Proc. Estonian Acad. Sci. Biol. Ecol., 2007, **56**, 3, 239–250

Fossil pigments in surface sediments of some Estonian lakes

Annika Mikomägi and Jaan-Mati Punning*

Institute of Ecology, Tallinn University, Uus-Sadama 5, 10120 Tallinn, Estonia

Received 12 May 2006, in revised form 21 December 2006

Abstract. We applied a complex of methods (spectrophotometry, HPLC, sediment oxygen demand) for the study of fossil pigments in lake sediment. The methods were tested on well-monitored lakes of different trophic status. It was found that the variations in pigment concentrations in the surface sediments of the studied lakes were mainly determined by their degradation before final burial. In the oligotrophic lakes of high Secchi transparency the concentration of fossil carotenoids and chlorophyll derivatives was the lowest and it increased when the photooxidation conditions deteriorated (decreasing transparency, higher trophicity). The individual pigments identified by HPLC analysis were in good correspondence with monitoring data.

Key words: fossil pigments, lake sediments, spectrophotometrical analyses, HPLC, chlorophylls, carotenoids, SOD.

INTRODUCTION

The nature and intensity of factors and processes influencing lake ecosystems and their impact are extremely complicated, and the temporal and spatial variability of monitoring data of water masses in lakes is great. Therefore, to distinguish and better understand the long-term development of lake ecosystems it is necessary to perform observations at different temporal scales. Some of the most direct indicators of lake development are the kinetics of carbon turnover and net primary production. As many researchers have demonstrated, the organic matter in sediments is often determined by preservation rather than production (Wetzel, 1983; Dean, 1999). Bloesch et al. (1988) showed that about 10% of the estimated net primary production is deposited as organic carbon in eutrophic lakes. The deposition rate of organic carbon in the sediment varies over-proportionally with changes in net primary production (Gruber et al., 2000).

* Corresponding author, punning@tlu.ee

Detailed studies of chlorophylls, carotenoids, and their derivatives in aquatic sediments and efforts in their isolation and identification (Leavitt & Hodgson, 2001) have made it possible to use fossil pigments to reconstruct past changes in lake production. Because pigments are very sensitive to degradation by dissolved oxygen, in most lakes more than 90% of the pigments are degraded to colourless compounds before permanent burial and the degradation of pigments continues in surface sediment layers (Watts & Maxwell, 1977; Repeta & Gagosian, 1987; Hurley & Armstrong, 1990; Leavitt & Carpenter, 1990; Leavitt, 1993). Thus, fossil pigment records reflect the sedimentation history and simultaneously give indirect information about the dynamics of the abundance of algae in lakes. The main problems in applying data on the distribution of fossil carotenoids and chlorophyll derivatives in reconstructing the development of planktonic populations in lakes are related to the understanding of the degradation and preservation of living organisms in lake sediments (Sanger, 1988; Leavitt et al., 1999).

Thus, quantification of pigment degradation needs to be studied very comprehensively due to the complicated control over pigment deposition and fossil abundance in different lakes. One way to achieve this is to study the traces of well monitored or historically documented events in accumulative sediments.

The main aim of the current research was to study factors that determine the distribution of fossil pigments and their taphonomy in surface sediments in four well-monitored Estonian lakes with different trophic status and topography. To complete the study, comprehensive methods for the isolation and identification of fossil pigments were worked out.

STUDY SITES

Surface sediments from four Estonian lakes (Table 1) of different trophic status, Secchi transparencies, catchment characteristics, and the nature and intensity of human impact were studied.

All the lakes studied are closed and small, lying in relatively deep glaciokarstic hollows, fed by groundwater and atmospheric precipitation, and have small dynamic ratios (see Håkanson & Jansson, 1983), which means that sedimentation is very weakly influenced by wind and wave activities. They are situated in areas of limnoglacial sediments and there is no active agricultural activity in the catchment. All lakes are dimictic and a strong thermal stratification develops in summer, while the depth of the epilimnion stays rather constant at about 2–4 m. The cooling period starts with slow convective erosion of the stratification and subsequent deepening of the thermocline. At the end of the year lake waters become mixed and remain so until the beginning of March. The concentration of oxygen in the studied lakes has a very distinct seasonal cycle. Its vertical gradient during the period of convective mixing is a consequence of higher consumption in the deeper layers compared to the supply by vertical transport. With the onset of stratification, organic matter rapidly uses oxygen in the hypolimnion.

