Estonian Journal of Earth Sciences, 2011, **60**, 2, 91–101 doi: 10.3176/earth.2011.2.03

Dynamics of phytoplankton pigments in water and surface sediments of a large shallow lake

Rene Freiberg[a], Monika Nõmm[a], Ilmar Tõnno[a], Tiiu Alliksaar[b], Tiina Nõges[a] and Anu Kisand[a,b]

[a] Centre for Limnology, Institute of Agricultural and Environmental Sciences, Estonian University of Life Sciences, 61101 Rannu, Tartumaa, Estonia; rene.freiberg@limnos.ee
[b] Institute of Geology, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

Received 7 July 2010, accepted 9 February 2011

Abstract. Our aim was to find out to which extent fossil phytoplankton pigments in the large shallow and turbid Lake Võrtsjärv carry information on the history of phytoplankton communities. For this purpose we examined how the changes in the pigment composition of surface sediments follow their changes in the water column. Depth-integrated lake water and surface sediment samples were collected weekly in May–October 2007. Considering cyanobacterial and diatom dominance in phytoplankton, we analysed fucoxanthin, diadinoxanthin and diatoxanthin as marker pigments for diatoms, zeaxanthin as a marker pigment for total cyanobacteria and canthaxanthin as a marker pigment for colonial cyanobacteria. Chlorophyll *a* and its derivative pheophytin *a* were applied as indicators for total phytoplankton.

The dynamics of phytoplankton pigments in surface sediments generally did not follow their dynamics in the water column, possibly due to intensive resuspension and a high sedimentation rate in a large and shallow lake. It was noticed that the surface sediment carries information on pigment degradation intensity and on weight and size characteristics of phytoplankton cells, which affect their sinking and floating velocities. Higher pigment contents of sediment in spring were presumably caused by lower resuspension due to high water level and slower degradation in cold water. Pheophytin *a* and the marker pigments of cyanobacteria were found to be persistent against degradation in upper sediment layers, which makes them useful indicators for tracking the historical changes in phytoplankton communities also in a shallow lake. Sharp decrease in chemically unstable pigment contents between the sediment surface and deeper layers indicates that only the uppermost sediment surface is resuspended in Lake Võrtsjärv. The transformation of the diatom marker carotenoid diadinoxanthin to diatoxanthin was found to occur mainly in sediments and not in the water column, and the process is not induced by excess light.

Key words: phytoplankton pigments, large shallow lake, surface sediment layers, resuspension, Lake Võrtsjärv.

INTRODUCTION

Phytoplankton pigments (PhPs) that capture and transform solar energy in the water column (Hall et al. 1999) store valuable palaeoclimatic and palaeoenvironmental information if buried in sediments (Fietz et al. 2007; Soma et al. 2007). Carotenoids are useful biomarkers of different classes of phytoplankton, while chlorophyll *a* (Chl *a*) is not class-specific and is commonly used to estimate the total amount of phytoplankton in aquatic systems (Jeffrey et al. 1997; Bianchi et al. 2002; Reuss et al. 2005).

Planktic and benthic algal communities are common for shallow lakes. Benthic algae can be substantial primary producers in pelagic and benthic food webs in non-stratified lakes (Zimba 1995; Bonilla et al. 2005). However, the development of benthic algae is limited in turbid shallow lakes where the euphotic zone does not penetrate to the sediment surface (Nõges & Laugaste 1998).

Contrary to anaerobic sediments where PhPs may preserve for a long period, the aerobic degradation of PhPs in the water column is usually very rapid and extensive (Leavitt & Carpenter 1990a, 1990b; Leavitt 1993; Patoine & Leavitt 2006). The composition of PhPs preserved in sediments commonly differs from that in the water as the sensibility to decomposition varies among different pigments (Bianchi et al. 2002). Each lake represents a unique environment for deposition and preservation of PhPs, depending on its oxygen and light penetration characteristics, resuspension intensity, digestion through zooplankton grazing and phytoplankton abundance. In anaerobic sediments of deep lakes, where resuspension and bioturbation are negligible, PhPs or their ratios might reflect the history of phytoplankton composition and primary production (Cohen 2003, pp. 257–260; Reuss et al. 2005). In deep lakes the stratification depth is also an important factor for conservation of sediment pigments as their degradation in the water column is rapid (>90%) due to photo-oxidation,

grazing by invertebrates, etc. (Leavitt & Carpenter 1990a, 1990b; Leavitt 1993; Descy et al. 1999; Patoine & Leavitt 2006). In shallow lakes resuspension and aerobic conditions in surface sediments enhance the transformation processes of organic matter, including PhPs, which strongly complicates the interpretation of palaeolimnological information stored in sediments (Leavitt & Carpenter 1989). However, as most of the World's lakes are shallow (Scheffer 1998), the evaluation of the possibilities of tracking historical changes in shallow lakes by using fossil sediment records is highly needed. This has become extremely relevant during the last decade in the light of the challenging tasks posed by the EU Water Framework Directive (Directive 2000) requesting the improvement of the ecological status of water bodies considering the type-specific reference conditions. If no historical data or reference water bodies are available, only palaeolimnology and modelling could enable assessment of the historical status of the water body. Despite various methodological problems, some successful palaeolimnological studies of shallow lakes have been published within the last years (Eilers et al. 2004; Engstrom et al. 2006; Leeben et al. 2008). Our aim was to find out to which extent the fossil PhPs in such a large shallow and turbid lake as Võrtsjärv carry the information on the history of phytoplankton communities. For this purpose we examined how the changes in the PhP composition of surface sediments follow their changes in the water column.

STUDY SITE

Lake Võrtsjärv (Fig. 1), the third largest lake (270 km^2) in Eastern Europe, excluding large lakes in Russia, is situated in the Central Estonian depression of preglacial origin. The bedrock is comprised of Middle Devonian deposits, mainly sandstone, and covered with diverse Quaternary sediments. The southern part of the lake bottom is covered with gyttja overlying lake marl. Northwards the mud is gradually replaced by sandy mud and sand. No sediment accumulation occurs in the wind-exposed northern part of the lake and the bottom (Fig. 2) is mainly sandy or stony (Raukas 1995).

Lake Võrtsjärv is very shallow, with a mean depth of 2.8 m (maximum 6 m). Due to bad outflow conditions, water level in the lake fluctuates strongly (annual mean amplitude 1.38 m), depending on the amount of precipitation in the catchment area (3374 km^2). The renewal of the 750 million m^3 water mass takes place on average once a year. Due to shallowness and the large wind-exposed area, L. Võrtsjärv is unstratified and very turbid. The Secchi depth ranges from 0.5 to 1.0 m during the ice-free period. The lake is eutrophic, characterized by mean concentrations of about 2 mg L^{-1} for total nitrogen and about 50 μg L^{-1} for total phosphorus. The dominant phytoplankton groups in the lake are cyanobacteria (CY) and diatoms, forming ~90% of the total phytoplankton biomass (Jaani 1973; Haberman et al. 1998; Nõges et al. 2004).

