

Assessment of the effect of anthropogenic pollution on the ecology of small shallow lakes using the palaeolimnological approach

Tiiu Koff, Egert Vandel, Agáta Marzecová, Egle Avi and Annika Mikomägi

^a Institute of Ecology, Tallinn University, Uus-Sadama 5, Tallinn 10120, Estonia; tiiu.koff@tlu.ee, egert.vandel@tlu.ee, agata.marzecova@tlu.ee, egleke1@tlu.ee, annika.mikomagi@tlu.ee

Received 26 August 2016, accepted 1 November 2016

Abstract. Palaeolimnological techniques were utilized to determine the extent of the effect of anthropogenic pollutants or other environmental stressors on three lake ecosystems over the last 200 years. The ecology of the study sites has experienced significant changes due to various activities such as (1) extensive catchment drainage and using poisoning as a fish management measure, (2) seepage of urban waste water due to establishment and growth of a town and (3) artificial inflow of oil-shale mining waters. Sediment geochemical composition, fossil pigments and Cladocera remains from the sediment cores were analysed to demonstrate that sufficient information can be derived from sediments to permit a historical reconstruction. The integrated use of archival maps, historical records and lake monitoring data confirmed links to anthropogenic pollutants, primarily on the catchment level. The examples show how the sediment indicators provide unique insights into the causes and temporal dynamics of lake ecosystem changes relevant for environmental management decisions. This study demonstrates that palaeolimnology has great potential to assist in eutrophication assessment and management efforts in waterbodies.

Key words: Cladocera, environmental management, geochemistry, lake sediments, palaeorecords, pigments.

INTRODUCTION

The pollution of lakes and reservoirs constitutes a major threat to the world freshwater resources. The most widely discussed causes of water quality deterioration are the discharge of wastewater from commercial and industrial waste (intentionally or through spills) into surface waters, but also chemical contamination from treated sewage and release of waste and contaminants into surface runoff flowing to surface waters (including urban runoff and agricultural runoff, which may contain chemical fertilizers and pesticides) (Moss 2008; Yang et al. 2010). As a consequence of this pollution the ecological state of the freshwater ecosystem may change. It is important to identify the processes that determine the ability of the ecosystem to stay within a desired state or how the slowly changing variables and abrupt impacts will determine the boundaries beyond which disturbances may push the system into another state (Scheffer & Carpenter 2003). The resilience of the aquatic ecosystems, which we understand according to Folke et al. (2004), is the capacity of a system to absorb disturbance and reorganize while undergoing a change so as to retain essentially the same function, structure, identity and feedbacks. Many of these responses have been non-linear, with aquatic ecosystems responding abruptly or showing a certain level of resilience to forces until a threshold is breached.

Although environmental monitoring has been essential in detecting eutrophication, biodiversity loss or water quality deterioration, the monitoring activities are limited in time and thus not sufficient in their scope to identify the causality and thresholds. The contaminants discharged to the environment are washed by rainwater, transported to aquatic ecosystems and deposited and preserved in sediments that continuously accumulate with time. Therefore the historical records of anthropogenic pollutants in aquatic environments can be reconstructed by studying lake sediments (Bindler et al. 2008; Battarbee & Bennion 2011). The characterization and the quantification of the pollutants entrapped in well-dated sediment cores allow (1) the quantification of the natural content of trace elements (geochemical background) that can further be used to calculate the anthropogenic enrichment signal, (2) the evaluation of the modern pollution level with regard to natural (climate-induced) and (pre-)historical variations and (3) the assessment of the temporal evolution of the contamination and its relationship with past human activities (settlement, land-use) (Thevenon & Poté 2012).

Distinguishing the anthropogenic and natural signals is particularly important when defining reference conditions, because inappropriate restoration targets might prove unachievable. Palaeolimnological studies increasingly show that the response of lakes to climatic

© 2016 Authors. This is an Open Access article distributed under the terms and conditions of the Creative Commons Attribution 4.0 International Licence (<http://creativecommons.org/licenses/by/4.0>).

and human influences are complex, multidimensional and often indirectly mediated through watershed and in-lake processes. In some instances changes have been more profound than might be anticipated from an apparently simple driver, and some lakes fail to recover fully. The EU Water Framework Directive (WFD, Directive 2000/60/EC) requires member states to establish type-specific reference conditions that will show no or minimal anthropogenic impact. For establishing these conditions the palaeolimnological approach has been used in several cases (Taylor et al. 2006; Battarbee & Bennion 2011; Battarbee et al. 2011), also in Estonia (Heinsalu & Alliksaar 2009).

A combination of the new ecosystem state and continual pressure by pollution can lead to further deterioration of a lake. Therefore it is important to identify possible regime shifts (e.g. the shift from oligotrophic to eutrophic states in lakes) and find out preventive measures for possible ecosystem management. It is also crucial to consider ecological information from several lines of evidence rather than to reduce all information to a univariate water-quality inference (Whitmore & Riedinger-Whitmore 2014). For identifying the regime shift we need an appropriate timescale and good indicators partly provided by palaeolimnological methods. Multi-indicator palaeolimnological studies have helped to establish temporal patterns of change in ecological structure and function in response to multiple drivers such as eutrophication (Sayer et al. 2010, 2012; Davidson & Jeppesen 2013; Bennion et al. 2015), climate (Leng & Barker 2006; Holmes et al. 2016), hydrology and chemistry (Tropea et al. 2010).

In this paper, we present recent sediment records from three lakes located in Estonia (Eastern Europe), for which historical monitoring data were available. According to these records, the lake ecosystems were deteriorated by various anthropogenic disturbances: (1) use of poisoning as a fish management measure and extensive catchment drainage, (2) seepage of urban waste water due to the establishment and growth of

urban areas and (3) artificial inflow of oil-shale mining waters. The objective of this study is to investigate the historical pollution of three well-dated lacustrine records in order to evaluate the impact of anthropogenic pollution on ecosystem deterioration. We will focus mostly on major shifts reflected across several indicators and compare them with the historical data on land-use and lake monitoring. We will explore the usefulness of lake sediment analysis for the integrative assessment of ecosystem deterioration and the environmental management decision-making by addressing hypothetical questions for lake management.

MATERIAL AND METHODS

Studied lakes

The study sites are shallow (average depth under 4 m) and small lakes (with size below 60 ha) (Table 1) located in Estonia, in the eastern part of the Baltic area (Fig. 1). They were selected based on the following criteria: known events of pollution confirmed by the availability of multiple monitoring data, the archival documents, maps and high sediment accumulation rates.

Lake Lohja (Fig. 1) was originally a clear- and soft-water ecosystem with rare *Lobelia dortmanna* L. During the late 1960s the lake rapidly transitioned to an algal-dominated, turbid state, characterized by strong cyanobacterial blooms and fish decimation (Mäemets 1968). These changes occurred shortly after the lake management measures in 1963–64 that aimed at changing the lake conditions and fish population in order to create suitable conditions for sea trout farming. The attempt involved treatment by a toxic pesticide (bicyclic terpene) and liming with oil-shale ash. The experiment was unsuccessful; the introduced trouts did not adapt and the initial population of perch, roach and pike was replaced with carp which survived the poisoning and was dominant until the 1970s (Mäemets 1977). Furthermore, it has been assumed that the lake quality deteriorated as

Table 1. Main parameters of the studied lakes

	Lake Lohja	Lake Verevi	Lake Nõmmejärv
Location	59°32'N; 25°41'E	58°13'N; 26°24'E	58°03'N; 26°30'E
Area (ha)	56.8	12.6	15
Max depth (m)	2.9	11	7
Mean depth (m)	2.2	3.7	3.1
Mixing regime	Not stratified	Stratified, dimictic	Stratified, dimictic
Recent trophic status	Mesotrophic	Hypertrophic	Eutrophic
Water hardness	Soft-water	Hard-water	Hard-water
Flow-through	Yes	Seasonal	Yes