Table 1. Studied lakes

Parameter	Ahnejärv	Martiska	Kuradijärv	Linajärv
Area, ha	1.5	2.7	1.9	3.8
Maximum depth, m	8.2	7.8	7.1	5.0
Thermocline depth, m	2–3	3–4	3–4	2–3
Maximum Chl *a* concentration in 0–1 m, mg m^{-3} (Ott et al., 1987)	2.8	5.5	10.3	80
pH during stratification period:				
Epilimnion (0–1 m from surface)	7.5	7.2	7.0	7.6
Hypolimnion (0.5–1 m from bottom)	7.3	7.0	7.0	7.7
Oxygen content (mg L^{-1}) during stratification period:				
Epilimnion (0–1 m from surface)	8.9	9.2	8.5	12
Hypolimnion (0.5–1 m from bottom)	0.2	1.4	1.3	0.5
Summer Secchi transparency, m	4.4	2.4	0.9	0.6
Trophic status	Oligo(meso?)-trophic	Oligo-mesotrophic	Oligo-mesotrophic	Meso-trophic

The analysed sediments consisted of brownish gyttja of high organic matter content (loss-of-ignition (LOI) 60–86%) and high porosity (95–98% of water). Detailed sediment studies in Lake Viitna Linajärv (Punning et al., 2003) and Lake Martiska (Punning et al., 2007) show that during the last decades the mean accumulation rates in the deepest areas of these lakes were respectively 25 and 9 mg cm^{-2} yr^{-1}.

Three lakes (Martiska, Ahnejärv, Kuradijärv) are situated in north-eastern Estonia in the Kurtna Kame Field area. The area has been severely affected by oil shale mining and processing (Punning, 1994). The fourth lake, Lake Viitna Linajärv, is situated in northernmost Estonia, in an area of limno- and fluvioglacial sediments and at present it is intensively used for swimming and recreation.

METHODS

Sampling of the upper 3 centimetres of sediments at different depths of the studied lakes was performed in October 2005 using a gravity corer. From all lakes surface sediments were sampled from the deepest area of the lake, besides that from lakes Martiska, Ahnejärv, and Kuradijärv samples were taken from depths very close to the position of the thermocline. In Lake Viitna Linajärv sediment samples were taken at depths of 1 m intervals (see Table 2). The samples were immediately after sampling packed into special plastic boxes and transported in argon atmosphere in cooling boxes to the laboratory. In the laboratory the samples were stored prior to analysis in a cool box (approx. 4 °C) in a dark argon environment. Every sample was divided into four sub-samples. One part was used

Table 2. Content of fossil pigments (spectrophotometric units g^{-1} OM), SOD_7 (mg O_2 g^{-1} OM), and LOI (%) in the surface samples of the studied lakes

Lake	Depth, m	CD	Carotenes	Xanthophylls	TC	CD/TC	SOD_7	LOI, %
Ahnejärv	4.4	1.1	0.2	0.9	1.1	1.0	5	60
	8.2	1.4	0.3	1.2	1.5	0.9	18	60
Martiska	3.3	1.1	0.3	1.0	1.3	0.8	15	64
	7.8	2.7	2.2	3.9	6.1	0.4	68	63
Kuradijärv	3.0	1.7	0.7	1.3	2.0	0.8	14	66
	7.1	4.4	2.9	5.2	8.2	0.5	139	67
Viitna	1.0	0.9	0.5	1.0	1.5	0.6	30	85
Linajärv	2.0	1.9	0.8	1.3	2.1	0.9	47	72
	3.0	2.9	1.5	2.6	4.1	0.7	101	81
	4.0	3.4	1.8	2.9	4.8	0.7	78	84
	5.0	4.7	2.9	4.8	7.7	0.6	61	86

for the measurement of organic matter as LOI at 500 °C (Dean, 1999), the second for the spectrophotometrical analysis of chlorophyll derivates (CD) and total carotenoids (TC), the third for sediment oxygen demand (SOD), and the fourth for HPLC analysis of fossil pigments.

For spectrophotometrical analysis of pigments a standard method (Sanger, 1988) was applied. Approximately 2 g of wet sediment was used for extraction. Absorption of CD was measured at 665 nm. The carotenoids were extracted and divided into two groups: (1) epiphasic carotenoids (carotenes) and (2) hypophasic carotenoids (xanthophylls). The absorption of carotenes and xanthophylls was measured at 448 nm (Swain, 1985; Bengtsson & Enell, 1986). Measurements were carried out on a spectrophotometer "Cadas 100". The content of the pigments was expressed as spectrophotometric units per gram of organic matter.

