydrobiologia* 599: 49–58.
- Lepane V., Leeben A. & Malashenko O. 2004. Characterization of sediment pore-water dissolved organic matter of lakes by high-performance size exclusion chromatography. *Aquatic Science* 66: 185–194.
- Lepane V., Tönno I. & Alliksaar T. 2010. HPLC approach for revealing age-related changes of aquatic dissolved organic matter in sediment core. *Procedia Chemistry* 2: 101–108.
- McGowan S., Leavitt P.R., Hall R.I., Anderson J., Jeppesen E. & Odgaard B.V. 2005. Controls of algal abundance and community composition during ecosystem state change. *Ecology* 86: 2200–2211.
- Mooij W.M., Janse J.H., De Senerpont Domis L.N., Hülsmann S. & Ibelings B.W. 2007. Predicting the effect of climate change on temperate shallow lakes with the ecosystem model PCLake. *Hydrobiologia* 584: 443–454.
- Mori S. & Barth H.G. 1999. *Size exclusion chromatography*. Springer-Verlag, Berlin Heidelberg.
- Moss B., McKee D., Atkinson D., Collings S.E., Eaton J.W., Gill A.B., Harvey I., Hatton K., Heyes T. & Wilson D. 2003. How important is climate? Effects of warming, nutrient addition and fish on phytoplankton in shallow lake microcosms. *Journal of Applied Ecology* 40: 782–792.
- Murphy J. & Riley J.P. 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta* 27: 31–36.
- Münster U. & Chróst R.J. 1990. Origin, composition, and microbial utilization of dissolved organic matter. In: Overbeck J. & Chróst R.J. (eds.), *Aquatic microbial ecology*, Springer-Verlag, New York, pp. 8–46.
- Nõges P. & Järvalt A. 2004. Long-term changes in the ecosystem of Võrtsjärv and their causes. In: Haberman J., Pihu E. & Raukas A. (eds.), *Võrtsjärv*, Estonian Encyclopaedia Publishers, Tallinn, pp. 347–355.
- Nõges P. & Kisand A. 1999. Horizontal distribution of sediment phosphorus in shallow eutrophic Võrtsjärv (Estonia). *Hydrobiologia* 408–409: 167–174.
- Nõges P. & Laugaste R. 1998. Seasonal and long-term changes in phytoplankton of lake Võrtsjärv. *Limnologica* 28: 21–28.
- Nõges P. & Nõges T. 1998. The effect of fluctuating water level on the ecosystem of Võrtsjärv, central Estonia. *Proc. Estonian Acad. Sci. Biol. Ecol.* 47(2): 98–113.
- Nõges P., Laugaste R. & Nõges T. 2004. Phytoplankton. In: Haberman J., Pihu E. & Raukas A. (eds.), *Võrtsjärv*, Estonian Encyclopaedia Publishers, Tallinn, pp. 217–232.
- Nõges P., Nõges T. & Laas A. 2010b. Climate-related changes of phytoplankton seasonality in large shallow Võrtsjärv, Estonia. *Aquatic Ecosystem Health & Management* 13: 154–163.
- Nõges P., Mischke U., Laugaste R. & Solimini A.G. 2010a. Analysis of changes over 44 years in the phytoplankton of Võrtsjärv (Estonia): the effect of nutrients, climate and the investigator on phytoplankton-based water quality indices. *Hydrobiologia* 646: 33–48.
- Nõges P., Kangur K., Nõges T., Reinart A., Simola H. & Viljanen M. 2008. Highlights of large lake research and management in Europe. *Hydrobiologia* 599: 259–276.
- Nõges T. & Nõges P. 2006. Indicators and criteria to assess ecological status of the large shallow temperate polymictic lakes Peipsi (Estonia/Russia) and Võrtsjärv (Estonia). *Boreal Environment Research* 11: 67–80.
- Nõges T., Nõges P. & Laugaste R. 2003. Water level as the mediator between climate change and phytoplankton composition in a large shallow temperate lake. *Hydrobiologia* 506–509: 257–263.
- Nõges T., Alliksaar T., Heinsalu A. & Nõges P. 2006. A paleolimnological assessment of recent eutrophication history on large inland water body, Lake Peipsi, Estonia. *Verhandlungen der Internationalen Vereinigung für Theoretische und Angewandte Limnologie* 29: 1135–1138.
- Nõges T., Arst H., Laas A., Kauer T., Nõges P. & Toming K. 2011. Reconstructed long-term time series of phytoplankton primary production of a large shallow temperate lake: the basis to assess the carbon balance and its climate sensitivity. *Hydrobiologia* 667: 205–222.
- Nõges T., Järvet A., Laugaste R., Loigu E., Leisk Ü., Tönno I. & Nõges P. 2005. Consequences of catchment processes and climate changes on the ecological status of large shallow temperate lakes. In: Ramachandra T.V., Ahalya N. & Murty C.R. (eds.), *Aquatic ecosystems*,

- conservation, restoration and management*, Capital Publishing Company. New Dehli, Kolkata, Bangalore, pp. 88–99.
- Patoine A. & Leavitt P.R. 2006. Century-long synchrony of fossil algae in a chain of Canadian prairie lakes. *Ecology* 87: 1710–1721.
- Psenner R., Boström B., Dinka M., Pettersson K., Pucsko R. & Sager M. 1988. Fractionation of phosphorus in suspended matter and sediment. *Archiv für Hydrobiologie – Beiheft Ergebnisse der Limnologie* 30: 98–110.
- Reuss N., Conley D.J. & Bianchi T.S. 2005. Preservation conditions and the use of sediment pigments as a tool for recent ecological reconstruction in four northern European estuaries. *Marine Chemistry* 95: 283–302.
- Scheffer M. 1998. *Ecology of shallow lakes*. Chapman & Hall, London.
- Scheffer M., Hosper S.H., Meijer M.-L., Moss B. & Jeppesen E. 1993. Alternative equilibria in shallow lakes. *Trends in Ecology & Evolution* 8: 275–279.
- Sondergaard M., Jensen J.P. & Jeppesen E. 2003. Role of sediment and internal loading of phosphorus in shallow lakes. *Hydrobiologia* 506–509: 135–145.
- Toming K., Arst H., Paavel B., Laas A. & Nõges T. 2009. Spatial and temporal variations in coloured dissolved organic matter in large and shallow Estonian waterbodies. *Boreal Environment Research* 14: 959–970.
- Wetzel R.G. 2001. *Limnology. Lake and river ecosystems*. Academic Press, USA.
- Wright S., Jeffrey S., Mantoura R., Llewellyn C., Bjørnland T., Repeta D. & Welschmeyer N. 1991. Improved HPLC method for the analysis of chlorophylls and carotenoids from marine phytoplankton. *Marine Ecology Progress Series* 77: 183–196.
- Zapata M., Ayala A.M., Franco J.M. & Garrido J.L. 1987. Separation of chlorophylls and their degradation products in marine phytoplankton by reversed-phase high-performance liquid chromatography. *Chromatographia* 23: 26–30.