Sedimentary geochemical response to human impact on Lake Nõmmejärv, Estonia

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Abstract. In order to assess the geochemical and stable isotopic response of recent sediments to the changing anthropogenic influence on Lake Nõmmejärv, bulk geochemistry determined by XRF spectroscopy and carbon and oxygen stable isotopes in carbonates ($\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$) were analysed. A time scale was defined by the ^{210}Pb dating method. The most significant change in sediment composition was a steep transition from organic to mineral rich sediment at the beginning of the 1970s. Our data confirm that this shift was caused by an abrupt influx of allochthonous mineral matter (Si, Al, K, Rb, Ti, Zr) derived from mine waters that started to be drained from an oil shale mine into the lake through an artificial channel. Since then, the minerogenic sedimentation remains high but after the initial peak, the proportion of siliciclastic matter decreases in favour of $CaCO_3$ accumulation. During the last 40 years the carbonate content increased from 7% to 40%. Geochemical evidence supports the assumption that the key mechanism in the formation of carbonates was biologically mediated authigenic $CaCO_3$ precipitation. In addition, decrease in sediment organic matter due to high minerogenic sedimentation forms more favourable conditions for the preservation of the accumulated $CaCO_3$. The shift in the $\delta^{13}C_{carb}$ values during the 1970s and 1980s indicates potential links between $CaCO_3$ precipitation and the increase in lake productivity.

Key words: lake sediments, geochemical composition, X-ray fluorescence spectroscopy, carbonates accumulation, stable isotopes, human influence.

INTRODUCTION

A number of palaeoecological investigations have proved that the geochemical composition of lake sediments serves as a valuable archive of information for the reconstruction of natural as well as human-induced processes that shape the present character of a lake's ecosystem (Engstrom & Wright, 1984; Birks & Birks, 2006; Battarbee et al., 2007). The use of chemical proxies is particularly important for analysis of sediments that accumulated during the last centuries when intensified human activities began to alter natural biogeochemical pathways, causing disturbance of natural systems at an elemental level (Boyle, 2001; Tylmann, 2005; Punning et al., 2007).

Previous investigations show that during the last century the natural ecosystem of Lake Nõmmejärv in NE Estonia became affected by human activities that resulted in significant alterations in its sediment and water composition as well as in its ecological status (Vesiloo, 1987; Sagris, 1989; Varvas, 1994; Punning et al., 1997).

As a result of the implementation of environmental protection measures and the political transition at the beginning of the 1990s, the industrial impact in the area connected with oil shale mining and power plants has become less pronounced. A complex palaeoecological study, which was carried out at the beginning of the 1990s, showed that this factor seems to positively contribute to a decrease of pollution connected with atmospheric fallout as well as to the overall tendency of the lake ecosystem to return to pre-disturbance conditions (Punning et al., 1997).

Based on geochemical and stable isotope proxies, this study aims to describe the changes in the geochemical composition of the sediment as a response to the presumed reduction in the human impact on the lake during the last 20 years. It also attempts to detect what anthropogenic factors continue to control the present state of the lake. To document and understand the ways in which human impact on the ecosystems interacts with natural processes is one of the essential prerequisites for establishing sustainable and efficient land management (Oldfield & Dearing, 2003).

STUDY AREA

Lake Nõmmejärv is located in NE Estonia (58°03′ N and 26°30′ E) in the western part of the Kurtna lake district (Fig. 1). The lake is 15 ha in area and its maximum depth is 7 m (Varvas & Punning, 1993). Its catchment has a forested area in its western and eastern parts, peatland to the north, and arable land in the south (Fig. 1a). Human influence began to intensify at the end of the 19th century when drainage of the surrounding bogs and pastures started. During the 1920s, the natural flow of the Raudi Stream (Fig. 1a) was directed to the lake, changing it from a closed to an open system. Local human impact on the lake continued to increase with the construction of a military camp on the shore at the beginning of the 1930s, which was used then for military and later, including today, for tourist activities (Punning et al., 1997).