Pigments for chromatographic analyses were extracted from 100 mg freeze-dried sediment samples using 90% acetone. After that the extracts were centrifuged and filtered through a 0.45 µm pore size Whatman PTFE filter. A reverse-phase high performance liquid chromatography (RP-HPLC) system that includes a Perkin Elmer chromatograph, an Adsobsphere HS C18 column (3 µm particle size; 150 mm × 4.6 mm i.d.) with Alltech precolumn and UV-VIS detector was used. For better resolution an ion pairing reagent (IPR) (1.5 g tetrabutyl ammonium acetate and 7.7 g ammonium acetate in 100 mL HPLC-grade water) was added to the solvent (Mantoura & Llewellyn, 1983). The detection wavelength was 435 nm and the flow rate 1.5 mL min^{-1}. Pigments were identified by comparing their retention times and spectra against standards.

For sediment oxygen demand (SOD) measurements wet sediment samples (approximately 1–2 g each) were washed into SOD bottles, and the bottles were filled with distilled and aerated water. Initial dissolved oxygen contents were recorded during 10 days using an oxygen probe frequently each day. The control bottle was filled with the same (distilled and aerated) water and dissolved oxygen level was daily measured (Wang, 1980). Sediment oxygen demand was calculated as mg O_2 per gram of organic matter and results are presented on the seventh day (SOD_7).

RESULTS

The fossil pigment content values in surface samples (Table 2) varied significantly between lakes and within lakes at different sampling depths. The variability of the TC values was the largest – from 1.1 up to 7.7 units – and in all cases the TC values increased with the increase in water depth in the sampling sites. The TC values were especially high in samples taken from the deepest areas of lakes, where the concentrations of oxygen sharply diminish. There was also a strong correlation between water depth and content of carotenes and xanthophylls while the contrast in the concentrations in the shallower and deeper areas was generally greater in xantophylls. The variations of CD values at different depths were weaker than those of TC.

Surface sediment oxygen demand (SOD_7) was in good accordance with increasing depths in all lakes excluding Lake Viitna Linajärv where the highest SOD_7 values were measured in samples taken at a depth of 3.0 m (Fig. 1). The highest SOD_7 values (139 mg O_2 per gram of organic matter) were measured for surface sediments in the deeper areas of Lake Kuradijärv. There were no correlations between LOI and the SOD_7 or fossil pigment content values.

The differences between the studied lakes in the content of fossil pigments as well as in the SOD_7 values are clearly expressed. At equal depths, the lowest content of degradable pigments and SOD_7 was found in Lake Ahnejärv, the second lowest in Lake Martiska, and the highest values of these indices were prevalent in lakes Kuradijärv and Viitna Linajärv (Fig. 1). As seen in Table 1, the summer Secchi transparency decreases roughly in the same order.

In the works of many researchers, the content of fossil pigments (Swain, 1985; Sanger, 1988; Lami et al., 1994; Reuss et al., 2005) and SOD_7 (Wang, 1980; Stefan & Fang, 1994; Witek et al., 1999; Benoit et al., 2006) characterize mostly the level of degradation and preservation of organic matter. To characterize the production of a lake, HPLC analysis was used to examine the relative abundance of pigments in samples taken from the deepest areas of the studied lakes (Table 1).

In interpreting the obtained HPLC spectra and in examining the identification affinity of the fossil pigments, we used widely cited papers (Lami et al., 1994; Leavitt et al., 1999; Leavitt & Hodgson, 2001; Marchetto et al., 2004; Hodgson et al., 2006) (Table 3). The obtained HPLC spectra were quite different for different lakes and it was difficult to identify all peaks. Because of the relative abundance of some fossil pigments, those which were most definitely identified are given in Fig. 2 (calculated as the proportion of individual peak areas in the total area). The concentrations of β-carotene, chlorophyll *a* (Chl *a*), and pheophytin *a* are valuable