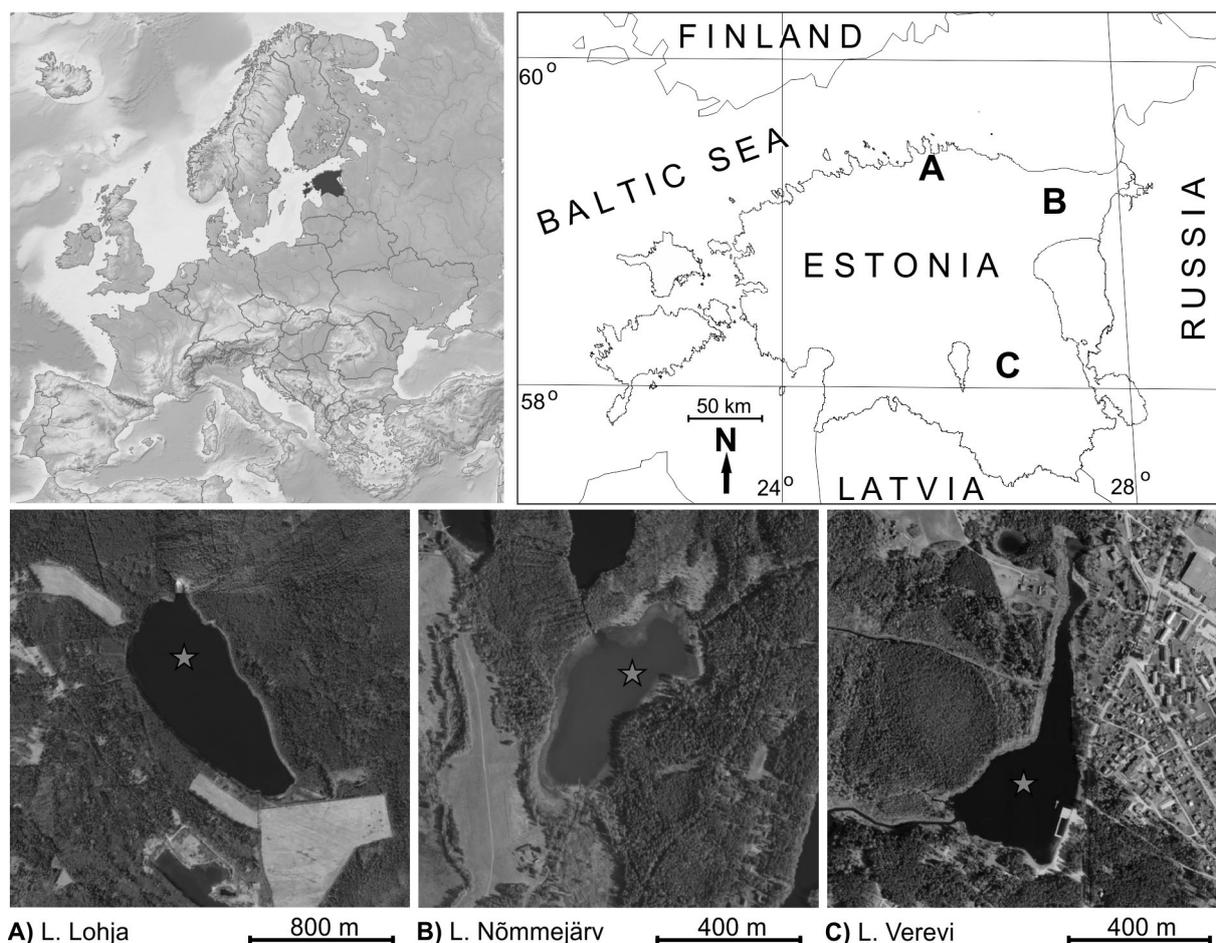


Fig. 1. Regional location of Estonia (top left). Location of the study sites (top right): A, Lake Lohja; B, Lake Nõmmejärv; C, Lake Verevi and aerial photos of the studied lakes and coring points.

a consequence of these measures (Mäemets 1968). The cyanobacterial blooms were most severe during the 1970s–1980s; however, the lake has remained meso-eutrophic until present (Ott 2008). There is a need to confirm the hypothesis that the unsuccessful lake management plan caused the deterioration of lake conditions.

Lake Nõmmejärv (Fig. 1) represents a hard-water lake which has since 1972 become heavily influenced by discharges of alkaline oil-shale mine waters through an artificial channel. The lake was already influenced by anthropogenic activities of an army camp in the mid-20th century (Marzecová et al. 2011). However, due to the large contents of minerogenic particles and sulphates, the mine water discharge represents a major risk factor for the lake ecosystem. Since the 1960s, the phytoplankton changes have indicated an increase in the occurrence of cyanobacteria (Ott 2006). At present, the phosphorus concentrations in water are low; however, several other ecological factors indicate less favourable,

eutrophic, conditions. In the light of the changing land management planning that could potentially lead to the closure of the water inflow that flushes through the lake, there is a need to evaluate its possible impacts on the ecological functioning of the lake.

Lake Verevi (Fig. 1) is an example of a hard-water hypertrophic lake affected by urban waste waters and intensive recreational activities. The region around the lake was sparsely populated until the opening of the railway in the 1880s, which gave an impetus for establishing a small town of Elva. The first lake monitoring survey in the 1920s characterized the ecological status of the lake as naturally moderately eutrophic (Ott et al. 2005). The lake trophic state has changed in the following stages: naturally mesotrophic (until the late 1950s), eutrophic (late 1950s–mid-1980s), hypertrophic (mid-1980s–2002) (Kangro et al. 2005). The hypertrophic conditions were characterized by a significant increase in algal productivity, strong cyano-

bacteria blooms and reduced water mixing. From the 2000s, the remediation activities (reduction of external loads, removal of macrophytes, lakeshore bed cleaning) led to temporary improvements in the ecological status of the lake. However, the lake has been under the risk of nutrient loading from sediments and substantial further remediation actions have been considered (Ott et al. 2005). In order to evaluate the remediation and plan its future management, it is important to identify if these type of improvements have changed the lake status and are comparable with desirable reference conditions.

Sediment sampling and dating

Short sediment cores (50–70 cm) were sampled from the deepest points of the lakes with a modified Livingstone–Vallentyne piston corer. After the lithological description, the sediment cores were sectioned into 1–2 cm subsamples and placed in a cold, dark storage area until analysis. Samples for pigment analysis were stored separately under the argon atmosphere. Cladocera remains were analysed from 1 cm³ samples of wet sediment. Material for remaining analyses was freeze-dried and homogenized. The age of the sediment was established by ²¹⁰Pb dating (Appleby 2001). The dating analysis was performed by a specialized laboratory (Centre for Monitoring Study and Environment Technologies, Kiev, Ukraine). All three sites were impacted in the past by multiple anthropogenic activities and showed clear changes in sedimentation regime. The age–depth stratigraphy was therefore derived in all cases using a Constant Rate of Supply (CRS) model, which was developed for sites with changes in sedimentation dynamics (Appleby 2001). The age–depth models were verified by using information about activity–depth distribution of artificial radionuclide ¹³⁷Cs. The sediment data were analysed in parallel cores whose age–depth scales were correlated using their lithological features (e.g. Marzecová et al. 2011).

Geochemical, pigment and Cladocera analysis

The content of organic matter and carbonates in sediment was estimated using the loss on ignition (LOI) analysis at 550 °C and 950 °C, respectively (Boyle 2004). Sediment samples were analysed for metals using an energy dispersive X-ray fluorescence (XRF) spectrometry. The analysis was performed with a Bruker S2 Ranger XRF spectrometer at the Department of Geography, University of Liverpool according to the Boyle (2000) methodology. The sediment samples consisted of 3 g of dried and homogenized sediments. The instrument was calibrated for the sediment samples by a series of known standards (Boyle et al. 2016). For the purpose of

this study we evaluated the changes in the following elements: Ca, K, Mg, Pb, Ti, Zn and Zr. Changes in metals were investigated in terms of catchment-derived erosion and pollution (Boyle 2001). The analysis of fossil pigments was conducted using high-performance liquid chromatography (HPLC). Analytical measurement followed the methodology by Airs et al. (2001) and for L. Nömmejärv, by Leavitt & Hodgson (2001). Pigment identification and quantification of concentrations were done using pigment standards from the International Agency for ¹⁴C Determination, DHI, Denmark. Fossil pigments were used as biomarkers of lake productivity and algal blooms. Because of the differential preservation of pigments, only comparatively stable carotenoids were used in this study. Cladocera (zooplankton) remains were analysed using a light microscope following the methodology described by Szeroczyńska & Sarmaja-Korjonen (2007). Species identification followed standard reference collections and descriptive manuals. Cladocera assemblages were used to infer information about lake trophic status and deterioration.