At the beginning of the 1950s, oil shale mining began in the vicinity of the Kurtna lake district. Expansion of oil shale mining and related industries such as oil-shale-based power engineering became a strong industrial factor in the region (Erg, 2003). Local kukersite oil shale forms horizontal sequences in the limestone from which it has been extracted in underground mines. To facilitate the discharge of groundwater from mines, several Kurtna lakes have been utilized and interconnected with channels. In 1970 the Raudi Stream was completely transformed into an artificial channel and mine water started to flow through Lake Nõmmejärv. Variation in the discharge has been largely governed by seasonal fluctuations and the volume of mining waters (from 25 000 to 54 000 $m^3 h^{-1}$)
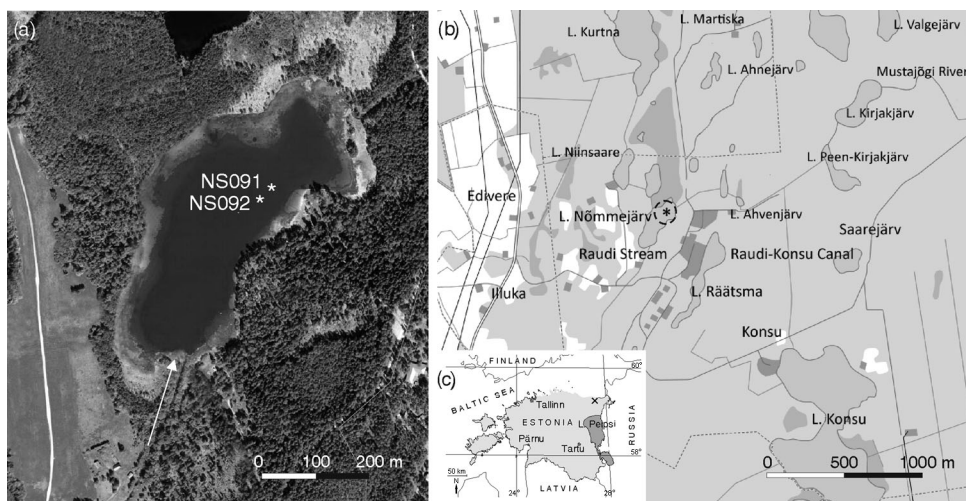
Fig. 1. Location of Lake Nõmmejärv with two coring points NS091 and NS092 (a). The arrow indicates the inflow of the Raudi Stream to the lake located in the Kurtna lake district (b) in the north-eastern part of Estonia (c).

(Sagris, 1989). Water is also carrying mine clastic mineral debris, which consists of carbonate matter, siliciclastic (silica-bearing sedimentary rock) particles, and oil shale remains and is high in sulphate ions and calcium (Bauert & Kattai, 1997; Erg, 2003).

Fly-ash pollution from oil shale combustion peaked between the 1940s and 1980s, resulting in elevated accumulation rates of several trace elements (Varvas & Punning, 1993). In addition to industrial influence, Lake Nõmmejärv has been also extensively used as a recreation and swimming area for the region.

Lake Nõmmejärv has been studied since the 1940s. Then it was described as a nutrient-poor lake (Riikoja, 1940). Since then the monitoring of the lake has shown changes in water chemistry (Table 1) as well as in its ecological characteristics.

Table 1. Lake water chemistry measurements from different studies ([a] Riikoja, 1940; [b] Mäemets, 1968; [c] Mäemets, 1977; [d] Sagris, 1989; [e] Ott, 2006) during the last 80 years

Water chemistry parameter	1937[a]	1954[b]	1974[c]	1987[d]	2006[e]
HCO_3^-, mg L^{-1}	210	235–247	235–263	227	286–342
SO_4^{2-}, mg L^{-1}	5.8	16–21	–	201	325–355
Cl^-, mg L^{-1}	1	3.2–3.5	–	12.4	5.9–7.2
Mg^{2+}, mg L^{-1}	20.3	16.3	–	42.9	–
Fe^{2+}; Fe^{3+}, mg L^{-1}	0.1 (1)	0–1	1	–	–
pH	7.8	7.7–8.2	7.3–8.4	–	7.7–8.1

– No data.

The lake gradually became mesotrophic (Mäemets, 1968; Ott, 2006). Although the most recent monitoring data show that there is no thermal stratification (Ott, 2006), older studies mention oxygen stratification in summer (Mäemets, 1968; Punning et al., 1997).

MATERIALS AND METHODS

In 2009, two 52 cm long cores of unconsolidated sediments (NS091 and NS092) were collected from the central part of the lake (Fig. 1a) using a modified Livingstone–Vallentyne piston corer. The cores were continuously sampled in 2 cm intervals, with the exception of the upper 10 cm of core NS092, which was sampled at 1 cm intervals. Information about the water content was obtained by heating the samples at 105 °C to constant weight. In order to assess total organic matter and carbonate content, loss on ignition (LOI) analysis at 550 °C (LOI550) and 950 °C (LOI950) was performed for both cores according to standard methodologies (Boyle, 2000, 2001; Heiri et al., 2001). Samples from core NS091 were used to determine bulk chemistry by X-ray fluorescence (XRF) spectroscopy. Sediment samples from core NS092 were used to measure carbon and oxygen stable isotopes in carbonates ($\delta^{13}C_{carb}$, $\delta^{18}O_{carb}$) and for ^{210}Pb dating.