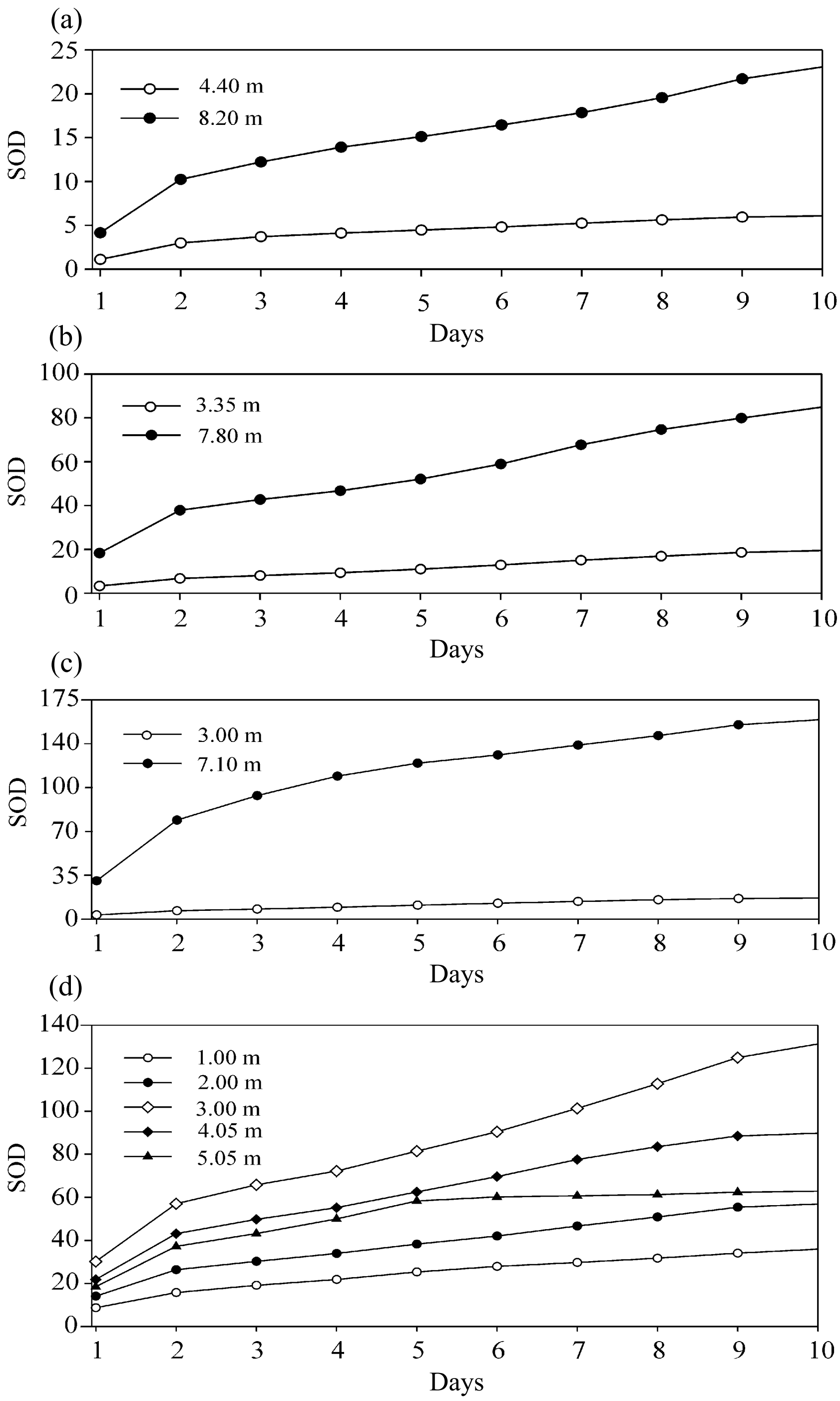

Fig. 1. Dynamics of SOD (mg O_2 g^{-1} OM) in surface sediments from the deepest areas of the studied lakes (a – Ahnejärv; b – Martiska; c – Kuradijärv; d – Viitna Linajärv) and from different depths.

