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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, $CaCO_3$ 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-

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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 Hosper 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 temperatures 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 km^2 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 km^2). 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 HCO_3^- 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 ^{210}Pb and ^{226}Ra, and the artificial radionuclides of ^{137}Cs and ^{241}Am by gamma spectrometry using a low background germanium detector (Appleby *et al*. 1986). The ^{210}Pb radiometric ages were calculated applying the constant rate of supply model and corrected by ^{137}Cs and ^{241}Am 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 (Nõges *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 Võrtsjärv, ca. 90% of the total phytoplankton biomass is formed by cyanobacteria (mainly filamentous forms) and diatoms (Nõges and Laugaste 1998, Nõges *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 Võrtsjärv 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 N_2. Thereafter, the pigment extracts were clarified by filtration through a 0.45 μm 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 μl flow cell. Injection was done using a Rheodyne model 7725 manual valve (Cotati, California, USA) fitted with a 50 μl 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 μm column (150 mm × 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 μl sample loop. A BioSep-SEC-S 2000 PEEK analytical column (300 × 7.50 mm, Phenomenex, USA) preceded by a suitable guard column (75 × 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 μm and pore size of 145Å. The mobile phase consisted of 0.10 M $NH_4H_2PO_4$–$(NH_4)_2HPO_4$ 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 μm 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 NH_4Cl, pH 7), bicarbonate-dithionite (BD; both $NaHCO_3$ and $Na_2S_2O_4$ 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 (NH_4Cl-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 $\mu g\ g^{-1}$ DW, ranging from 460 to 1360 $\mu g\ g^{-1}$ 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 (NH_4Cl-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-

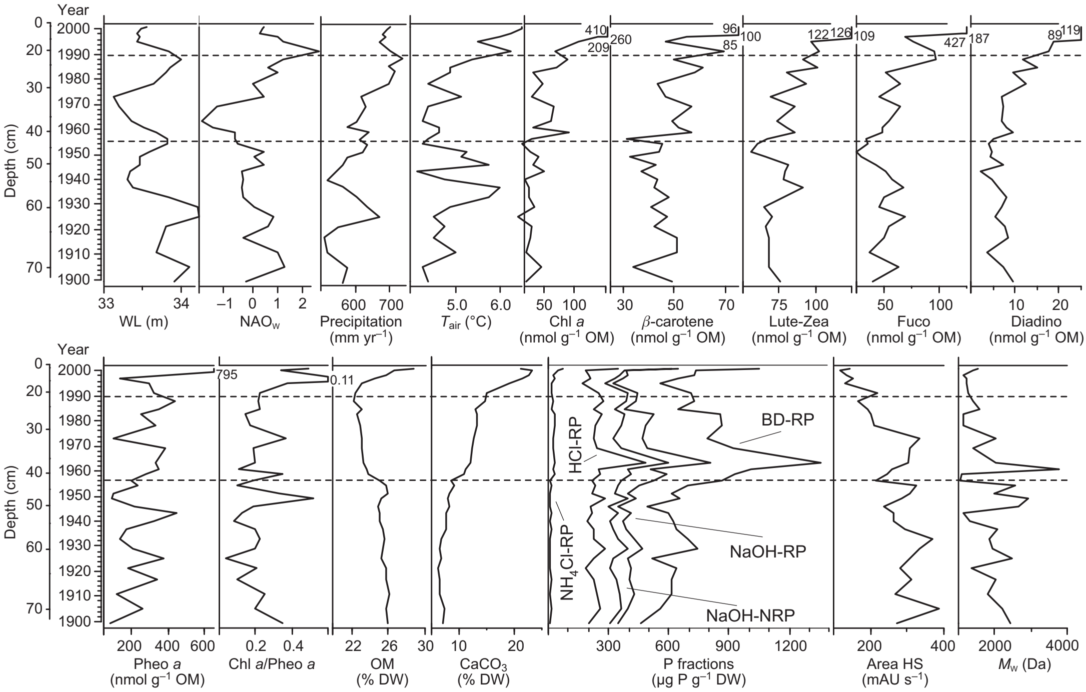

Fig. 2. The dynamics of palaeoparameters in sediments and water level oscillation (WL) in Võrtsjärv together with the fluctuation of annual mean air temperature (T_{air}), North Atlantic Oscillation winter index (NAO_w) and amount of precipitation for the period 1900–2001. Chl *a* = chlorophyll *a*; 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).