Statistical analyses

Diagrams were plotted using Tilia (version 1.7.16) (Grimm 1990). The Constrained Incremental Sums of Squares (CONISS) stratigraphical cluster analysis was conducted in Tilia in order to determine the periods of different environmental conditions. For this purpose all palaeolimnological data including LOI, geochemistry, pigments and Cladocera were used, making a total of 40 variables in Lake Nömmejärv, 77 in Lake Lohja and 84 in Lake Verevi.

RESULTS AND DISCUSSION

In this study, we have evaluated the ecological changes in three lakes which were exposed to anthropogenic pressures for over a century. We shall first discuss the chronostratigraphy and individual case studies, then summarize the main changes in the trajectories of anthropogenic disturbance from the 19th to 21st centuries and finally consider the crucial anthropogenic transformations that have contributed to the changes in the ecological status in these lakes.

Chronostratigraphy of sediments from the studied lakes

In all three cases, ²¹⁰Pb showed a nearly monotonic decrease down the core, with few subtle variations (Fig. 2). The ²¹⁰Pb/²²⁶Ra equilibrium corresponding to about 130–150 years of accumulation was reached at the

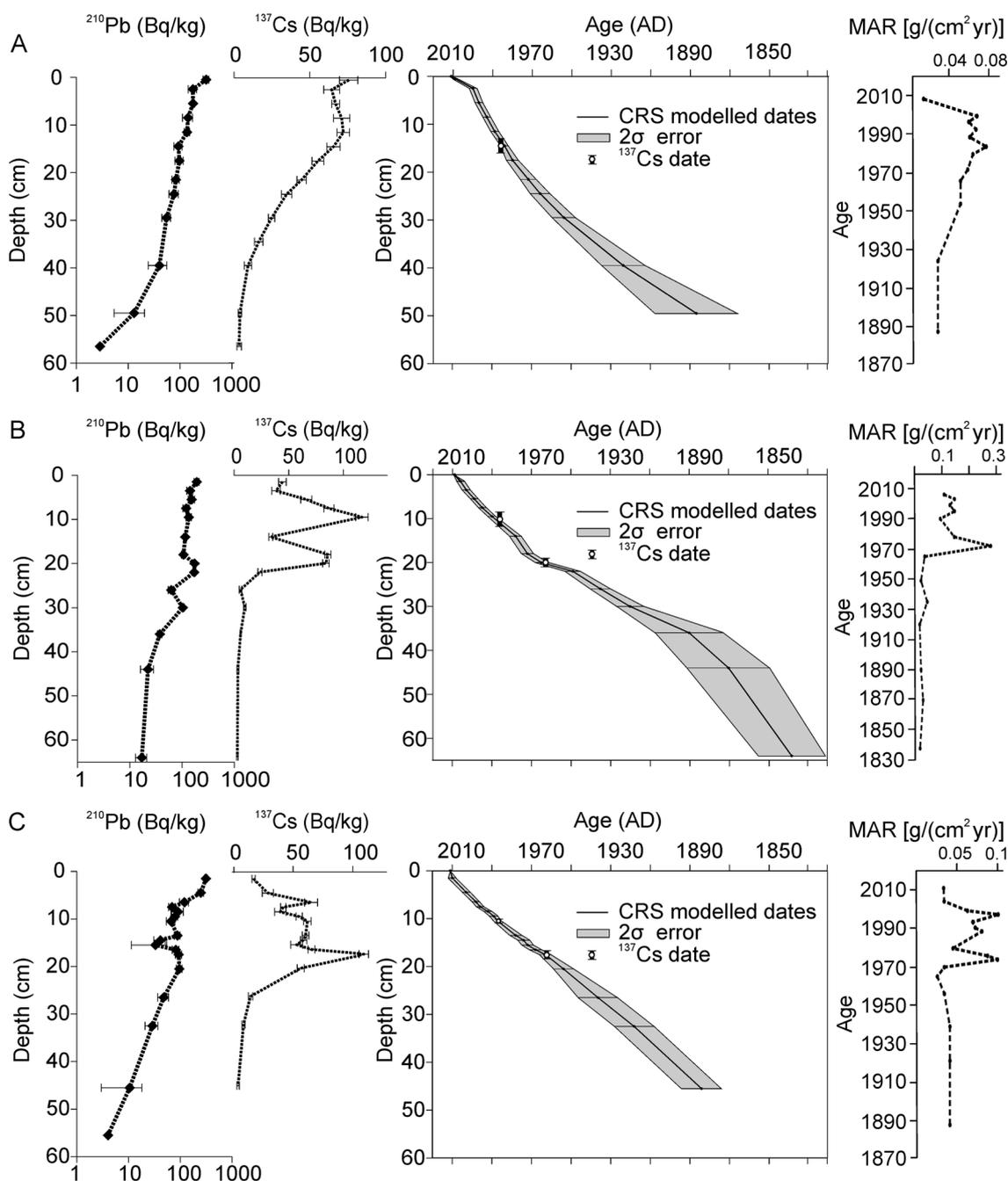


Fig. 2. Activity profiles of ^{210}Pb and ^{137}Cs versus depth in sediments from the studied lakes (A, Lake Lohja; B, Lake Nõmmejärv; C, Lake Verevi). Age–depth diagram with modelled ^{210}Pb dates. Black squares represent ^{210}Pb dates from the revised CRS model fitted to the ^{137}Cs peak (white circle). MAR – mass accumulation rate in the studied lakes.

following depths: 50 cm in Lake Lohja, 36 cm in Lake Nõmmejärv and 45 cm in Lake Verevi. In Lake Lohja, the ^{137}Cs profile showed only one peak from 1986 which was integrated with the ^{210}Pb profile. In case of deeper lakes, Nõmmejärv and Verevi, the ^{137}Cs dates (AD 1963 and AD 1986) corroborated with the

CRS-modelled ^{210}Pb dates. The CRS-modelled mass accumulation rates (MARs), presented in Fig. 2, show that an increase in Lake Lohja started ca 1930 and increased three-fold during the 20th century. The highest MARs of sediments were observed in Lake Nõmmejärv during the 1970s. This event was connected with

the onset of the mine water discharge that brought large amounts of minerogenic particles to the lake ecosystem and influenced also the sedimentation processes (Marzecová et al. 2011). In Lake Verevi, the MAR increase was most pronounced in 1970 during the reconstruction of the lake shores with new sand deposits (Mikomägi et al. 2016).

Sedimentary data from Lake Lohja

Based on the results of the cluster analysis of all palaeolimnological data the sediment core was divided into two zones with the main shift occurring in the 1930s (Fig. 3). The LOI 550 curve is very stable and shows no abrupt changes. The values of LOI 950 were very low (not shown in Fig. 3), indicating lack of carbonates (Boyle 2004). The metal concentrations were low and stable until ca 1900. At the beginning of the 20th century, all metal profiles began to increase gradually. A three-fold increase in sediment accumulation rates (Fig. 2), which occurred between ca 1930s and 2000, was paralleled in the synchronous increase in Ti followed by similar changes in all metals (zone L1; Fig. 3). The conservative Ti is typically associated with minerogenic matter, thus the changes in the Ti profile indicate increasing erosion from the catchment. Overall, the metal profiles showed similar trends between lithogenic elements such as Ti, K/Ti ratio and trace

metals (such as Pb), suggesting the catchment to be the main material source of metals. The concentrations of Ca remained low throughout the core and showed a similar trend as the other lithogenic components. Cladocera assemblages indicate loss of macrophyte-related species (e.g. *Disparalona rostrata*, *Sida crystallina* and *Leydigia leydigi*) (not shown in Fig. 3) and high relative abundances of species indicative of eutrophication *Bosmina (Eubosmina) coregoni* and *Chydorus sphaericus*. The interval in fossil pigment record is characterized by a peak in β -carotene (total productivity) in the 1970s and gradual increase in cantaxanthin (cyanobacterial pigments) from the 1930s. However, the main shifts in all datasets occur already before the algal bloom period in the 1970s.