Table 3. Determined fossil pigments, their preservation (1 is highest and 3 lowest level), and taxonomic affinities

Pigment	Stability	Affinity (after Leavitt & Hodgson, 2001; Hodgson et al., 2006)
Chlorophyll *a*	3	Plantae, Algae
Pheophytin *b*	2	Chl *b* derivative (Plantae, Chlorophyta, Euglenophyta)
Pheophytin *a*	1	Chl *a* derivative (Plantae, Algae)
β-Carotene	1	Plantae, Algae
Lutein	1	Chlorophyta, Euglenophyta, Plantae
Alloxanthin	1	Cryptophyta
Diatoxanthin	2	Bacillariophyta, Dinophyta, Chrysophyta
Zeaxanthin	1	Cyanobacteria (Chlorophyta)
Echinenone	1	Cyanobacteria
Myxoxanthophyll	2	Colonial Cyanobacteria

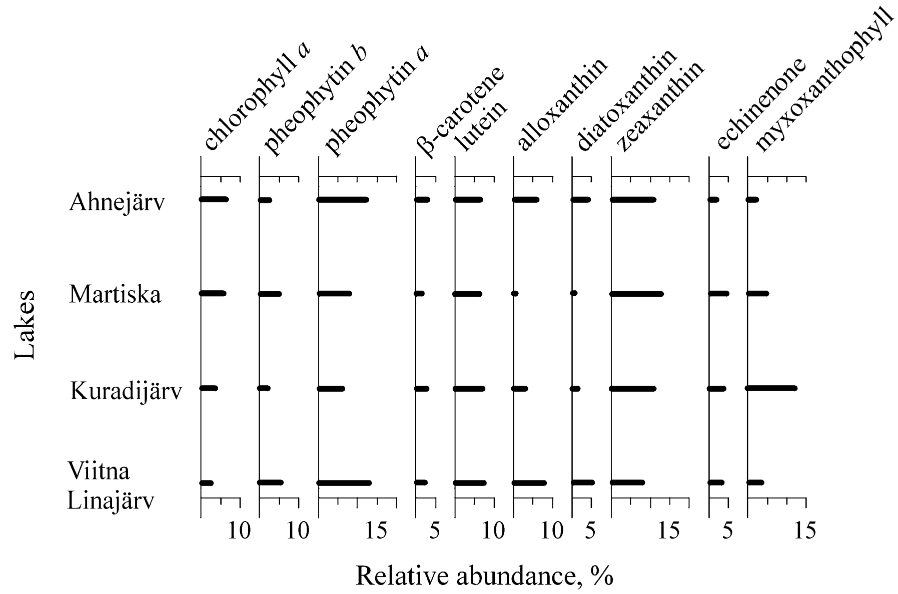

Fig. 2. Relative abundance of the identified fossil pigments in the surface sediments from the deepest areas of the studied lakes.

indicators of total algae abundance. Unaltered marker carotenoids, e.g. alloxanthin, lutein, and echinenone, can be used for distinguishing algae divisions. Analysis of carotenoid alloxanthin allows for the distinguishing of the relative importance of cryptophytes. The main cyanobacteria pigments in the sediment samples are echinenone, zeaxanthin, and myxoxanthophyll (indicates colonial cyanobacteria). The abundance of myxoxanthophyll was much higher in Lake Kuradijärv than in the other lakes studied.

DISCUSSION

The reliability of the methods used was proved by comprehensive analysis of organic matter degradation products in different small Estonian lakes. There was a logical connection between the results that were obtained using the different methods (spectrophotometric, HPLC, SOD) and the physical, chemical, and biological parameters of lakes. The obtained results indicated a good relation between CD and TC variations and pigment peak areas, which were identified using HPLC chromatograms. Although the concentration of fossil pigments and taphonomy in lake sediments were determined through production and destruction, interpretation of the results remained complicated. Each parameter verifies an event, reduces the uncertainty, and contributes to the reconstruction of the past development of the lake. It is often difficult to predict the factors determining pigment concentration in sediments – whether they are due to productivity or preservation conditions. However, the spectrophotometric, chromatographic, and SOD data make this possible.

Sedimentary CD and TC concentrations in Lake Ahnejärv were compared to other investigated lakes. The ratio of CD/TC was directly related to the amounts of pigments that were originally deposited, because carotenoids degrade slightly more rapidly than chlorophyll derivatives (Swain, 1985). The CD/TC values were higher in oligotrophic lakes like Lake Ahnejärv, where primary production is lower and preservation conditions are worse (better transparency and higher oxygen content). The value of LOI in Lake Ahnejärv sediment was lower (60%) than in the other investigated lakes. Lake Ahnejärv's bottom vegetation is relatively rich and the lake is almost oligotrophic (Mäemets & Teder, 1987). Also HPLC analysis results confirmed this. The contents of cyanobacteria pigments (echinenone, myxoxanthophyll) in all samples were very small compared with pigments that derive from higher plants and from many algae groups (Chl *a*, pheophytin *b*, pheophytin *a*, β-carotene, lutein).