Total element concentrations of major and trace elements (Al, Si, Ca, K, Mg, Ti, Zr, Fe, Mn, S, P, Pb, Br, Sr, Cu, Zn, Ni, Cs, Nb) that indicate bulk composition of sediment were measured from loose powder samples by an X-ray fluorescence spectrometer with energy dispersive (EDXRF) detection. Analyses were carried out according to the methodology established by Boyle (2000) in the laboratories of the Department of Geography at Liverpool University. Analytical performance was calibrated with known reference standards. Element concentration is expressed as mg per g of dry weight (mg g^{-1}). The geochemical data set ($n = 26$) was further standardized to zero mean and unit variance and processed in program ZONE 1.2 (Juggins, 2005) for stratigraphically constrained cluster analyses to assess stratigraphic zonation. To detect the associations among chemical elements, principal component analysis (PCA) in CANOCO for Windows 4.5 (ter Braak & Smilauer, 2002) was used.

Stable isotope analysis was performed in the Department of Isotope-Palaeoclimatology of the Institute of Geology at Tallinn University of Technology. The sediment samples were homogenized prior to analysis. Stable isotopes were analysed using a Thermo Fisher Scientific mass spectrometer Delta V Advantage and GasBench II. Isotope results are reported, using the usual δ-notation, as per mil (‰) on the VPDB (Vienna Pee Dee Belemnite) scale. The reproducibility of results is ±0.1‰. Stable isotope values were also measured from two samples of lake water. The samples were collected with a bathometer from top and bottom

water layers. Results of water analyses are reported at the VSMOW (Vienna Standard Mean Ocean Water) scale.

The age–depth scale was determined by ^{210}Pb dating analysis of 14 samples from core NS092. The analysis was performed by the Centre for Monitoring Study and Environment Technologies, Kiev, Ukraine.

RESULTS

Lithology

The lower sections of sediment cores NS091 and NS092 consist of black gyttja, which changes to light-grey gyttja in the uppermost part of both cores. The results of LOI analysis show that the lower part is highly organic with LOI550 values reaching up to 85% (Fig. 2a). In both cores the organic matter content sharply decreases to about 20% at a depth of 15 cm in NS091 and at 19 cm in NS092 in favour of mineral matter. From these depths the carbonate content, calculated from LOI950 values, steeply rises from ca 7% and reaches 40% in the uppermost sediment (Fig. 2a). The LOI profiles of the cores are similar, with a 3–4 cm vertical shift between profiles, which seems to be caused by the uneven microtopography of the lake bottom. The cores were correlated on the basis of the water content profiles (Fig. 2b).
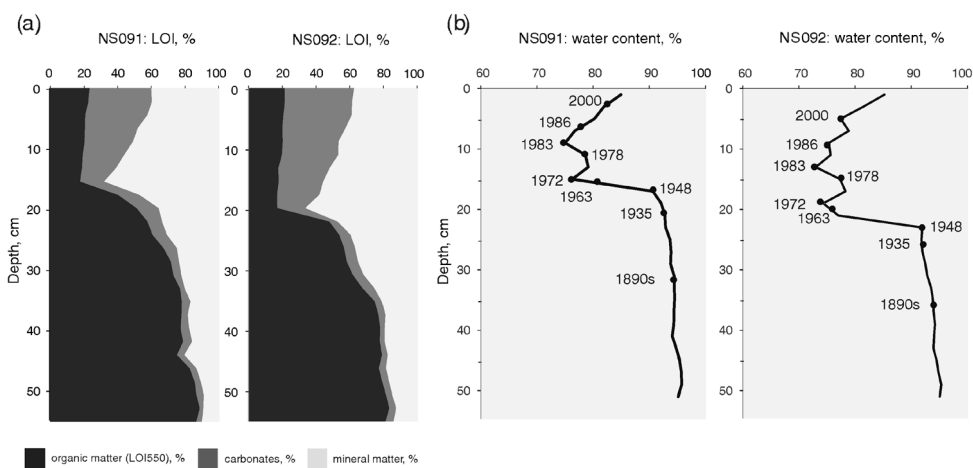

Fig. 2. Lithology of cores NS091 and NS092: vertical distribution of organic matter (LOI550), carbonates, and mineral matter in sediment cores estimated by loss on ignition. Values are expressed as a percentage per dry weight (a). Correlation of water content profiles between cores NS091 and NS092 was used to infer age–depth chronology for core NS091 (b). Chronological data were obtained from ^{210}Pb dating of core NS092 (Fig. 3).