Lake Lohja – Was the poisoning of the lake the cause of the worsening of the ecological status of the lake?

Although monitoring reports tend to focus mainly on the effects of lake poisoning (Mäemets 1968, 1977), the cartographic analysis of the archival maps indicate multiple land-use changes in the catchment since the beginning of the 20th century, specifically the intensification of the drainage system (1930s and 1980s), deforestation (in the 1940s), the opening of the quarry with an inflow to Lake Lohja (mid-20th century–1990)

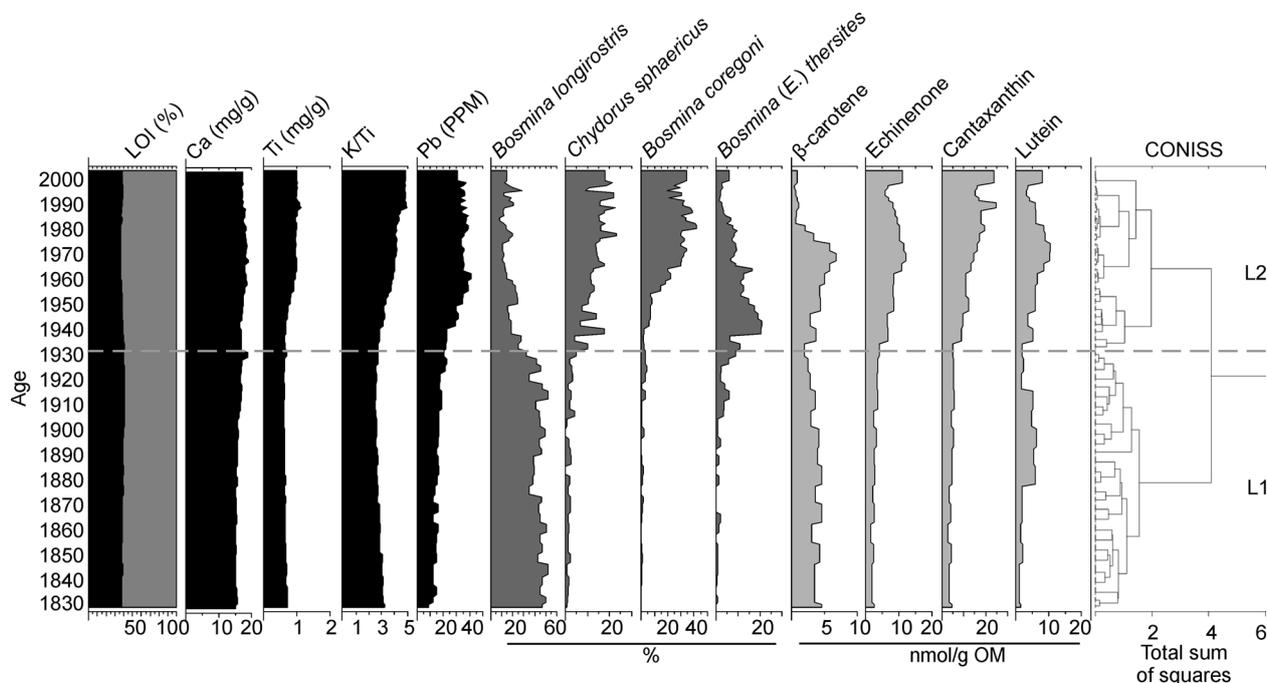


Fig. 3. Selected variables from the sediment of Lake Lohja in age scale and results of CONISS analysis of all data (77 variables). Loss on ignition (LOI 550) data are marked as follows: black – organic matter; grey – mineral matter.

(Marzecová et al. 2016). Depth profiles of the pigment and Cladocera indicators show ecological deterioration already in the late 1930s, suggesting a steep transition to the eutrophic and algal-dominated state (Fig. 3). At the same time, the increase in conservative metals such as Ti indicates an increase in soil erosion (Hobbs et al. 2014). Overall, the sedimentary profiles show consistent changes before the poisoning event and connect the increase in algal production with the erosional changes. This is in agreement with many other studies from anthropogenically-transformed watersheds which linked the extensive changes in the surroundings (drainage ditching, deforestation, change in land-use) that have influenced the lake properties (Hobbs et al. 2014). In total, the combination of the available evidence suggests that although poor lake management might have worsened the ecological status of the lake, the temporal dynamics of eutrophication and algal blooms have been primarily driven by the land-use activities in the catchment, which have been a constant source of nutrients and turbidity from eroded particles.

Sedimentary data from Lake Nömmejärv

The sediment composition of Lake Nömmejärv shows three distinct zones (Fig. 4). The lowermost part of the core (zone N1, Fig. 4), which consists of sediments

accumulated before the 1910s, is organic-rich gyttja. The first change in the element chemistry (a subtle increase in Ti and Zr) occurred already in zone N1 at around 1870. The increase in Ti, Zr and Zn becomes clearly visible at around 1910 and their concentrations continue to increase upwards (zone N2). At the same time, a gradual increase in the K/Ti ratio upwards in the core suggests the coarsening of minerogenic matter (Boyle 2001). The greatest changes in element chemistry occur between the late 1950s and early 1970s (shift between zones N2 and N3), showing a most pronounced peak in lithogenic metals, Ti and Zr. In 1970, the period of minerogenic sedimentation is followed by a significant increase in CaCO₃, as well as high concentrations of Ca. In addition, the uppermost sediments (zone N3) are characterized by the high Ca/Mg ratio, which can be expected in authigenic carbonates (Marzecová et al. 2011). In the same interval, the Pb profile shows a significant decrease, most likely due to the diluting effect caused by large accumulations of carbonates.

Prior to the artificial channel (zones N1 and N2; Fig. 4), the low values of β -carotene reflect low total productivity, although stable values of cyanobacterial pigments (echinenone, myxoxanthophyll) indicate the presence of some cyanobacterial groups in Lake Nömmejärv. The monitored increase in cyanobacteria during the 1960s is reflected in the increasing abundance

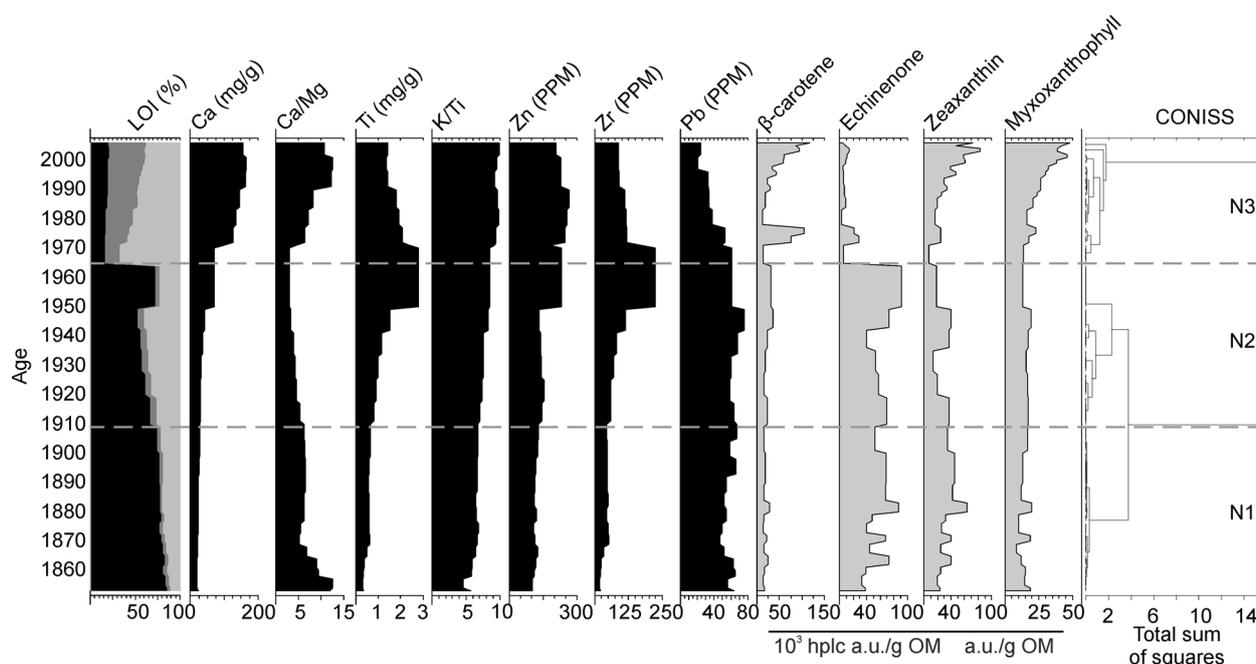


Fig. 4. Selected variables from the sediment of Lake Nömmejärv in age scale and results of CONISS analysis of all data (40 variables). Loss on ignition (LOI 550 and 950) data are marked as follows: black – organic matter; dark grey – CaCO₃; light grey – siliciclastic mineral matter.

of echinenone. From the 1990s, the gradual increase in zeaxanthin, myxoxanthophyll and β -carotene indicates the rise in lake productivity.