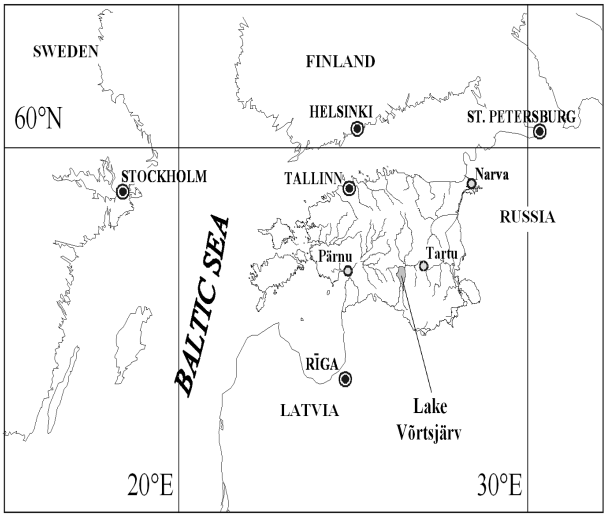

Fig. 1. Location map of L. Võrtsjärv.

MATERIALS AND METHODS

Considering CY and diatom dominance in phytoplankton of L. Võrtsjärv (Nõges et al. 2004), fucoxanthin (Fuco), diadinoxanthin (Diadino) and diatoxanthin (Diato) were analysed as marker pigments for diatoms (Leavitt & Hodgson 2001; Buchaca & Catalan 2007a, 2007b), zeaxanthin (Zea) as a marker pigment for total CY and canthaxanthin (Cantha) as a marker pigment for colonial CY (Leavitt & Hodgson 2001; McGowan et al. 2005; Carreto et al. 2008) to track phytoplankton community changes in water and in upper sediment layers. Diatoxanthin and Diadino were both analysed to track diatoms as in their xanthophyll cycle Diadino could be transformed to Diato at intensive light (Patoine & Leavitt 2006). Chlorophyll *a* and pheophytin *a* (Pheo *a*) were applied as marker pigments for total phytoplankton and for general Chl *a* derivative, respectively (Leavitt & Hodgson 2001). However, one should consider that Chl *a* is also the major pigment in higher plants.

Field sampling

The sampling site is situated in the southern part of L. Võrtsjärv between the eastern shore and the island of

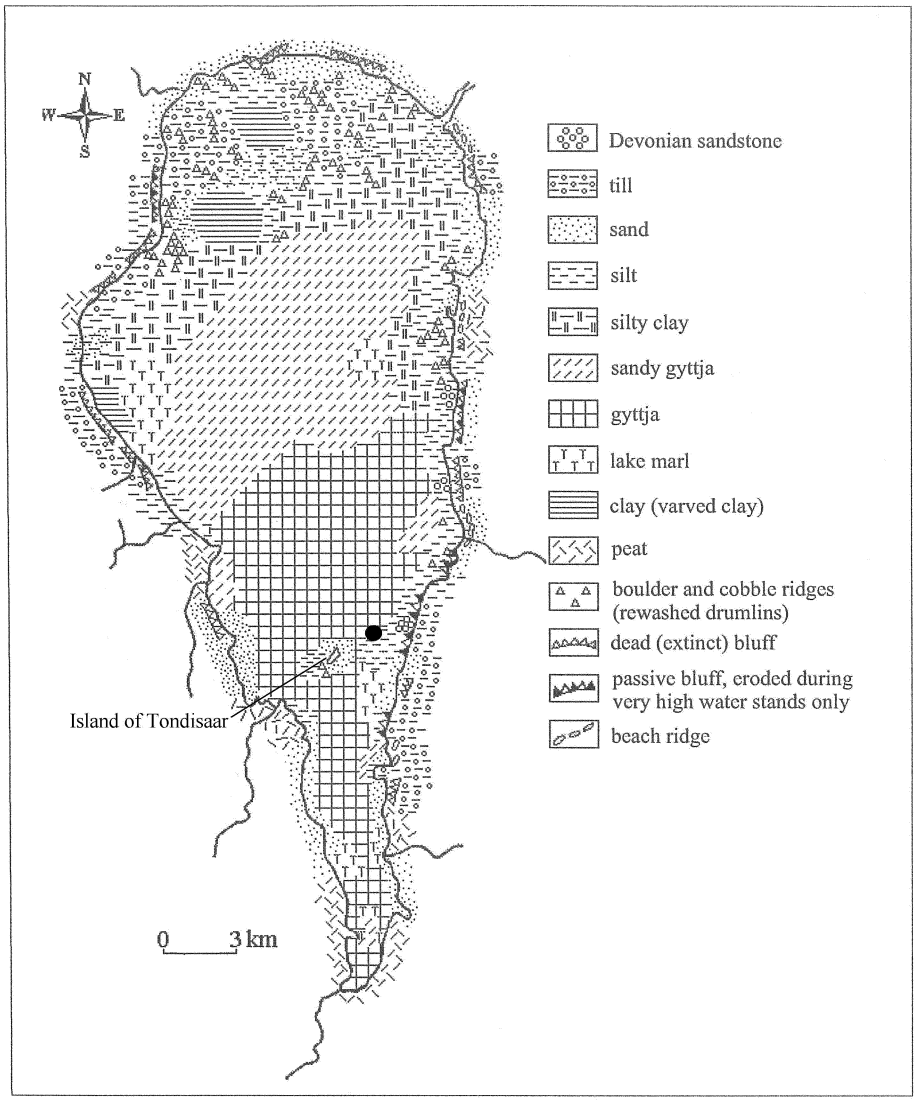

Fig. 2. Bottom sediments in L. Võrtsjärv after R. Pirrus, A. Raukas and E. Tavast (modified from Raukas & Tavast 2002). The solid circle marks the photosynthetic pigments sampling station.

Tondisaar (58°12.573′ N, 026°05.742′ E; Fig. 2), where the mean water depth is 2.5 m. Phytoplankton of L. Võrtsjärv has usually two biomass maxima (Nõges et al. 2004) – in spring (diatoms) and in autumn (CY and diatoms), and the sampling periods of PhPs were selected accordingly. From the sampling site depth-integrated lake water samples and surface sediment samples were collected weekly in 2007 during two periods – from 15 May to 03 July and from 07 August to 30 October. A Willner-type gravity corer was used for sediment coring (Uppsala University). All samples were placed into an insulated box and immediately transported to the laboratory.