Chronology

Calculation of radiometric dates and assessment of sedimentation rate was based on ^{210}Pb dating of sediment core NS092 using a CRS (Constant Rate of Supply) dating model (Appleby & Oldfield, 1978). Unsupported ^{210}Pb activity was calculated from total ^{210}Pb activity by subtracting the background activity measured in the sediment sequence below 36 cm where constant ^{210}Pb activity was reached. The depth 36 cm was considered as the limit for reliable age assessment. The sediment at this depth was calculated to be 120 years old (Fig. 3). Artificial radionuclides, ^{137}Cs and [241]Am, were also detected. The activity of ^{137}Cs measured over the profile showed two peaks, a broad peak in the interval 18 to 20 cm and a clear peak at a depth of 9.5 cm. A distinctive [241]Am peak was detected at 20 cm. The peak in the ^{137}Cs/[241]Am ratio at a depth of 20 cm can be associated to the atmospheric fallout after nuclear weapon tests in 1963, but the ^{137}Cs peak at 9.5 cm most likely represents the ^{137}Cs fallout caused by the Chernobyl accident in 1986.

   The CRS dating model was preferred because the ^{210}Pb data calculated with this model more closely correspond with chronostratigraphic records of ^{137}Cs and [241]Am (Fig. 3) than those calculated with the CIC (Constant Initial Concentration) model.
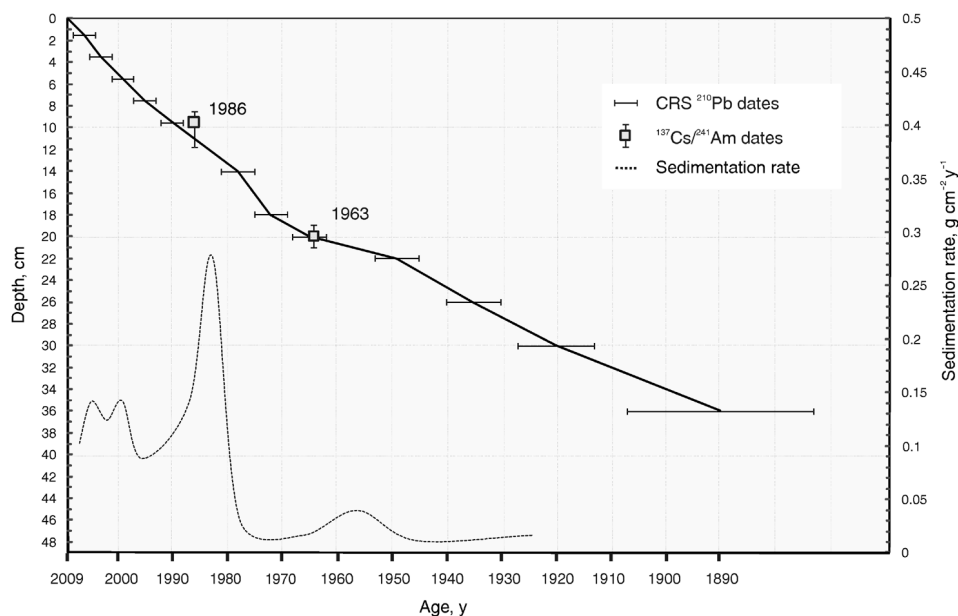

Fig. 3. Age–depth plot of sediment core NS092 based on ^{210}Pb analysis. [210]Pb chronology and sedimentation rates were estimated with the CRS model. The age scale was verified with ^{137}Cs and [241]Am chronostratigraphic dates.

Sediment accumulation rates gradually increased from $0.013 \text{ g cm}^{-2} \text{ y}^{-1}$ to $0.102 \text{ g cm}^{-2} \text{ y}^{-1}$ in the uppermost part of the core with a strong disruptive interval around 20 cm depth where sediment accumulation rates were estimated to reach $0.277 \text{ g cm}^{-2} \text{ y}^{-1}$ (Fig. 3). Due to the disruptive character of this event caused by an abrupt mineral sediment influx the measurement error is high and therefore this estimation should be considered with caution. This issue was already noted previously (Punning et al., 1997).

Geochemistry

Stratigraphically constrained cluster analysis (CONISS) of the geochemical dataset measured from core NS091 showed three main zones with contrasting patterns of elemental composition (Fig. 4). An exception is a group of closely correlated lithophile elements, most specifically Al, Si, Ti, K, Rb, and Zr (less closely correlated Mg, Zn, Cu). Their profiles change congruently in all zones, and they represent the mineral fraction that consists of siliciclastic particles derived from catchment mineral sources (Boyle, 2001).