According to Sanger (1988), carotenoids are more sensitive to photo- and chemical oxidation, and microbial activity. Therefore the CD/TC ratio, which shows the level of degradation of organic matter, is as a rule higher in sediments from shallower areas of lakes than from deeper areas. This regularity was invalidated by samples taken from Lake Viitna Linajärv where TC and xanthophylls content in sediments from depths of 3.0 and 4.05 m were inversed and CD/TC ratios did not decrease with increasing depth.

As the data of limnological monitoring show, the trophic status of Lake Martiska and especially of Lake Kuradijärv worsened significantly since the 1970s due to the atmospheric load of fly ash and the lowering of water levels (Punning, 1994). The transparency of these lakes is much less than in Lake Ahnejärv (Table 1) and the anoxic hypolimnion has caused strong degradation of the bottom vegetation. Limnologically characterized differences appear also in sedimentary pigment diversities and in sediment oxygen demand. The CD and TC concentrations in Lake Martiska and Lake Kuradijärv are greater than in Lake Ahnejärv. This may be due to larger production or better preservation of pigments.

The water transparency of Lake Kuradijärv is low (0.9 m) and the oxygen saturation in the hypolimnion extremely low (1–3%). This kind of environment tends to promote the preservation of pigments, and the low CD/TC ratio (0.54) in Lake Kuradijärv also confirms this. The SOD_7 value was higher than in the other lakes. The great abundance of carotenes in sediments indicates good preservation conditions and high phytoplankton production.

The HPLC spectra showed that lutein, zeaxanthin, and myxoxanthophyll were more abundant than other sedimentary pigments in Lake Kuradijärv (Fig. 2). Zeaxanthin and myxoxanthophyll are typical cyanobacteria pigments and they indicate that the phytoplankton is dominated by cyanobacteria (Leavitt & Hodgson, 2001), which refer to eutrophication of the lake.

Sedimentary pigment data from Lake Martiska showed a predominance of carotenoids with regard to CD. The ratio of CD/TC in the sediments from the deepest area of the lake is the lowest compared to the other studied lakes and indicates good pigment preservation conditions and a relatively high phytoplankton production. Earlier investigations have shown dominance of chlorophyta (*Oocystis* spp. and *Fusola* spp.) and cyanobacteria (*Aphanocapsa* spp. and *Cyanodictyon* spp.) in this lake.

Lake Viitna Linajärv is now a meso-eutrophic lake. Limnological studies in 1999 and 2000 (Punning & Leeben, 2003) showed a marked increase in the Chl *a* concentration during this time (45 and 25 $\mu g\ L^{-1}$, respectively). The cyanobacterial blooms (up to 120 μg Chl *a* L^{-1}), lasting to late autumn, were caused mainly by *Anabaena contorta* and *A. flos-aquae*. The concentration of organic matter in Lake Viitna Linajärv's sediment was significantly higher (86%) than in other investigated lakes. The CD and TC values were relatively high (respectively 4.7 and 7.7) and the CD/TC ratio was 0.61. The low ratio indicates good pigment preservation conditions in Lake Viitna Linajärv's bottom sediments and agrees with the strongly anoxic hypolimnion and high SOD_7 values. Spectrophotometric and HPLC analyses allow us to conclude that phytoplankton production in the lake is high. The concentration of various pigments (pheophytin *b*, pheophytin *a*, lutein, alloxanthin, zeaxanthin) indicates lake eutrophication. If phytoplankton dominates the lake, then carotenoids, especially xanthophylls, will prevail over CD (Sanger, 1988). This is typical of Lake Viitna Linajärv where the CD/TC ratio in sediments from the deepest area is higher than in the surface sediments in lakes Martiska and Kuradijärv. High values of chlorophyll and carotenoids and higher relative abundance of lutein, zeaxanthin, and alloxanthin in HPLC spectra indicate high productivity in Lake Viitna Linajärv, as well as a rather high sedimentation rate in this lake (Punning & Leeben, 2003).