Extraction of pigments

Analysis of PhPs followed the recommendations of Leavitt & Hodgson (2001) and Mantoura & Llewellyn (1983). Depth-integrated water samples (50–100 mL, depending on water turbidity) were filtered through Whatman GF/C glass microfibre (1.2 µm) filters (precombusted at 400 °C for 4 h) and frozen (–20 °C) until PhP analyses. From the sediment cores three subsamples from depths of 0–1, 2–3 and 4–5 cm were sectioned. From each homogenized subsample approximately 5 g of wet sediment was weighed and immediately frozen (–20 °C) prior to PhP analyses.

Thereafter frozen sediment samples were freeze-dried. Residual sediment from the subsamples was heated at 550 °C for 4 h for measurements of sediment organic matter content as loss on ignition (Heiri et al. 2001) relevant for PhP calculations. Acetone–methanol mixture (80 : 20 v : v) was added to the frozen GF/C glass-fibre filters and the freeze-dried sediment samples in order to extract PhPs, thereafter the filtered samples were sonicated (Branson 1210) for 10 min. All PhP samples were extracted at −20 °C in the dark for 24 h. Finally the PhP extracts were clarified by filtration through a 0.45 µm pore-size filter (Millex LCR, Millipore).

High-performance liquid chromatography analyses

Reversed-phase high-performance liquid chromatography (RP-HPLC) was applied, using a Shimadzu Prominence (Japan) series system with a photodiode array (PDA) detector to separate the PhPs. The method was adapted from Airs et al. (2001) and slightly modified. As an ion-pairing reagent 0.5 M ammonium acetate was added in a volume ratio of 2 : 3 to each PhP sample. To avoid chemical decomposition of pigments, the autosampler was cooled down to +5 °C (Reuss & Conley 2005) and a maximum of 10 samples were loaded at a time. The sample injection volume was 50 µL.

Separations were performed in a reversed-phase mode by using two Waters Spherisorb ODS2 3 µm columns (150 mm × 4.6 mm I.D.) in-line with a pre-column (10 mm × 5 mm I.D.) containing the same phase. A binary gradient elution method (Table 1) was used with isocratic holds between 0–2 and 30–43 min. The flow rate remained constant during the elution, 0.8 mL min^{-1}. Absorbance was detected at wavelengths from 350 to 700 nm. The software 'LC solution ver. 1.22' (Shimadzu) was applied to collect and analyse the data. The integration of peak areas was made at each pigment absorbance maximum (Jeffrey et al. 1997). Commercially available external standards from DHI (Denmark) were used for peak identification and quantification. Spearman rank order correlation and the program 'Statistica for Windows 6.0' were applied in statistical analyses.

Table 1. Elution scheme and solvents used in the separation of phytoplankton pigments by HPLC

	Time, min				
	0	2	30	43	50
Solvent A, %	50	50	100	100	50
Solvent B, %	50	50	0	0	50

Solvent A = 80% methanol : 20% 0.5 M ammonium acetate (pH 7.2) (v : v).
Solvent B = 80% methanol : 20% acetone (v : v).

RESULTS

Lake sediments at the sampling site were characterized by water-rich (>90%) gyttja, consisting mainly of mineral matter (>60% in dried sediment) and less organic matter and carbonates (about 25% and 11%, respectively).

The concentrations of all studied PhPs in the water samples were lower from May to July than from August to October in 2007. However, in the upper sediment layers the contents of Chl *a*, Pheo *a*, Fuco, Diadino and Diato were higher from May to July than from August to October (Fig. 3A–G). Zea content in the studied sediment layers remained similar within the investigated periods, while Cantha increased towards autumn (Fig. 3F, G). Chl *a*, Fuco and Diadino generally decreased, while Diato increased from the sediment surface (0–1 cm) towards deeper sediment layers. Concentrations of Pheo *a*, Zea and Cantha were rather similar in all investigated sediment layers (Fig. 3A–G).

Chlorophyll *a* was the dominant pigment in water and in surface sediment layers within the whole investigated period. In water Chl *a* was followed by Zea, Fuco, Diadino, Pheo *a*, Cantha and Diato. In upper sediment layers the concentrations of Zea, Diato and Pheo *a* were similar, followed by Fuco and Diadino, while Cantha concentration was the lowest. The mean concentration of Chl *a* in water was 17 times higher than that of Pheo *a*, while in upper sediment layers the difference was ~3 times (Fig. 4A, B).

Chlorophyll *a* concentration in water was inversely correlated with that in surface sediment layers, and the same was valid also for Pheo *a* and Diato. No correlation was detected between Fuco, Diadino, Zea and Cantha concentrations in water and in upper sediment layers except the positive correlation between Cantha in water and in the 0–1 cm sediment layer. The contents of the same pigment in different sediment layers were generally positively correlated (Table 2). The water level in L. Võrtsjärv was decreasing during our study period from May to November (Fig. 3H). The concentrations of Chl *a*, Pheo *a*, Diato, Zea and Cantha in water were significantly negatively correlated with the water depth, while for Fuco and Diadino this correlation was weak and insignificant. Sediment pigment contents in all studied layers were significantly positively correlated with water depth except for Zea and Cantha. The content of Cantha in sediment was negatively correlated with water depth, while for Zea the correlation was insignificant (Fig. 5).