The chemical composition of sediment below 25 cm (zone Z3) is strongly influenced by a high proportion of organic matter (80%) (Fig. 2a). In this zone the concentrations of measured elements are low (Fig. 4). At a depth of 35 cm (end of the 19th century), a gradual, uniform increase in element profiles becomes apparent.

In the interval from 25 cm to 9 cm, which corresponds with the period from the early 1930s to the late 1980s (zone Z2), the concentrations of elements continue to rise, but differences among individual profiles begin to show. Some elements (Fe, Mn, S, and P) increase already in the 1930s but changes in their profiles are not synchronous. Elements of the siliciclastic mineral fraction (Al, Si, K, Ti, Rb, Zr) form a steep peak and reach the highest values at a depth of 15 cm (early 1970s). Concentrations of elements from both these groups remain elevated up to 9 cm depth (late 1980s).

In the lower part of the sediment core, Ca and Sr closely follow the trend of siliciclastic elements. From a depth of 15 cm onwards, the correlation between Ca or Sr and the siliciclastic elements becomes negative and Ca and Sr values continuously rise.

In the uppermost 9 cm interval, which corresponds with the time period since the late 1980s (zone Z1), the majority of elements show decreasing concentrations and declining fluctuations compared with the underlying zone (Z2). An exception is Ca and Sr values, which remain high and their profiles follow the trend of the carbonate content curve.

Having similar chemical properties, Sr readily substitutes for Ca in the structure of carbonate minerals. The substitution of Sr for Ca is well described in carbonate rocks but their co-precipitation has been observed also in lake marl (Treese et al., 1981). In the whole core, Ca and Sr are highly correlated ($r = 0.98$, $p = 0.0001$) and they likely represent the sediment carbonate matter.
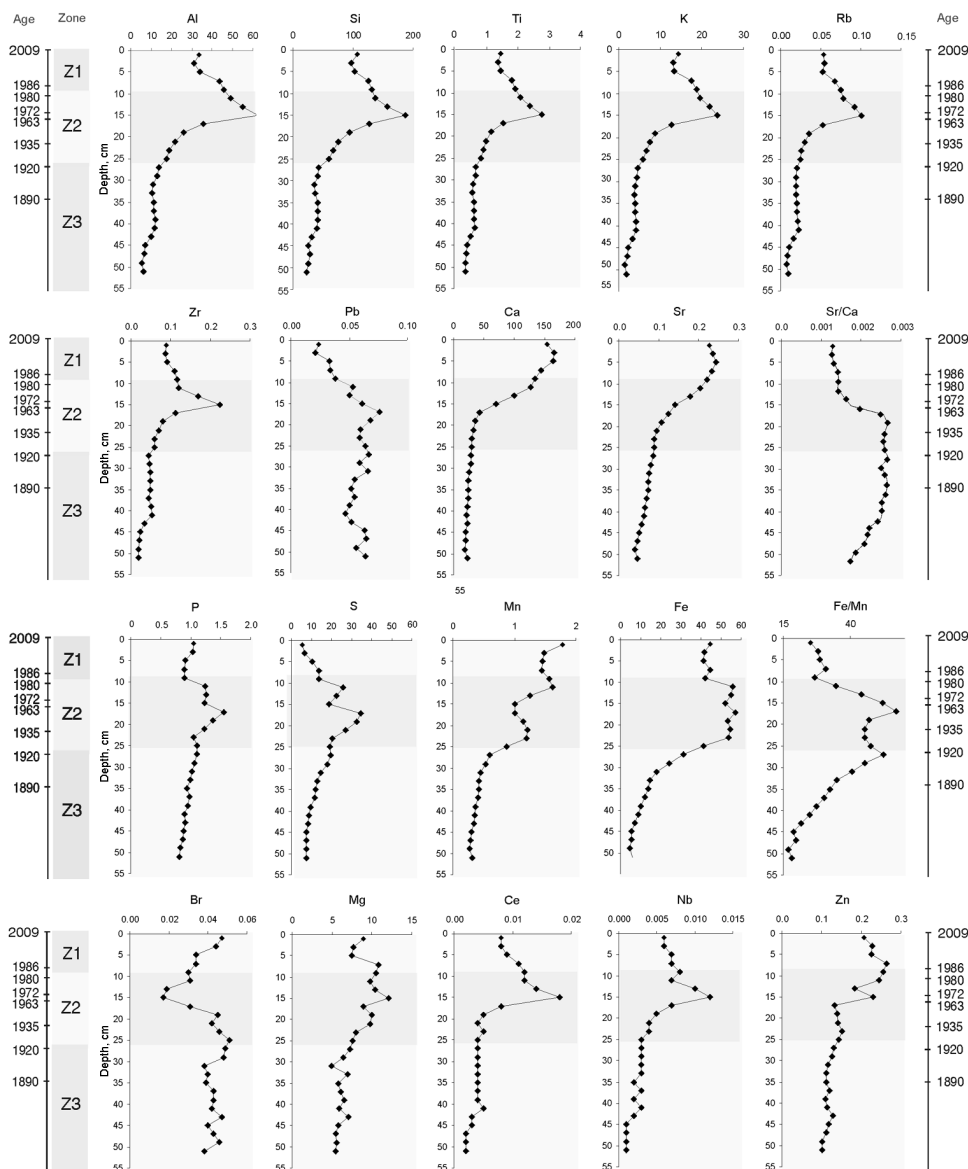
Fig. 4. Selected element concentrations measured by XRF spectroscopy in sediment core NS091 plotted against depth. Concentrations are presented in mg g^{-1}. The age scale is inferred from the ^{210}Pb dating of core NS092 (Fig. 2). Vertical profiles can be divided into three zones of different chemical composition (Z1, Z2, Z3).