Lake Nõmmejärv – Would the closing of the inflow from the mining area restore the previous status of the lake?

Sediment data indicate that the water inflow has had multiple influences on the lake ecosystem. An abrupt increase in mass accumulation rates (Fig. 2), increased the sedimentation of carbonates. Major shifts in sediment chemistry and pigments (Fig. 4) point to alterations in the sedimentation regime as well as in the ecological status. In terms of biological changes, the peak in pigment concentrations during the 1980s and subsequent rise in β -carotene and myxoxanthophyll suggest temporary peaks in total productivity. The comparatively low abundance of echinenone suggests that the fossil pigment record may be influenced by shifts in vegetation. As the distribution of macrophytes largely depends on the substrate conditions (Jones et al. 2012), the changes in lake ecology may be primarily driven by the more minerogenic sedimentation. Thus, the combination of evidence suggests that in spite of the hazardous levels of minerals and sulphates, which represent a potential risk for the ecosystem, the current negative impact of the artificial channel is limited to suspended solids and silting dynamics. The inflow may also have had a positive effect on the lake ecosystem, or rather balancing the negative part. In Lake Nõmmejärv, carbonate increase is reflected in the increase in Ca values and the Ca/Mg ratio remains low, suggesting an in-lake precipitation linked to biological productivity (Marzecová et al. 2011). Carbonate sedimentation may be considered as beneficial because lake marl acts as a phosphorus sink (Otsuki & Wetzel 1972), in case of eutrophication processes. The shortening of the water retention time (circulation up to 40 times per year) by increased flow-through rate prevents the formation of anoxic conditions in the lake bottom. At the moment, after the closedown of Viru mine (summer 2013), the water circulation is much slower (approximately 17 times a year) (Terasmaa et al. 2014), making the conditions more likely become anoxic. If the artificial inflow ceases completely, critical limits for water circulation can be reached, resulting in the release of phosphorus from the sediments. The water pH has also started to decline during recent years, which can be linked to the smaller proportion of alkaline mine water in the whole water budget (Terasmaa et al. 2014). Therefore, the plan to decrease the inflow of mining water in order to make the water regime more natural, may lead to the opposite situation, i.e., deterioration of

the ecosystem given that the lake has already shifted to another stable state with artificial inflow.

Sedimentary data from Lake Verevi

In the 20th century, Lake Verevi underwent significant changes in the sedimentation regime, which in the 1960s shifted from organic-rich sediment to carbonate-rich sediments. The CONISS analysis revealed three zones of change. The transition between zones V1 and V2 is marked by a stepwise increase in Ti concentrations, typical for an increase in catchment erosion (Fig. 5). Zone V2 is characterized by an increase in Pb values, which starts ca 1930 and has a peak in the 1950s–1960s. After the 1960s, there is an increase in the K/Ti ratio, which can be associated with the coarsening of the sediment (Boyle 2001). The most pronounced change in element chemistry is a steep increase in Ca concentrations that corresponds to the increase in carbonates. The fluctuations in the Ca/Mg ratio suggest multiple sources of carbonates. The presence of Mg in the 1960s–1980s (low Ca/Mg ratio) suggests that some of the carbonate material had been delivered from the catchment. From the 1990s, the Ca/Mg ratio increases, suggesting the predominance of authigenic calcite.

The profiles of the pigment and Cladocera indicators show the onset of increase already before the 1900s. The shift towards the Cladocera species indicative of eutrophication, such as *Bosmina longirostris*, *Chydorus sphaericus* and *Bosmina (E.) kessleri*, occurs already in the 1860s, slightly earlier than eutrophication indicated by fossil pigment data. The second change in the Cladocera assemblages is in zone V3, where decrease in *C. sphaericus* and the disappearance of macrophyte-related Cladocera (not shown in Fig. 5), started after the onset of remediation in 2000. Fossil pigment data revealed a slight increase in total productivity (β -carotene) and cyanobacteria (zeaxanthin) in the 1890s, confirming the results of Cladocera analysis and the suggestion that the lake experienced a period of eutrophication already in the 19th century. The most dramatic changes occurred in the uppermost zone V3. This period (1980s–2000s), for which also the monitoring data confirmed the hypertrophic status of the lake, showed an increase in the total productivity (β -carotene) and cyanobacteria (zeaxanthin), accompanied by the accumulations of carbonates (concomitant increase in carbonates and Ca). Such a significant correlation between the fossil pigment indicators for algal productivity and the CaCO_3 signal suggests that carbonate accumulations are caused by authigenic precipitation of marl due to intensive photosynthesis.

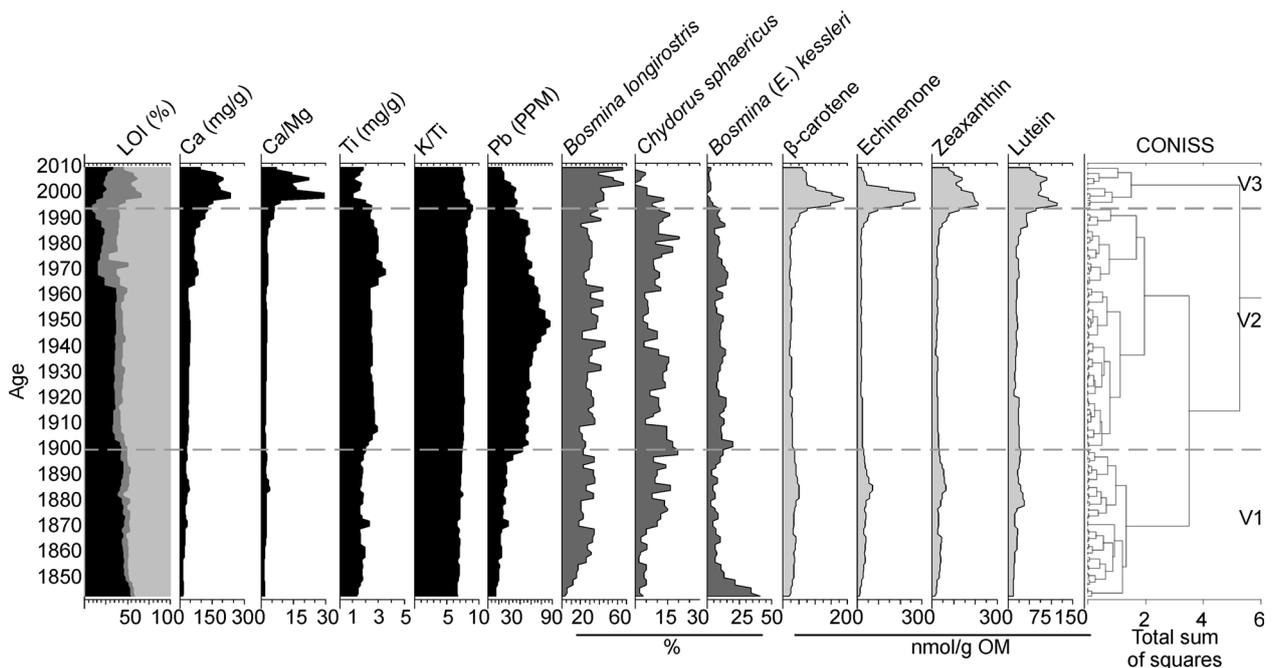


Fig. 5. Selected variables from the sediment of Lake Verevi in age scale and results of CONISS analysis of all data (84 variables). Loss on ignition (LOI 550 and 950) data are marked as follows: black – organic matter; dark grey – CaCO_3 ; light grey – siliciclastic mineral matter.