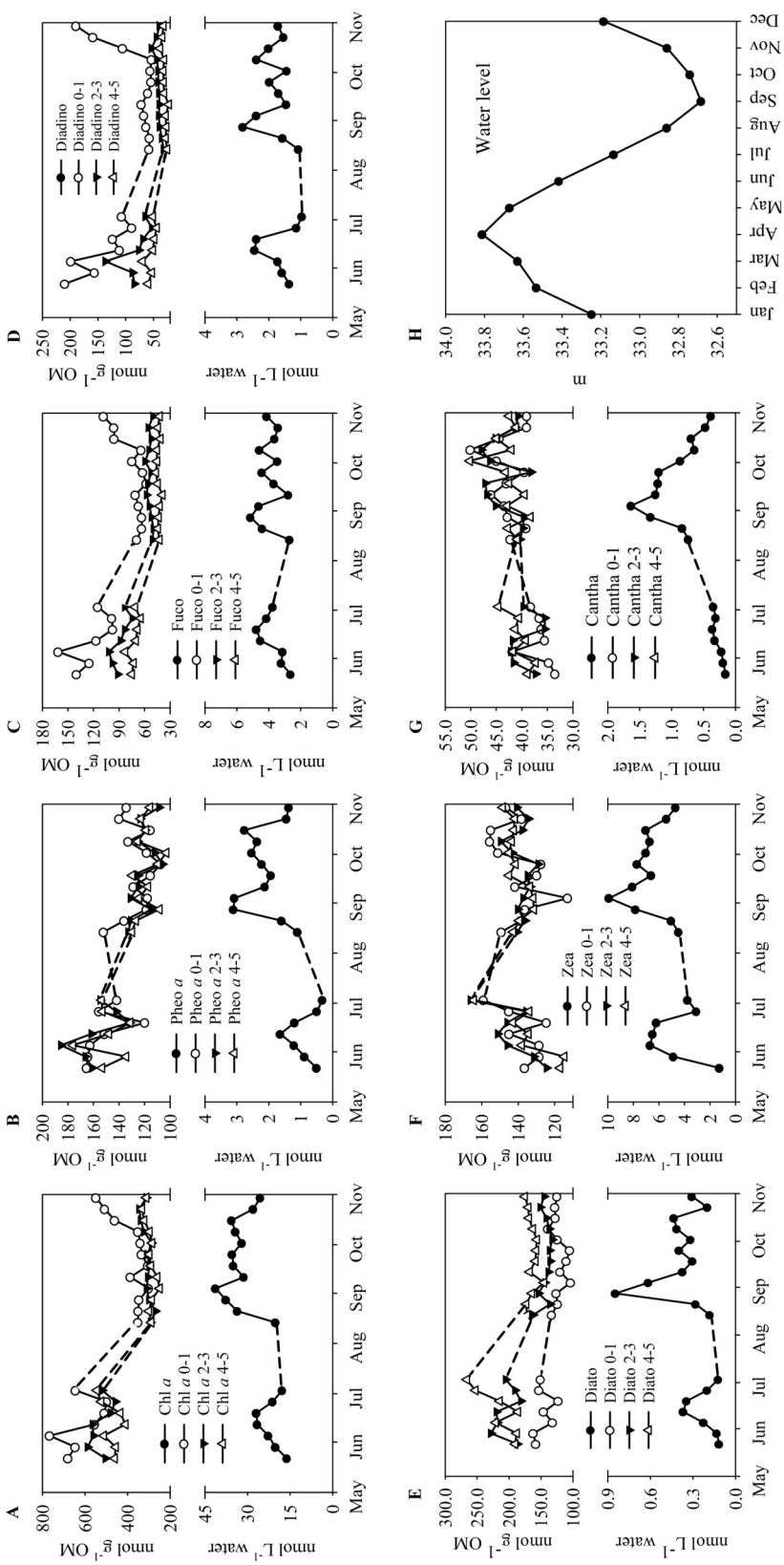

Fig. 3. Dynamics of phytoplankton pigments in L. Võrtsjärv water (nmol L^{-1} water) and in upper sediment layers (nmol g^{-1} OM; OM – organic matter) in 2007 (A–G). The timespan between two analysed periods is marked with dashed lines. (A) Chl *a* – chlorophyll *a*; (B) Pheo *a* – pheophytin *a*; (C) Fuco – fucoxanthin; (D) Diadino – diadinoxanthin; (E) Diato – diatoxanthin; (F) Zea – zeaxanthin; (G) Cantha – canthaxanthin. 0–1, 2–3 and 4–5 – investigated sediment layers (in cm); (H) Water level dynamics (metres above sea level) in L. Võrtsjärv in 2007 (http://www.emhi.ee/).

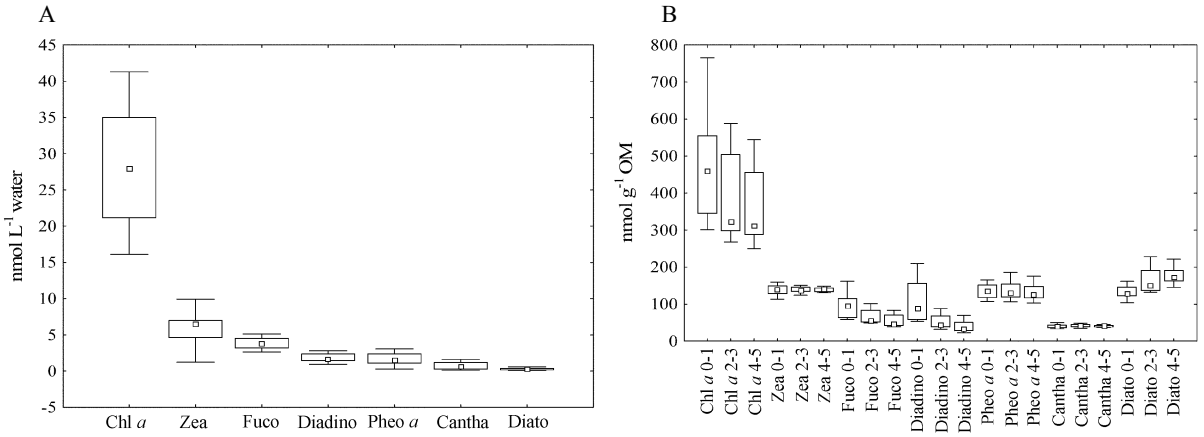

Fig. 4. Concentrations of phytoplankton pigments in L. Võrtsjärv water (A; nmol L^{-1} water) and in upper sediment layers (B; nmol g^{-1} OM; OM – organic matter) in 2007. Median, 25th and 75th percentiles as vertical boxes with error bars are presented. Chl *a* – chlorophyll *a*; Pheo *a* – pheophytin *a*; Fuco – fucoxanthin; Diadino – diadinoxanthin; Diato – diatoxanthin; Zea – zeaxanthin; Cantha – canthaxanthin. 0–1, 2–3 and 4–5 – investigated sediment layers (in cm).