To further examine the major trends in the sediment composition, principal component analysis (PCA) of geochemical data was carried out (Fig. 5). The first two PCA axes together account for 87.7% of the total variance within the data set (F1 76%, F2 11.7%). Positive factor loadings on axis F1 represent a group of
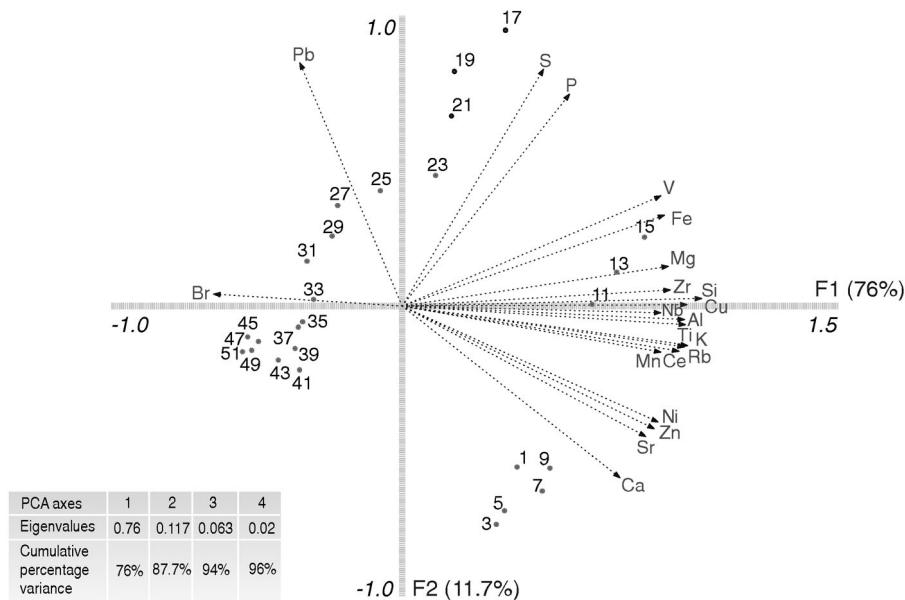
Fig. 5. Biplot of F1 axis vs. F2 axis based on the principal component analysis of element concentrations measured by XRF spectroscopy of samples ($n = 26$) from core NS092. Arrows represent explanatory variables and points represent sample scores. Component loadings of variables are given in F1 and F2 eigenvalues. Eigenvalues and cumulative percentage variance of the variables for the first four PCA axes are presented in the table next to the biplot.

elements and trace metals typical for the siliciclastic fraction. The negative side of PCA axis F1 is marked by a high loading of Br together with a cluster of scores for organic rich samples from the lowermost part (zone Z3). As Br is known to have a strong affinity to humic substances (Punning, 1994, Alvisi & Dinelli, 2002), the positioning of the Br axis in the sector with organic rich samples supports Br being a suitable tracer of organic matter. The second PCA axis (F2) has a high positive loading of Pb in the second sector of the biplot followed by high negative loadings of Ca, Sr, and sample scores from the uppermost carbonate rich zone (Z1). The PCA biplot shows that sample scores from zone Z1 are loosely clustered whereas the sample scores of zone Z2 form a successive line.