Lake Verevi – Was the effort to improve the lake status successful?

The limnological survey data considered the ecological status of Lake Verevi as ‘natural’ until the 1950s (Ott et al. 2005), but the sediment indicators had detected a series of changes already a century earlier (Fig. 5). Temporal increase in all measured carotenoids, including indicators of total productivity and cyanobacteria, shows that the lake experienced a period of eutrophication in the first half of the 19th century. A short-lived peak in the minerogenic component suggests that the eutrophication could be connected to an erosional event. Unfortunately, the event precedes the historical records and therefore it is not possible to link the erosion and eutrophication to a certain event. Although the total algal productivity decreased by the 1880s, all carotenoid concentrations remained relatively high during the whole interval from the 1880s until the late 1970s. Alternatively, it is possible that the monitoring data underrepresented the anthropogenic eutrophication. In addition, it should be noted that some differences arise in using different proxies. The shift towards the Cladocera species indicative of eutrophication, *Bosmina longirostris*, *Chydorus sphaericus* (Fig. 5) and *Bosmina (E.) kessleri*, occurs already in the mid-19th century, slightly earlier than indicated by fossil pigment data. A second change in

the Cladocera assemblages is a relative decrease in *C. sphaericus* (Fig. 5) and the disappearance of numerous macrophytes-related Cladocera (not shown in Fig. 5), immediately after the onset of remediation in the 2000s. In this sense, the Cladocera record proved to be the most sensitive in indicating the first water quality changes. In addition to Cladocera, the remediation shows also positive results in pigment records, as the values start to decrease abruptly. But as the period of improved conditions has been relatively short, it would be hasty to give a final evaluation for the possible recovery of the lake ecosystem.

The trajectories of anthropogenic disturbance in small Estonian lakes revealed from sediment studies

Overall, several lines of evidence from sediments confirm long-term changes in the productivity and ecological changes of lakes that correspond to the timing of different sources of anthropogenic pollution (Fig. 6). In all three cases, the pigments and Cladocera data, when available, attest that lakes underwent significant changes in the communities of primary producers, changing from a low-productive system to algae- and cyanobacteria-dominated systems. These findings correspond to the region-wide history of the intensification of land-use,

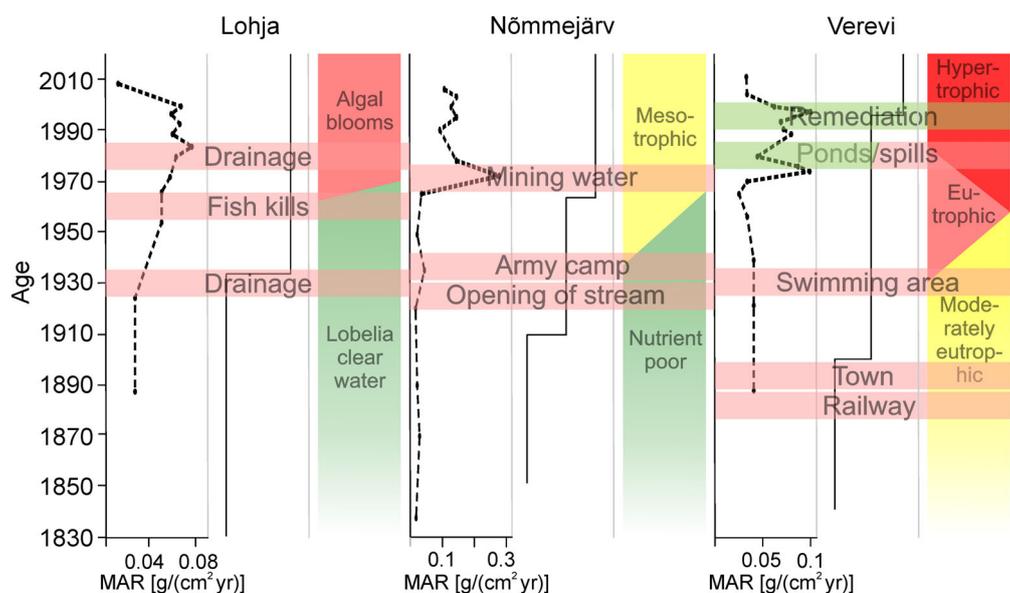


Fig. 6. Summary of our analysis of mass accumulation rates (MAR) of sediments (dashed line). Main zones of CONISS stratigraphical cluster analysis showed periods of different environmental conditions based on the data (solid line). The principal disturbances historically present (pink colour) for different lakes, such as drainage and fish kills for Lake Lohja (Marzecová et al. 2016), building of new streams, presence of army camps and discharge of mining waters for Lake Nõmmejärv (Marzecová et al. 2011) and the establishment of a railway, town and swimming area, as well as spills from ponds for Lake Verevi (Mikomägi et al. 2016). The periods of remediation measures for Lake Verevi are shown in green colour. The description of the ecological status of lakes is based on lake monitoring data (Ott 2006).

which started in the 1930s by the mechanization of the ditching processes and was followed by the intensification of the agriculture during the Soviet collectivization of farms (Lillak 2003). Moreover, in case of the two hard-water lakes (Verevi and Nõmmejärv), the eutrophication has resulted in changes in the accumulation of carbonates (as confirmed by high Ca concentrations as well as high LOI 950 values), a process caused by intense biological production. The precipitation of carbonates can be linked to the higher pH values during the vegetative period caused by increased primary production due to eutrophication. At the same time, increased primary production can also lead to a higher MAR of organic matter. In case of Lake Lohja, the amount of carbonates is low but still MAR increases after intensive human impact. This increase cannot be explained only by higher amounts of autochthonous organic matter as the share of organic matter does not increase (Fig. 3).

In addition, the main commonality in the response of lakes to anthropogenic pressure is an intensification of minerogenic erosion. In all three lakes, the concentrations of measured metals were low and stable until ca 1850–1900. From the beginning of the 20th century until present, the metal profiles exhibited a higher variability and increase in concentrations. These changes are clearly visible in Ti profiles. Titanium is a conservative

lithogenic element associated with mineral matter, therefore the increasing concentrations suggest an erosion from the catchment (Boyle 2001; Boës et al. 2011). In all three instances, the changes in Ti were found to be contemporaneous with the increases in algal abundances, as evidenced by algal specific pigments, suggesting that the eutrophication of lakes can be linked with the catchment disturbance. A town was constructed on the shore of Lake Verevi at around 1900, and the catchment was affected by deforestation (Mikomägi et al. 2016). The historical maps of lakes Nõmmejärv (Marzecová et al. 2011) and Lohja (Marzecová et al. 2016) show that the sedimentary signatures of erosion coincide with the period of the construction of drainage ditches. The connectivity to the catchment and the erosion seem to be one of the important factors contributing to the increased productivity and algal abundance of lakes. It seems that the sedimentation rates of organic as well as minerogenic matter have increased evenly, resulting in more extensive allochthonous input due to the mismanagement of the lake catchment. In all lakes studied the MAR has decreased during last decades, showing possible signs of recovery and relief from anthropogenic stress.