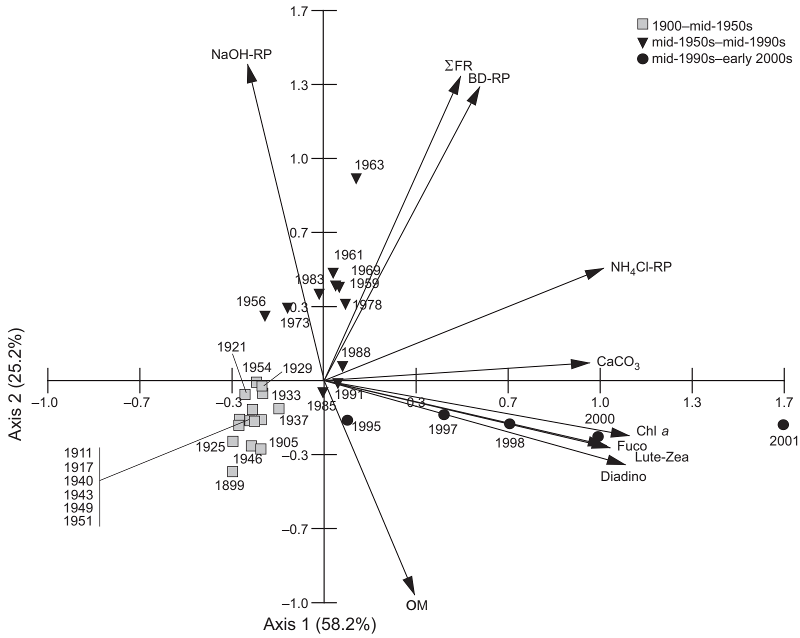

Fig. 3. Principal Component Analysis (PCA) biplot indicating three periods distinguished using selected palaeoparameters (arrows) from the 1900–2001 Võrtsjärv sediment core. For abbreviations *see* Fig. 2. ΣFR = sum of sedimentary phosphorus fractions.

Discussion

The palaeopigment composition in Võrtsjärv 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 Võrtsjärv phytoplankton at that time. The large catchment area ensures naturally higher nutrient inflow to Võrtsjärv 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 Võrtsjärv. 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 Võrtsjärv 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 Võrtsjärv 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 Võrtsjärv 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 (Nõges *et al.* 2003, Nõges *et al.* 2010a). In Võrtsjärv, 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 Võrtsjärv the sediment surface consists of very fine floating material which is not the best substrate for phytobenthos. Phytoplankton investigations in Võrtsjärv 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 (Nõges *et al.* 2004). Thus the proportion of pigments derived from phytobentos is negligible in the pigment content accumulated in the Võrtsjärv 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 Võrtsjärv 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 (Nõges *et al.* 2003, Nõges *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 Võrtsjärv 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 *a*	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 Võrtsjärv 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 Võrtsjärv 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 (Nõges and Laugaste 1998, Nõges and Nõges 2006). Moreover, the analysis of phytoplankton taxonomic indices showed a continuous deterioration of Võrtsjärv ecological status during the 44-year period of limnological investigations (1964–2007; Nõges *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 NH_4Cl-RP and $CaCO_3$ indicate accelerated eutrophication of the lake (Table 4). NH_4Cl-RP includes phosphates dissolved in sediment porewater and loosely sorbed on sediment particles. Higher concentration of NH_4Cl-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 Võrtsjärv 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 Võrtsjärv, the NAO_w index is positively correlated with biomass of cyanobacteria and diatoms as well as with total biomass of phytoplankton in spring (Nõges and Järvalt 2004, Nõges *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 Võrtsjärv 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; NH_4Cl-RP = loosely sorbed sedimentary phosphorus fraction.

Palaeopigments	$CaCO_3$ content	Area HS	NH_4Cl-RP
Chlorophyll *a*	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 (ΣFR, 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 (Nõges and Järvalt 2004). This could be one possible explanation for negative correlation of NAO_w and T_{air} with ΣFR, 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, Nõges *et al*. 2008). In case of Võrtsjärv, 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 Võrtsjärv induce changes in the composition of dominant phytoplankton species: during high-water period shadow-tolerant species are favoured and vice versa (Nõges *et al*. 2003, Nõges *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 Võrtsjärv.

Together with the collapse of extensive agriculture in the early 1990s, the external load of nutrients to Võrtsjärv 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; Nõges *et al*. 2011). According to the monitoring data, the biomass of the filamentous cyanobacteria *Limnothrix planctonica* has increased in Võrtsjärv 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 (Nõges *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 resulted from increasing T_{air}.

Conclusions

Our palaeolimnological investigation revealed that distinct changes in the Võrtsjärv 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 Võrtsjärv 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 autochthonous 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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