CONCLUSIONS

The application of a complex methodology (spectrophotometric, HPLC, SOD) for the study of surface sediments from Estonian lakes shows good correspondence with data obtained by other approaches. The values of TC and SOD_7 are the most sensitive to increasing depth and decreasing Secchi transparency. The variations in pigment concentrations in the sediments might be explained by changes in the trophic status of the lakes, initially by photooxidation conditions that determine the degradation of TC and CD before final burial. In the HPLC spectra Chl *a*, pheophytin *b*, pheophytin *a*, β-carotene, lutein, alloxanthin, diatoxanthin, zeaxanthin, echineoen, and myxoxanthophyll were present in all the studied lakes. The differences between the lakes are in good correlation with monitoring data indicating advanced eutrophication in lakes Viitna Linajärv and Kuradijärv.

ACKNOWLEDGEMENTS

This research was supported by the Estonian Ministry of Education and Research target-financed project 0282121s02 and the Estonian Science Foundation grant 5584. We are indebted to anonymous reviewers for their critical comments and valuable suggestions.

REFERENCES

Bengtsson, L. & Enell, M. 1986. Chemical analysis. In *Handbook of Holocene Palaeoecology and Palaeohydrology* (Berglund, B. E., ed.), pp. 423–451. John Wiley & Sons, Chichester, New York, Brisbane, Toronto, Singapore.

Benoit, P., Gratton, Y. & Mucci, A. 2006. Modelling of dissolved oxygen levels in the bottom waters of the Lower St. Lawrence Estuary: coupling of benthic and pelagic processes. *Mar. Chem.*, **102**(1–2), 13–32.

Bloesch, J., Stadelmann, P. & Bührer, H. 1988. Primary production, mineralization and sedimentation in the euphotic zone of the Swiss lake. *Limnol. Oceanogr.*, **22**, 511–526.

Dean, W. E. 1999. The carbon cycle and biogeochemical dynamics in lake sediments. *J. Paleolimnol.*, **21**, 375–393.

Gruber, N., Wehrli, B. & Wüest, A. 2000. The role of biogeochemical cycling for the formation and preservation of varved sediments in Soppensee (Switzerland). *J. Paleolimnol.*, **24**, 277–291.

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

Hodgson, D. A., Verleyen, E., Squier, A. H., Sabbe, K., Keely, B. J., Saunders, K. M. & Vyverman, W. 2006. Interglacial environments of coastal east Antarctica: comparison of MIS 1 (Holocene) and MIS 5e (last interglacial) lake-sediment records. *Quat. Sci. Rev.*, **25**, 179–197.

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

Lami, A., Niessen, F., Guilizzoni, P., Masaferro, J. & Belis, C. 1994. Palaeolimnological studies of the eutrophication of volcanic Lake Albano (Central Italy). *J. Palaeolimnol.*, **10**, 181–197.