The changes in metals in all three lakes were similar until the first decades of the 20th century, but as the land-use became more diversified, also the element

signature showed differences among lakes. Typically, the intensification of agriculture, deforestation, urbanization and industrialization will cause a significant increase in the concentrations of potentially toxic heavy metals (such as Pb, Zn, Ni or Cu) in sediments (Boyle 2001; Long et al. 2010). This is the only partial case in our study. In spite of significant changes in the catchment land-use (and also history of atmospheric pollution for oil-shale burning and intensified use of lakes for recreation), the traces of heavy metals have not greatly increased in comparison with many other sites influenced by a similar impact (e.g. Long et al. 2010). In Lake Lohja and Lake Nõmmejärv, Pb values remained relatively low throughout the core, whereas the strong positive correlation between Pb and Ti suggests the natural origin of Pb. In Lake Verevi, Pb records show a more pronounced increase between the 1940s and 1960s, hinting at some levels of lead accumulation from anthropogenic activity. However, in this lake, the decrease in Pb values around the 1960s coincides with the dramatic increase in carbonates, hence also in this case the Pb profile needs to be interpreted with caution. Considering the significant changes in the supply of bulk erosional matter, we conclude that the mass changes in sediment composition may have diluted the more subtle variations in trace metals.

CONCLUSIONS

The understanding of the mechanisms of human impact on the functioning of different aquatic ecosystems and the recognition of threshold limits are the ultimate prerequisite for sustainable use of natural waters and environmental management. The response of aquatic ecosystems to a certain source of pollution is usually not driven by one clear process, but rather is a consequence of the whole set of contributing issues – intensive land-use practices, urbanization, etc. As the historical monitoring data can be scarce and often only major sources of pollution are recorded, palaeodata can become handy when detecting the sources and consequences of different anthropogenic impacts.

In spite of the complex history of the anthropogenic drivers, the information derived from sediment indicators broadly agreed with the monitoring and historical evidence of eutrophication, catchment erosion and pollution. Furthermore, the palaeodata identified human-induced changes in lake ecosystems which were not recorded by monitoring and specified the onset of the events. The comparison of multi-proxy analysis of lake sediments with historical and monitoring data clearly confirms the usefulness of integrative analysis for under-

standing the dynamics of anthropogenic deterioration of lake ecosystem.

The sediment data extended the analysis in the past beyond the first monitoring data and helped to identify an earlier onset of cultural eutrophication, which is important for setting up reasonable reference target conditions in restoration schemes. The palaeolimnological approach revealed a significant impact of the erosion from the catchment on the deterioration of lake quality, particularly cyanobacterial blooms. In all three lakes, the signal of catchment erosion was accompanied by ecological changes – shift in algal groups (Lake Nõmmejärv), increase in total productivity (Lake Lohja and Lake Nõmmejärv), strong signal of cyanobacteria (Lake Lohja and Lake Verevi). These alterations affected also the sedimentation processes with a significance for internal biogeochemical cycling of nutrients. For example, the rise in lake productivity in hard-water lakes (Lake Verevi and Lake Nõmmejärv) resulted in the accumulation of carbonates which can be a relevant sink for phosphorus, thus serving for the mitigation of eutrophication processes. To some extent the use of complex palaeolimnological methods showed some signs of possible recovery of ecosystems (Lake Verevi).

The above-mentioned results will contribute to a better understanding of the development of lake ecosystems under increasing anthropogenic stress. They help to formulate effective regulations and measures for the recovering of lake ecosystems and preventing their further deterioration.

Acknowledgements. This study was supported by the Estonian Science Foundation under Grant 8189, Environmental Conservation and Environmental Technology R&D Programme Project ‘EDULOOD’, The Estonian Doctoral School of Earth Sciences and Ecology and Centre of Excellence ‘Studies of natural and man-made environments’ at Tallinn University. We are grateful to Peter Devins for revising the English. We thank the anonymous referees for valuable comments improving the final version of the manuscript.

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*, A917, 167–177.
- Appleby, P. G. 2001. Chronostratigraphic techniques in recent sediments. In *Tracking Environmental Change Using Lake Sediments. Volume 2: Physical and Geochemical Methods* (Last, W. M. & Smol, J. P., eds), pp. 171–203. Kluwer Academic Publishers, Dordrecht.

- Battarbee, R. W. & Bennion, H. 2011. Palaeolimnology and its developing role in assessing the history and extent of human impact on lake ecosystems. *Journal of Paleolimnology*, **45**, 399–404.
- Battarbee, R. W., Morley, D., Bennion, H., Simpson, G. L., Hughes, M. & Bauere, V. 2011. A palaeolimnological meta-database for assessing the ecological status of lakes. *Journal of Paleolimnology*, **45**, 405–414.
- Bennion, H., Davidson, T. A., Sayer, C. D., Simpson, G. L., Rose, N. L. & Sadler, J. P. 2015. Harnessing the potential of the multi-indicator palaeoecological approach: an assessment of the nature and causes of ecological change in a eutrophic shallow lake. *Freshwater Biology*, **60**, 1423–1442.
- Bindler, R., Renberg, I. & Klaminder, J. 2008. Bridging the gap between ancient metal pollution and contemporary biogeochemistry. *Journal of Paleolimnology*, **40**, 755–770.
- Boës, X., Rydberg, J., Martinez-Cortizas, A., Bindler, R. & Renberg, I. 2011. Evaluation of conservative lithogenic elements (Ti, Zr, Al, and Rb) to study anthropogenic element enrichments in lake sediments. *Journal of Paleolimnology*, **46**, 75–87.
- Boyle, J. F. 2000. Rapid elemental analysis of sediment samples by isotope source XRF. *Journal of Paleolimnology*, **23**, 213–221.
- Boyle, J. F. 2001. Inorganic geochemical methods in palaeolimnology. In *Tracking Environmental Change Using Lake Sediments. Volume 2: Physical and Geochemical Methods* (Last, W. M. & Smol, J. P., eds), pp. 83–141. Kluwer Academic Publishers, Dordrecht.
- Boyle, J. F. 2004. A comparison of two methods for estimating the organic matter content of sediments. *Journal of Paleolimnology*, **31**, 125–127.
- Boyle, J. F., Sayer, C. D., Hoare, D., Bennion, H., Heppel, K., Lambert, S. J., Appleby, P. G., Rose, N. L. & Davy, A. J. 2016. Toxic metal enrichment and boating intensity: sediment records of antifoulant copper in shallow lakes of eastern England. *Journal of Paleolimnology*, **55**, 195–208.
- Davidson, T. A. & Jeppesen, E. 2013. The role of palaeolimnology in assessing eutrophication and its impact on lakes. *Journal of Paleolimnology*, **49**, 391–410.
- Folke, C., Carpenter, S., Walker, B., Scheffer, M., Elmqvist, T., Gunderson, L. & Hollong, C. S. 2004. Regime shifts, resilience, and biodiversity in ecosystem management. *Annual Review of Ecology, Evolution, and Systematics*, **35**, 557–581.
- Grimm, E. C. 1990. Tilia and Tilia graph PC spreadsheet and graphics software for pollen data. *INQUA, Working Methods, Newsletter*, **4**, 5–7.
- Heinsalu, A. & Alliksaar, T. 2009. Palaeolimnological assessment of the reference conditions and ecological status of lakes in Estonia – implications for the European Union Water Framework Directive. *Estonian Journal of Earth Sciences*, **58**, 334–341.
- Hobbs, W. O., Theissen, K. M., Hagen, S. M., Bruchu, C. W., Czeck, B. C., Hobbs, J. M. R. & Zimmer, K. D. 2014. Persistence of clear-water, shallow-lake ecosystems: the role of protected areas and stable aquatic food webs. *Journal of Paleolimnology*, **51**, 405–420.
- Holmes, N., Langdon, C. J., Caseldine, C. J., Wastegard, S., Leng, M. J., Croudace, I. W. & Davies, S. M. 2016. Climatic variability during the last millennium in Western Iceland from lake sediment records. *The Holocene*, **26**, 756–771.
- Jones, J. I., Collins, L. A., Naden, P. S. & Sear, D. A. 2012. The relationship between fine sediment and macrophytes in rivers. *River Research and Applications*, **28**, 1006–1018.
- Kangro, K., Laugaste, R., Nõges, P. & Ott, I. 2005. Long-term changes and seasonal development of phytoplankton in a strongly stratified, hypertrophic lake. *Hydrobiologia*, **547**, 91–103.
- Leavitt, P. R. & Hodgson, D. A. 2001. Sedimentary pigments. In *Tracking Environmental Change Using Lake Sediments. Volume 2: Physical and Geochemical Methods* (Last, W. M. & Smol, J. P., eds), pp. 295–325. Kluwer Academic Publishers, Dordrecht.
- Leng, M. J. & Barker, P. A. 2006. A review of the oxygen isotope composition of lacustrine diatom silica for palaeoclimate reconstruction. *Earth-Science Reviews*, **75**, 5–27.
- Lillak, R. 2003. *Eesti põllumajanduse ajalugu [History of Estonian Agriculture]*. Eesti Põllumajandusülikool, Tartu, 240 pp.
- Long, D. T., Parsons, M. J., Yansa, C. H., Yohn, S. S., McLean, C. E. & Vannier, R. G. 2010. Assessing the response of watersheds to catastrophic (logging) and possible secular (global temperature change) perturbations using sediment-chemical chronologies. *Applied Geochemistry*, **25**, 143–158.
- Mäemets, A. 1968. *Eesti järved [Estonian lakes]*. Valgus, Tallinn, 548 pp.
- Mäemets, A. 1977. *Eesti NSV järved ja nende kaitse [Lakes of the Estonian SSR and Their Protection]*. Valgus, Tallinn, 263 pp.
- Marzecová, A., Mikomägi, A., Koff, T. & Martma, T. 2011. Sedimentary geochemical response to human impact on Lake Nõmmejärv, Estonia. *Estonian Journal of Ecology*, **60**, 54–69.
- Marzecová, A., Avi, E., Mikomägi, A. & Koff, T. 2016. Ecological response of a shallow boreal lake to bio-manipulation and catchment land-use: integrating paleolimnological evidence with information from limnological surveys and maps. *Journal of Paleolimnology* [accepted].
- Mikomägi, A., Koff, T., Martma, T. & Marzecová, A. 2016. Biological and geochemical records of human-induced eutrophication in a small hard-water lake. *Boreal Environment Research*, **21**, 513–527.
- Moss, B. 2008. Water pollution by agriculture. *Philosophical Transactions of the Royal Society of London. Series B, Biological Sciences*, **363**, 659–666.
- Ott, I. 2006. *Eesti väikejärvede seire [Survey of Estonia's Small Lakes]*. Estonian Environment Information Centre, Estonia, [http://seire.keskkonnainfo.ee/index.php?option=com_content&view=article&id=1891%3Faccessed 25 January 2016](http://seire.keskkonnainfo.ee/index.php?option=com_content&view=article&id=1891%3Faccessed%2025%20January%202016)].
- Ott, I. 2008. *Eesti väikejärvede seire [Survey of Estonia's Small Lakes]*. Estonian Environment Information Centre, Estonia, http://seire.keskkonnainfo.ee/index.php?option=com_content&view=article&id=2116&Itemid=429 [accessed 2 February 2016].
- Ott, I., Kõiv, T., Nõges, P., Kisand, A., Järvalt, A. & Kirt, E. 2005. General description of partly meromictic hypertrophic