Stable isotopes

In the sediment sequence below 19 cm, the carbonate content was less than 7% (Fig. 6). Because carbonate concentrations were close to the measurement limit, in this interval it was possible to analyse stable carbon and oxygen isotopes only
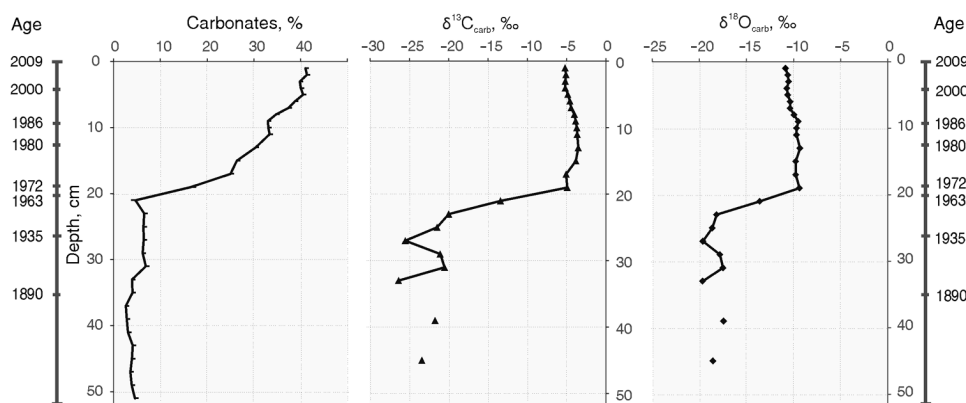
Fig. 6. Vertical profiles of carbonate content (percentage per dry weight) and stable isotope ($\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$) profiles measured from bulk carbonates in core NS092 plotted against depth. Isotope values are expressed in per mil (VPDB). The presented time scale is based on ^{210}Pb dating.

from six samples. The obtained $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values were unusually low, for both isotopes approximately −20‰. It is probable that isotope ratios were influenced by sediment diagenetic processes. These values were not interpreted further. In the upper 19 cm sequence (from the 1970s until present), the carbonate content in sediment increased up to 40%. In this interval, the $\delta^{18}O_{carb}$ values range from −10.8‰ to −9.4‰. The range of $\delta^{13}C_{carb}$ values is broader, from −5.2‰ to −3.5‰.

Stable carbon isotopes from dissolved inorganic carbon ($\delta^{13}C_{DIC}$) in lake water, measured during summer, were −7.7‰ in the top water layer (0.5 m) and −8.0‰ in the bottom layer (4.7 m). The $\delta^{18}O_{water}$ values in the same water layers were −11.6‰ and −11.8‰.

Sediment stable isotope values are in equilibrium with the $\delta^{13}C_{DIC}$ and $\delta^{18}O_{water}$ measured from the lake water. The narrow range in $\delta^{18}O_{carb}$ values and low covariance between stable isotopes probably reflect an open lake system (Gierlowski-Kordesch, 2010) where $\delta^{18}O$ values of lake water are controlled by the $\delta^{18}O$ of the mining water inflow.

DISCUSSION

The gradual and synchronous increase of elements typical for mineral matter, which began at the end of the 19th century, indicates a higher influx of eroded material from the catchment. The continuous increase in the sedimentation rate (Fig. 3) and concentrations of siliciclastic elements (Fig. 4) during the 1920s, after the Raudi Stream was directed into the lake, confirms that the chemistry of

lake sediment was predominantly influenced by erosional changes in the catchment governed by melioration activities.

During the early 1930s, an additional increase in the concentrations but a decline in the synchronicity of changes among element profiles indicate that along with the catchment impact other independent factors started to influence the sediment chemistry of Lake Nõmmejärv. A number of changes, such as an increase in the Fe/Mn ratio, variations in the Mn profile (Fig. 4), and weakening of the correlation between Fe and mineral matter, signal the rising importance of in-lake mechanisms. As under reducing conditions Mn tends to become mobile more readily than Fe, an increase in the Fe/Mn ratio has been often connected with prolonged periods of stratification or oxygen deficiency in the hypolimnion, conditions that are usually connected with increasing biological productivity in a lake (Engstrom & Wright, 1984; Punning et al., 1997). Taking into account that during the 1930s a military camp was built in the area, activities connected with its utilization (i.e. sewage, wastes) may have become a source of nutrients, which led to a biologically rich lake with sediment sensitive to hypolimnetic oxygen.

At the beginning of the 1970s, the sedimentation pattern became considerably altered by the steep peak in the accumulation rate caused by the dramatic increase in siliciclastic content. The occurrence of trace metals and rare earth elements (Zn, Cu, Nb, Ce) that are commonly associated with oil shale (Varvas, 1994) confirms that these changes were caused by sedimentation of detrital mineral matter derived from mine water that was directed to the lake during that time.