Leavitt, P. R. 1993. A review of factors that regulate carotenoid and chlorophyll deposition and fossil pigment abundance. *J. Palaeolimnol.*, **9**, 109–127.
Leavitt, P. R. & Carpenter, S. R. 1990. Aphotic pigment degradation in the hypolimnion: implications for sedimentation studies and paleolimnology. *Limnol. Oceanogr.*, **35**, 520–534.
Leavitt, P. R. & Hodgson, D. A. 2001. Sedimentary pigments. In *Tracking Environmental Change Using Lake Sediments. Vol. 3. Terrestrial, Algal and Siliceous Indicators* (Smol, J. P., Birks, H. J. B. & Last, W. M., eds), pp. 295–325. Kluwer Academic Publishers, Dordrecht.
Leavitt, P. R., Findlay, D. L., Hall, R. I. & Smol, J. P. 1999. Algal responses to dissolved organic carbon loss and pH decline during whole-lake acidification: evidence from paleolimnology. *Limnol. Oceanogr.*, **44**, 757–773.
Mäemets, A. & Teder, A. 1987. Kurtna vähetoiteliste järvede suurtaimestiku (makrofloora) muutustest viimastel aastakümnetel ja selle nüüdisseisund. In *Kurtna järvestiku looduslik seisund ja selle areng* (Ilomets, M., ed.), pp. 127–132. Tallinn.
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. *Anal. Chim. Acta*, **151**, 297–314.
Marchetto, A., Lami, A., Musazzi, S., Massaferro, J., Langone, L. & Guilizzoni, P. 2004. Lake Maggiore (N. Italy) trophic history: fossil diatom, plant pigments, and chironomids, and comparison with long-term limnological data. *Quat. Int.*, **113**, 97–110.
Ott, I., Nõges, T., Nõges, P., Järvalt, A., Tuvikene, A., Krause, T. & Kruus, U. 1987. Kurtna vähetoiteliste järvede seisundist. In *Kurtna järvestiku looduslik seisund ja selle areng* (Ilomets, M., ed.), pp. 172–177. Tallinn.
Punning, J. M. 1994. Influence of human activity on different ecosystems. In *The Influence of Natural and Anthropogenic Factors on the Development of Landscapes. The Results of a Comprehensive Study in NE Estonia. Inst. Ecol., Estonian Acad. Sci., Publ., No. 2* (Punning, J. M., ed.), pp. 190–227. Tallinn.
Punning, J. M. & Leeben, A. 2003. A comparison of sediment and monitoring data: implications for paleomonitoring a small lake. *Environ. Monit. Assess.*, **89**, 1–13.
Punning, J.-M., Kangur, M., Koff, T. & Possnert, G. 2003. Holocene lake-level changes and their reflection in the paleolimnological records of two lakes in northern Estonia. *J. Palaeolimnol.*, **29**, 167–178.
Punning, J.-M., Boyle, J. F., Terasmaa, J., Vaasma, T. & Mikomägi, A. 2007. Changes in lake sediment structure and composition caused by human-impact: repeated studies of Lake Martiska. *Holocene*, **17**(1), 145–151.
Repeta, D. J. & Gagosian, R. B. 1987. Carotenoid diagenesis in recent marine sediments – I. The Peru continental shelf (15° S, 75° W). *Geochim. Cosmochim. Acta*, **51**, 1001–1009.
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. *Mar. Chem.*, **95**, 283–302.
Sanger, J. E. 1988. Fossil pigments in paleoecology and paleolimnology. *Palaeogeogr. Palaeoclim. Palaeoecol.*, **62**, 343–359.
Stefan, H. G. & Fang, X. 1994. Dissolved oxygen model for regional lake analysis. *Ecol. Modell.*, **71**, 37–68.
Swain, E. B. 1985. Measurement and interpretation of sedimentary pigments. *Freshwater Biol.*, **15**, 53–75.
Wang, W. 1980. Fractionation of sediment oxygen demand. *Water Res.*, **14**, 603–612.
Watts, D. C. & Maxwell, J. R. 1977. Carotenoid diagenesis in a marine sediment. *Geochim. Cosmochim. Acta*, **41**, 493–497.
Wetzel, R. G. 1983. *Limnology*. Saunders College Publishing, Fort Worth, Philadelphia.
Witek, Z., Ochocki, S., Nakonieczny, J., Podgorska, B. & Drgas, A. 1999. Primary production and decomposition of organic matter in the epipelagic zone of the Gulf of Gdańsk, an estuary of the Vistula. *J. Mar. Sci.*, **56**, 3–14.

Fossiilsete pigmentide sisaldus Eesti järvede pindmistes setetes

Annika Mikomägi ja Jaan-Mati Punning

On juurutatud erinevad fossiilsete pigmentide määramismeetodid: spektrofotomeetriline meetod klorofülli derivaatide (CD) ning karotenoidide (TC) määramiseks ja kõrgsurve vedelikkromatograafiline meetod (HPLC) üksikute pigmentide identifitseerimiseks, samuti setteproovide hapnikutarbe määramismeetod. Meetodeid on testitud nelja järve (Ahnejärv, Kuradijärv ning Martiska järv Kurtna mõhnastikus ja Viitna Linajärv) erinevatest sügavustest võetud pindmistel setetel. Uurimistulemused näitavad, et CD ja TC sisaldus suureneb veesamba paksuse suurenemisega. Samuti on selge seos järve suvise läbipaistvuse (Secchi sügavus) ja pigmentide sisalduse vahel. Saadud tulemused ja nende võrdlev analüüs uuritud järvede pikaajalise monitooringuandmetega lubavad eeldada, et CD ja TC sisaldus setetes on põhiliselt määratud orgaanilise aine destruktsiooniga (eelkõige fotooksüdatsioon) settimisprotsessi käigus. Nii on kõige väiksemad CD ja TC hulgad määratud oligotroofse Ahnejärve pindmistes setetes. HPLC spektrid võimaldavad identifitseerida rea pigmente ja nende alusel hinnata järve floorat settimise ajal. Viitna Linajärve ja Kuradijärve pindmistes setetes fikseeritud luteiin, zeaksantiin ning müksoksantofüll viitavad kõrgele produktsioonile ja sinivetikate esinemisele, mis on heas kooskõlas monitooringu andmetega.