Table 2. Spearman rank order correlations for phytoplankton pigments analysed from L. Võrtsjärv water samples and upper sediment layers in 2007. Significant correlations at $p < 0.05$ are marked in bold. Chl *a* – chlorophyll *a*; Pheo *a* – pheophytin *a*; Fuco – fucoxanthin; Diadino – diadinoxanthin; Diato – diatoxanthin; Zea – zeaxanthin; Cantha – canthaxanthin. Sediment layers 0–1, 2–3 and 4–5 cm

	Chl *a* 0–1	Chl *a* 2–3	Chl *a* 4–5
Chl *a* water	**−0.805**	**−0.540**	**−0.695**
Chl *a* 0–1		**0.823**	**0.826**
Chl *a* 2–3			**0.807**
	Pheo *a* 0–1	Pheo *a* 2–3	Pheo *a* 4–5
Pheo *a* water	**−0.753**	**−0.697**	**−0.721**
Pheo *a* 0–1		**0.754**	**0.735**
Pheo *a* 2–3			**0.942**
	Fuco 0–1	Fuco 2–3	Fuco 4–5
Fuco water	−0.375	−0.274	−0.047
Fuco 0–1		**0.711**	**0.595**
Fuco 2–3			**0.798**
	Diadino 0–1	Diadino 2–3	Diadino 4–5
Diadino water	−0.068	0.052	−0.098
Diadino 0–1		**0.616**	**0.707**
Diadino 2–3			**0.928**
	Diato 0–1	Diato 2–3	Diato 4–5
Diato water	**−0.572**	−0.440	**−0.619**
Diato 0–1		**0.726**	**0.644**
Diato 2–3			**0.800**
	Zea 0–1	Zea 2–3	Zea 4–5
Zea water	−0.179	0.077	−0.214
Zea 0–1		0.446	**0.523**
Zea 2–3			**0.618**
	Cantha 0–1	Cantha 2–3	Cantha 4–5
Cantha water	**0.751**	0.353	0.314
Cantha 0–1		**0.730**	0.367
Cantha 2–3			0.295

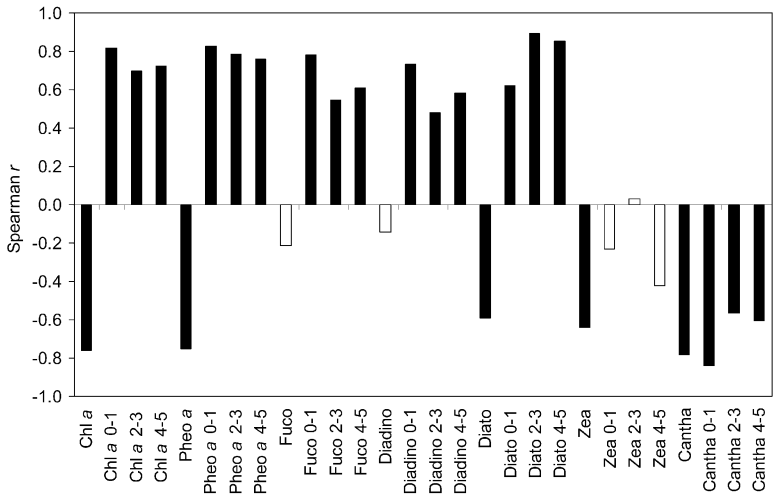

Fig. 5. Spearman correlation coefficients (black bars significant at $p < 0.05$, white bars nonsignificant) of phytoplankton pigment concentrations (marked as in Fig. 4) and water level in L. Võrtsjärv in 2007.

DISCUSSION

The dynamics of PhPs in the upper sediment layers of L. Võrtsjärv generally did not correspond to their dynamics in the water. Because of the morphology of the lake basin the water column is not stratified, sediments are subjected to mixing by waves and characterized by a high accumulation rate, especially the surface layers (Heinsalu et al. 2008, Fig. 1C). This can be the reason why short-term coupling with water and sediment PhPs was not detected in that large shallow and turbid lake. In stratified lakes where sediment layers are not disturbed by resuspension, such uncoupling could result from seasonal differences in the phytoplankton sinking rate, which is low during the phytoplankton population growing phase and high in the population decline phase (Sommer 1984). In large shallow lakes like L. Võrtsjärv sedimentation is accompanied by intensive resuspension (Scheffer 1998). Staying longer in the water column, more than 90% of PhPs could be degraded to colourless compounds before permanent burial, whereas the most rapid degradation occurs in dying cells and detritus (Leavitt & Carpenter 1990a, 1990b; Leavitt 1993). Resuspension is very strong in L. Võrtsjärv, and as the sediment trap experiments have shown, the major part (up to 96%) of the downward particle flux (including PhPs) is formed of resuspended material (Nõges et al. 1999). Wind speed and water level fluctuations have strong impact on resuspension intensity in large and shallow lakes, causing much higher resuspension and water turbidity at low water level during windy days. The water level of L. Võrtsjärv is typically low in winter and high in spring after the snowmelt, and its gradual decrease during summer and early autumn is followed by a small peak in late autumn (Haberman et al. 1998; Järvet 2004). In 2007 the difference between the minimum and maximum water levels was 1.28 m (Fig. 3H). Lake bottom morphometry changes at our sampling site, between the slopes of the shore and the island of Tondisaar (Fig. 2), which might cause varying sedimentation and resuspension conditions (Håkanson & Jansson 1983).

Higher sediment PhP contents (except Zea and Cantha) in spring (Fig. 3A–E) could partly originate from the previous autumn. After the formation of the ice cover the phytoplankton could calmly deposit on the bottom of the lake, and quite high PhP amounts were preserved in the sediments due to the low temperature and lack of resuspension under the ice. In spring, when the water level was high (Fig. 3H), the impact of resuspension was assumed to be relatively weak and therefore the deposited algal material of the spring phytoplankton maximum remained relatively less disturbed in the sediments. Also, the degradation of PhPs should be slow due to the still low water temperature. Together with the water level decrease towards autumn, the intensity of resuspension assumingly increased, as the earlier sediment trap experiments in L. Võrtsjärv have shown that the low water periods are characterized by a significantly higher sedimentation of resuspended material and, thus, more intensive resuspension than the high water periods (Nõges et al. 1999). The degradation of PhPs as well