- lake Verevi, its ecological status, changes during the past eight decades, and restoration problems. *Hydrobiologia*, **547**, 1–20.
- Otsuki, A. & Wetzel, R. G. 1972. Coprecipitation of phosphate with carbonates in a marl lake. *Limnology and Oceanography*, **17**, 763–767.
- Sayer, C. D., Burgess, A., Kari, K., Davidson, T. A., Peglar, S., Yang, H. & Rose, N. 2010. Long-term dynamics of submerged macrophytes and algae in a small and shallow, eutrophic lake: implications for the stability of macrophyte-dominance. *Freshwater Biology*, **55**, 565–583.
- Sayer, C. D., Bennion, H., Davidson, T., Burgess, A., Clarke, G., Hoare, D., Frings, P. & Hatton-Ellis, T. 2012. The application of palaeolimnology to evidence-based lake management and conservation: examples from UK lakes. *Aquatic Conservation: Marine and Freshwater Ecosystems*, **22**, 165–180.
- Scheffer, M. & Carpenter, S. R. 2003. Catastrophic regime shifts in ecosystems: linking theory to observation. *Trends in Ecology and Evolution*, **18**, 648–656.
- Szeroczyńska, K. & Sarmaja-Korjonen, K. 2007. *Atlas of Subfossil Cladocera from Central and Northern Europe*. Friends of the Lower Vistula Society, 84 pp.
- Taylor, D., Dalton, D., Leira, M., Jordan, P., Chen, G., León-Vintró, L., Irvine, K., Bennion, H. & Nolan, T. 2006. Recent histories of six productive lakes in the Irish Ecoregion based on multiproxy palaeolimnological evidence. *Hydrobiologia*, **571**, 237–259.
- Terasmaa, J., Mikomägi, A., Vandel, E., Vaasma, T., Vainu, M. & Heinsoo, M. 2014. Hydrotechnogenical influence of the oil shale mines to the water quality of the natural lakes in the Kurtna Lake District, Estonia. In *2nd International Conference – Water Resources and Wetlands, 11–13 September, 2014 Tulcea (Romania), Proceedings* (Gâstescu, P., Marszelewski, W. & Bretcan, P., eds), pp. 181–188, http://www.limnology.ro/water2014/proceedings/24_Terasmaa.pdf [accessed 8 July 2016].
- Thevenon, F. & Poté, J. 2012. Water pollution history of Switzerland recorded by sediments of the large and deep perialpine lakes Lucerne and Geneva. *Water, Air, and Soil Pollution*, **223**, 6157–6169.
- Tropea, A. E., Paterson, A. M., Keller, W. & Smol, J. P. 2010. Sudbury sediments revisited: evaluating limnological recovery in a multiple-stressor environment. *Water, Air, and Soil Pollution*, **210**, 317–333.
- Whitmore, T. J. & Riedinger-Whitmore, M. A. 2014. Topical advances and recent studies in paleolimnological research. *Journal of Limnology*, **73**, 149–160.
- Yang, Y.-H., Zhou, F., Guo, H.-C., Sheng, H., Liu, H., Dao, X. & He, C.-J. 2010. Analysis of spatial and temporal water pollution patterns in Lake Dianchi using multivariate statistical methods. *Environmental Monitoring and Assessment*, **170**, 407–416.

Paleolimnoloogiliste uuringute rakendamise reostuse mõju hindamisel väikejärvede ökosüsteemile

Tiiu Koff, Egert Vandel, Agáta Marzecová, Egle Avi ja Annika Mikomägi

Looduslike veekogude jätkusuutliku kasutuse ja haldamise aluseks on inimõju võimalike mõjude mõistmine antud ökosüsteemidele ning nende toimimisele. Vee ökosüsteemi reaktsioon teatud reostusallikale ei pruugi olla ühene lineaarne protsess, vaid selle kulgu võivad mõjutada varasemad survetegurid (maakasutus, linnastumine jne) ja ökosüsteemi enda puhverduvõime. Kasutades paleolimnoloogilisi meetodeid, tehti kindlaks, mil määral on inimtekkeliste saasteainete sissevool või muud keskkonnastressorid mõjutanud kolme järve ökosüsteeme viimase paarisaja aasta jooksul. Uuringud viidi läbi järvedel, mille kohta olid olemas nii ajaloolised kui ka seireandmed peamiste võimalike mõjurite kohta: 1) kalade mürgitamine ja muutused valgla maakasutuses (Lohja), 2) linnastumine ja linna reovete järve valgumine (Verevi) ja 3) põlevkivi kaevandusvete läbivool (Nõmmejärv). Selgitati, et setete geokeemilise koostise, fossiilsete pigmentide ja vesikirbuliste analüüsi alusel tehtud rekonstruktsioonid langevad suures osas kokku ajalooliste ning seireandmetega eutrofeerumise kulgemisest ja reostusest. Samas saab setteuuringute põhjal teha järeldusi muutuste ajalisest dünaamikast. Leiti, et esmased muutused järvede produktsioonis toimusid juba 19. sajandi keskpaigas ja need on olnud suuresti mõjutatud valgala maakasutuse muutustest. Uuring näitas, et paleolimnoloogial on veekogude eutrofeerumise hindamisel ja edaspidistel keskkonnakorralduslike kavade koostamisel suur potentsiaal.