obviously intensified towards autumn owing to higher water temperature and also because due to resuspension the pigments stayed for a relatively longer period in the illuminated and oxygenated water column. We found a strong positive correlation between sediment carotenoids associated with diatoms and the water level of the lake (Fig. 5). This could indicate that the changes in the water depth are first of all important for settling and resuspension processes of rather heavy cells of diatoms (Stoermer & Smol 1999). As diatoms in L. Võrtsjärv have a biomass peak in spring when the water level is high, this correlation could also be caused by periodicity. While biostratigraphic diatom analysis showed great potential of the planktonic/periphytic diatom ratio in the sediment for reconstructing the historical water level changes in L. Võrtsjärv (Heinsalu et al. 2008), the use of diatom marker pigments in sediment for that purpose is questionable. The coupling of the water level with the sediment pigments associated with CY (Zea, Cantha) proved to be different from the coupling with diatoms (Fig. 5). The biomass and proportion of CY in phytoplankton of L. Võrtsjärv generally increase towards the autumn (Nõges et al. 2004). The concentration of the marker pigment of colonial CY (Cantha) both in water and in surface sediments increased markedly towards the autumn (Fig. 3G), causing probably negative coupling with the decreasing water level in the lake (Fig. 5). Another marker pigment for CY, Zea, associated with their total concentration, did not show any relationship with the water level. As the cells of CY are lighter than those of diatoms, the changes in the sedimentation/resuspension pattern due to the variations in water depth are not as important for CY as they are for diatoms. Due to relatively large cell dimensions, the sinking and floating velocities of colonial CY are enhanced if compared to other non-aggregated CY. *Microcystis* species (one of the dominant colonial CY also in L. Võrtsjärv) produce large colonies that could actively control their buoyancy and settling rate (Walsby & McAllister 1987; Nõges & Laugaste 1998; Roderick et al. 2000; Reynolds 2006). The positive correlation between Cantha concentration in water and in the sediment top surface layer (0–1 cm) could indicate active migration of colonial CY between water and the sediment surface. The lack of correlation between Cantha concentration in water and in sediment subsurface layers of 2–5 cm (Table 2) could also support this hypothesis. Phytobenthos of L. Võrtsjärv, consisting mainly of CY and diatoms (Pork & Kõvask 1973), might also confuse the coupling of CY and diatom marker pigment between the water and upper sediment layers. The development of benthic algae in lakes depends on light penetrating to the sediment surface. In the very turbid L. Võrtsjärv the estimated euphotic zone varied from 1.6 to 3.2 m, remaining lower than the mean (2.8 m) or maximum (6.0 m) water depth (Haberman et al. 1998; Reinart & Nõges 2004). Monthly phytoplankton monitoring indicates that in the period of low water level resuspended algae from the sediment surface enrich phytoplankton species composition in the water column but do not contribute much to biomass (Nõges et al. 2004). Therefore the development of the benthic algae community in L. Võrtsjärv is limited. Unfortunately, the HPLC technique does not allow identifying whether PhPs in sediments are from phytoplankton or from phytobenthos (Greisberger & Teubner 2007).

Decrease in Chl *a*, Fuco and Diadino contents towards the deeper layers of the sediment core might be explained by chemical instability of these PhPs (Fig. 3A, C, D), e.g., both Fuco and Diadino contain a 5,6-epoxide group which enhances their quick degradation (Hurley & Armstrong 1990; Reuss & Conley 2005). Considerable decrease in unstable PhPs content between the sediment surface and other investigated layers indicates that mainly only the top of the sediment surface is included to resuspension in L. Võrtsjärv (Fig. 3A, C, D). Consequently, in case of unstable pigments the 'older' PhPs stored in deeper sediments are assumably more degraded than the pigments in the upper sediment layers. In comparison with diatom marker pigments, Zea and Cantha are chemically very stable, whereas Zea could be preserved even in aerobic environment (Hurley & Armstrong 1990; Bianchi et al. 2000; Leavitt & Hodgson 2001; Fietz et al. 2005; Reuss et al. 2005; Buchaca & Catalan 2007a, 2007b). That could explain why there was no distinct difference between Zea and Cantha concentrations in different sediment layers. As Pheo *a* is the degradation product of Chl *a*, its content was assumed to increase towards the deeper sediment layers. Contrary to unstable Chl *a*, Pheo *a* is very persistent in sediments (Leavitt & Hodgson 2001). However, Pheo *a* content did not show any distinct downward pattern in sediments and we could not track the degradation of Chl *a* on the basis of Pheo *a* content. Consequently, Pheo *a* and the marker pigments of CY (Cantha and Zea) in the upper sediment layers of L. Võrtsjärv seem to be rather conservative against degradation and could be used to track the historical changes in total phytoplankton and CY.

The water column irradiance is rather low in the shallow and turbid L. Võrtsjärv (Nõges & Laugaste 1998; Reinart & Nõges 2004). The diatom carotenoid Diadino that is active in the xanthophyll cycle could be transformed into Diato at high light to reduce the amount of energy reaching the photosynthetic reaction centres (Louda et al. 2002). Diatoms in L. Võrtsjärv are probably not under light stress as Diato concentration in the water column was nearly an order of magnitude lower than that of Diadino (Fig. 3D, E). On the contrary, in the upper sediment layers the content of Diato was higher

than that of Diadino. Moreover, Diato content increased and Diadino content decreased downwards in the sediment core (Figs 3D, E; 4B). Although part of the light in L. Võrtsjärv penetrates to the sediment surface, it is obvious that Diadino transformation to Diato in upper sediment layers could not be caused by excess light and should take place also in darkness. Consequently, transformation of the investigated diatoms marker carotenoids in L. Võrtsjärv occurs mainly in sediments, not in the water column. Several other studies have found that the xanthophyll cycle is not necessarily linked to protection against excess light (Morales et al. 1990; Torsten et al. 2001; Fietz et al. 2005). Louda et al. (2002) established that Diadino disappeared and transformed to Diato within the first two weeks of dark incubation. The inter-molecular Diadino–Diato transformation mechanism has been described by Patoine & Leavitt (2006).

Previous investigations in L. Võrtsjärv have shown a rather high sedimentation rate, especially for the upper sediment layers where the compaction of sediments has not occurred yet (Heinsalu et al. 2008). A high sedimentation rate means quick final burial of PhPs, which ensures rather similar preservation conditions within several years. This could explain positive correlations of the contents of the same pigment in different sediment layers (Table 2). Quick final burial of chemically stable palaeoindicators favours preservation of the historical information in L. Võrtsjärv sediments and allows palaeolimnological reconstructions of the lake ecosystem (Heinsalu et al. 2008).

CONCLUSIONS

- The dynamics of phytoplankton pigments (PhPs) in the upper sediment layers of L. Võrtsjärv generally did not correspond to their dynamics in the water. Sediments mixing by waves and characterized by a high accumulation rate in such a large and shallow lake could be the reasons for this phenomenon.
- Higher sediment PhP contents in spring were assumably caused by lower resuspension due to high water level and slow degradation due to low water temperature.
- Decrease in chemically unstable PhP contents between the sediment surface and deeper layers indicates that only the sediment surface is resuspended in L. Võrtsjärv.
- Pheophytin *a* and the marker pigments of cyanobacteria (Cantha and Zea) in the upper sediment layers of L. Võrtsjärv seem to be rather conservative against degradation and could be used to track the historical changes in total phytoplankton and cyanobacteria.
- Transformation of the diatom carotenoid Diadino to Diato in L. Võrtsjärv occurs mainly in sediments and is not induced by excess light.

Acknowledgements. The study was supported by the Estonian Ministry of Education and Research (projects SF0170011s08 and SF0332710s06), European Social Fund 'Mobilitas' (grant MJD51) and the Estonian Science Foundation (grants 6720, 6741, 8373 and G6020PKPK06). We are grateful to A. Leeben, P. Nõges and two anonymous referees for valuable comments and suggestions.

REFERENCES

Airs, R. L., Atkinson, J. E. & Keely, B. J. 2001. Development and application of a high resolution liquid chromatographic method for the analysis of complex pigment distributions. *Journal of Chromatography A*, **917**, 167–177.

Bianchi, T. S., Engelhaupt, E., Westman, P., Andren, T., Rolff, C. & Elmgren, R. 2000. Cyanobacterial blooms in the Baltic Sea: natural or human induced? *Limnology and Oceanography*, **45**, 716–726.

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.

Bonilla, S., Villeneuve, V. & Vincent, W. F. 2005. Benthic and planktonic algal communities in a high Arctic lake: pigment structure and contrasting responses to nutrient enrichment. *Journal of Phycology*, **41**, 1120–1130.

Buchaca, T. & Catalan, J. 2007a. Factors influencing the variability of pigments in the surface sediments of mountain lakes. *Freshwater Biology*, **52**, 1365–1379.

Buchaca, T. & Catalan, J. 2007b. On the contribution of phytoplankton and benthic biofilms to the sediment record of marker pigments in high mountain lakes. *Journal of Paleolimnology*, **40**, 369–383.

Carreto, J. I., Montoya, N., Akselman, R., Carignan, M. O., Silva, R. I. & Colleoni, D. A. C. 2008. Algal pigment patterns and phytoplankton assemblages in different water masses of the Rio de la Plata maritime front. *Continental Shelf Research*, **28**, 1589–1606.

Cohen, A. S. 2003. *Paleolimnology: The History and Evolution of Lake Systems*. Oxford University Press, New York, 528 pp.

Descy, J. P., Frost, T. M. & Hurley, J. P. 1999. Assessment of grazing by the freshwater copepod *Diaptomus minutus* using carotenoid pigments: a caution. *Journal of Plankton Research*, **21**, 127–145.

Directive, 2000. Directive 2000/60/EC of the European Parliament and of the council of 23 October 2000 establishing a framework for community action in the field of water policy. *Official Journal of the European Communities*, L **327**, 1–72.

Eilers, J. M., Kann, J., Cornett, J., Moser, K. & St. Amand, A. 2004. Paleolimnological evidence of change in a shallow, hypereutrophic lake: Upper Klamath Lake, Oregon, USA. *Hydrobiologia*, **520**, 7–18.

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.

Fietz, S., Sturm, M. & Nicklisch, A. 2005. Flux of lipophilic photosynthetic pigments to the surface sediments of Lake Baikal. *Global and Planetary Change*, **46**, 29–44.

Fietz, S., Nicklisch, A. & Oberhansli, H. 2007. Phytoplankton response to climate changes in Lake Baikal during the Holocene and Kazantsevo Interglacials assessed from sedimentary pigments. *Journal of Paleolimnology*, **37**, 177–203.

Greisberger, S. & Teubner, K. 2007. Does pigment composition reflect phytoplankton community structure in differing temperature and light conditions in a deep alpine lake? An approach using HPLC and delayed fluorescence techniques. *Journal of Phycology*, **43**, 1108–1119.

Haberman, J., Nõges, P., Nõges, T., Pihu, E., Kangur, K., Kangur, A. & Kisand, V. 1998. Characterization of Lake Võrtsjärv. *Limnologica*, **28**, 3–11.

Håkanson, L. & Jansson, M. 1983. *Principles of Lake Sedimentology*. Springer-Verlag, Berlin, 315 pp.

Hall, R. I., Leavitt, P. R., Quinlan, R., Dixit, A. S. & Smol, J. P. 1999. Effects of agriculture, urbanisation, and climate on water quality in the northern Great Plains. *Limnology and Oceanography*, **44**, 739–756.

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.

Hurley, J. P. & Armstrong, D. E. 1990. Fluxes and transformations of aquatic pigments in lake Mendota, Wisconsin. *Limnology and Oceanography*, **35**, 384–398.

Jaani, A. 1973. Hüdroloogia [Hydrology]. In *Võrtsjärv* [*Lake Võrtsjärv*] (Timm, T., ed.), pp. 37–60. Valgus, Tallinn [in Estonian].

Järvet, A. 2004. Hydrology of Lake Võrtsjärv. In *Lake Võrtsjärv* (Haberman, J., Pihu, E. & Raukas, A., eds), pp. 105–139. Estonian Encyclopaedia Publishers, Tallinn.

Jeffrey, S. W., Mantoura, R. F. C. & Bjørnland, T. 1997. Data for the identification of 47 key phytoplankton pigments. In *Phytoplankton Pigments in Oceanography: Guidelines to Modern Methods* (Jeffrey, S. W., Mantoura, R. F. C. & Wright, S. W., eds), pp. 449–559. UNESCO Publishing, Paris.

Leavitt, P. R. 1993. A review of factors that regulate carotenoid and chlorophyll deposition and fossil pigment abundance. *Journal of Paleolimnology*, **9**, 109–127.

Leavitt, P. R. & Carpenter, S. R. 1989. Effects of sediment mixing and benthic algal production on fossil pigment stratigraphies. *Journal of Paleolimnology*, **2**, 147–158.

Leavitt, P. R. & Carpenter, S. R. 1990a. Aphotic pigment degradation in the hypolimnion: implications for sedimentation studies and paleolimnology. *Limnology and Oceanography*, **35**, 520–534.

Leavitt, P. R. & Carpenter, S. R. 1990b. Regulation of pigment sedimentation by photooxidation and herbivore grazing. *Canadian Journal of Fisheries and Aquatic Sciences*, **47**, 1166–1176.

Leavitt, P. R. & Hodgson, D. A. 2001. Sedimentary pigments. In *Tracking Environmental Change Using Lake Sediments. Volume 3: Terrestrial, Algal, and Siliceous Indicators* (Smol, J. P., Birks, H. J. B. & Last, W. M., eds), pp. 295–325. Kluwer Academic Publishers, Dordrecht, The Netherlands.

Leeben, A., Tõnno, 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.

Louda, J. W., Liu, L. & Baker, E. W. 2002. Senescence- and death-related alteration of chlorophylls and carotenoids in marine phytoplankton. *Organic Geochemistry*, **33**, 1635–1653.

Mantoura, R. F. C. & Llewellyn, C. A. 1983. The rapid determination of algal chlorophyll and carotenoid pigments and their breakdown products in natural waters by reverse-phase high-performance liquid chromatography. *Analytica Chimica Acta*, **151**, 297–314.

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.

Morales, F., Abadia, A. & Abadia, J. 1990. Characterization of the xanthophyll cycle and other photosynthetic pigment changes induced by iron deficiency in sugar beet (*Beta vulgaris* L.). *Plant Physiology*, **94**, 607–613.

Nõges, P. & Laugaste, R. 1998. Seasonal and long-term changes in phytoplankton of lake Võrtsjärv. *Limnologica*, **28**, 21–28.

Nõges, P., Tuvikene, L., Nõges, T. & Kisand, A. 1999. Primary production, sedimentation and resuspension in large shallow Lake Võrtsjärv. *Aquatic Sciences*, **61**, 168–182.

Nõges, P., Laugaste, R. & Nõges, T. 2004. Phytoplankton. In *Lake Võrtsjärv* (Haberman, J., Pihu, E. & Raukas, A., eds), pp. 217–232. Estonian Encyclopaedia Publishers, Tallinn.

Patoine, A. & Leavitt, P. R. 2006. Century-long synchrony of fossil algae in a chain of Canadian prairie lakes. *Ecology*, **87**, 1710–1721.

Pork, M. & Kõvask, V. 1973. Vetikad [Algae]. In *Võrtsjärv* [*Lake Võrtsjärv*] (Timm, T., ed.), pp. 95–99. Valgus, Tallinn [in Estonian].

Raukas, A. 1995. *Estonian Nature*. Valgus, Estonian Encyclopaedia Publishers, Tallinn, 608 pp.

Raukas, A. & Tavast, E. 2002. The Holocene sedimentation history of Lake Võrtsjärv, central Estonia. *Geological Quarterly*, **46**, 199–206.

Reinart, A. & Nõges, P. 2004. Light conditions in Lake Võrtsjärv. In *Lake Võrtsjärv* (Haberman, J., Pihu, E. & Raukas, A., eds), pp. 141–149. Estonian Encyclopaedia Publishers, Tallinn.

Reuss, N. & Conley, D. J. 2005. Effects of sediment storage conditions on pigment analyses. *Limnology and Oceanography Methods*, **3**, 477–487.

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.

Reynolds, C. S. 2006. *The Ecology of Phytoplankton*. Cambridge University Press, New York, 552 pp.

Roderick, L., Oliver, L. & Ganf, G. G. 2000. Freshwater blooms. In *The Ecology of Cyanobacteria. Their Diversity in Time and Space* (Whitton, B. A. & Potts, M., eds), pp. 149–194. Kluwer Academic Publishers, Dordrecht, The Netherlands.

Scheffer, M. 1998. *Ecology of Shallow Lakes*. Chapman & Hall, London, 357 pp.

Soma, Y., Tani, Y., Soma, M., Mitake, H., Kurihara, R., Hashomoto, S., Watanabe, T. & Nakamura, T. 2007. Sedimentary steryl chlorin esters (SCEs) and other photosynthetic pigments as indicators of paleolimnological change over the last 28,000 years from the Buguldeika Saddle of Lake Baikal. *Journal of Paleolimnology*, **37**, 163–175.

Sommer, U. 1984. Sedimentation of principal phytoplankton species in Lake Constance. *Journal of Plankton Research*, **6**, 1–14.

Stoermer, E. F. & Smol, J. P. 1999. *The Diatoms. Applications for the Environmental and Earth Sciences*. Cambridge University Press, Cambridge, 469 pp.

Torsten, J., Reimund, G. & Wilhelma, C. 2001. Unusual pH-dependence of diadinoxanthin de-epoxidase activation causes chlororespiratory induced accumulation of diatoxanthin in the diatom *Phaeodactylum tricornutum*. *Journal of Plant Physiology*, **158**, 383–390.

Walsby, A. E. & McAllister, G. K. 1987. Buoyancy regulation by *Microcystis* in Lake Okaro. *New Zealand Journal of Marine and Freshwater Research*, **21**, 521–524.

Zimba, P. V. 1995. Epiphytic algal biomass of the littoral zone, Lake Okeechobee, Florida (USA). *Archiv fuer Hydrobiologie, Advances in Limnology*, **45**, 233–240.

Suure ja madala järve fütoplanktoni pigmentide dünaamika settes ning veesambas

Rene Freiberg, Monika Nõmm, Ilmar Tõnno, Tiiu Alliksaar, Tiina Nõges ja Anu Kisand

On kindlaks tehtud, mil määral annavad settes talletunud fossiilsed fütoplanktoni pigmendid teavet suure ja madala Võrtsjärve ajaloolise fütoplanktoni koosluse kohta. Selle väljaselgitamiseks võrreldi pindmiste settekihtide ja veesamba pigmentide sisaldusi ühenädalase intervalliga perioodil maist juunini ning augustist oktoobrini 2007. aastal. Arvestades sini- ja ränivetikate domineerimist järves, mõõdeti järgmisi pigmente: fukoksantiin, diadinoksantiin ning diatoksantiin kui ränivetikate, zeaksantiin kui sinivetikate ja kantaksantiin kui koloniaalsete sinivetikate marker. Kogu fütoplanktoni biomassi hindamiseks mõõdeti klorofüll *a* ja selle laguprodukti feofütiin *a* sisaldusi.

Uuringu tulemusena selgus, et settes olevate pigmentide sisaldus enamasti ei järginud veesambas toimunud pigmentide sisalduse muutusi. Peamised põhjused selleks on oletatavasti järves toimuv intensiivne resuspensioon ja suur settimiskiirus. Tulemused kinnitavad, et settes olevate pigmentide sisaldus peegeldab nende lagunemise intensiivsust ja vetikarakkude ujuvust. Kevadperioodil täheldati settes suuremat pigmentide sisaldust, mis oli tingitud järve kõrgest veetasemest ja madalast veetemperatuurist. Feofütiin *a* ja sinivetikate markerpigmendid on lagunemisele vastupidavamad ning kasutatavad ajalooliste muutuste kindlakstegemisel ka madalates järvedes. Kergemini lagunevate pigmentide sisalduse järsk vähenemine sügavamates settekihtides kinnitab, et resuspensioon mõjutab Võrtsjärves oluliselt vaid pindmist settekihti. Samuti selgus mõõtmise tulemusena, et ränivetikate markerpigmendi diadinoksantiini muutumine diatoksantiiniks toimub peamiselt settes ja see protsess ei ole põhjustatud liigtugevast päikesevalgusest.