Since the early 1990s, when the industrial impact started to decline, the variations in the element profiles decreased and the majority of elements attained more stable values. In the PCA biplot (Fig. 5) the clustered position of the sample scores that represent the uppermost zone Z1 indicates a tendency towards a stabilized chemical composition. These findings are in accordance with the prognosis from earlier sediment studies (Punning et al., 1997). However, it is important to stress that the composition of the uppermost sediment significantly differs from the stable period prior to anthropogenic forcing. It contains considerably less organic matter (20%) and it is high in siliciclastic (Al, Si, K, Ti, Rb, Zr) and carbonate (Ca, Sr) fractions.

According to PCA analysis (Fig. 5), the organization of variables along axis F1 is clearly defined by an abrupt shift from organic rich (Br) to minerogenic (Al, Si, K, Rb, Zr, Ti) sediment. On the basis of this evidence it can be concluded that the chemical composition of the studied sediment has been most strongly affected by human-induced sedimentation of mineral debris from mine water directed through the lake since the early 1970s.

The second PCA axis (F2; Fig. 5) emphasizes the opposite orientation of Pb and Ca and Sr. The correlation of Ca and Pb calculated in the whole sediment core is not statistically significant; however, from the 1970s the correlation became highly negative ($r = -0.95$, $p < 0.001$). A similar connection was observed in

Rõuge Liinjärv, a mesoeutrophic lake with an inflow of hard water and high carbonate accumulation in which Pb depletion in upper sediments was explained by the dilution due to higher carbonate accumulation (Lepane et al., 2007). For this reason we assume that another governing mechanism that influences the chemical composition of the sediment has been an accumulation of carbonates, which became apparent at the beginning of the 1970s and reached the maximum values in the uppermost zone.

Lacustrine carbonates may originate from multiple sources and their precipitation is controlled by multiple mechanisms, including sediment input, temperature, hydrology, and biological mediation (Gierlowski-Kordesch, 2010). In addition, also conditions of the sedimentation environment may limit the amounts of $CaCO_3$ that remain preserved in the sediment. In case of organic rich sediment, the decomposition of the accumulated organic matter in the hypolimnion tends to decrease the pH, thus influencing dissolution of $CaCO_3$, which settles from the epilimnion (Schlesinger, 1991; Dean, 1999). For these reasons it is often difficult to determine the main control mechanisms of changes in carbonate content. The stable isotope signature of carbonates reflects primary factors of $CaCO_3$ formation and may provide important evidence for the reconstruction of carbonate changes (Leng & Marshall, 2004; Gierlowski-Kordesch, 2010).

Taking into account that oil shale has been extracted from limestone bedrock it can be hypothesized that the increase of the carbonate content in lake sediment was caused by sedimentation of carbonate clastic debris from mine water. However, $\delta^{13}C_{carb}$ values of Ordovician limestone ($\delta^{13}C_{carb} = -1.6$‰ to 0‰ in the Kukruse Stage) from oil shale mines (Kaljo et al., 2007) clearly differ from the stable carbon isotopic composition of lake sediment ($\delta^{13}C_{carb} = -5.2$‰ to -3.5‰) as well as lake water $\delta^{13}C_{DIC}$ values (-7.7‰ and -8.0‰). These differences suggest that carbonates in lake sediments are not of clastic origin. More likely, the dominant source of carbonates has been authigenic precipitation from lake water.

It has been suggested that partition coefficients for Sr may be highly dependent upon whether carbonate precipitation was inorganic or biomediated. The biochemically induced precipitation tends to produce lower Sr/Ca ratios than inorganic precipitation (Treese et al., 1981). The decrease in the Sr/Ca ratio (Fig. 4), which began in the early 1970s, suggests the possibility of compositional differences between carbonates accumulated prior and after the 1970s being linked to biological precipitation.

Studies dealing with processes of the carbon cycle in lakes have shown that in alkaline, biologically rich lakes the precipitation of $CaCO_3$ is commonly triggered by high phytoplankton productivity, which removes isotopically light CO_2 and leads to ^{13}C enrichment of precipitated carbonates (Schlesinger, 1991; Lu et al., 2010). Stable $\delta^{13}C_{carb}$ values from carbonates accumulated during the 1970s and 1980s show a slight increase (Fig. 6).

The presented evidence suggests that the carbonate increase was a result of authigenic precipitation connected with the productivity increase in the lake. This suggestion is in accordance with the monitoring data according to which the lake classified as mesotrophic from the 1960s. However, taking into account the substantial decrease in the organic matter caused by minerogenic sedimentation, it is possible that the pH of the water–sediment interface has increased, creating more favourable conditions for the preservation of carbonates (Dean, 1999).

In other Estonian lakes, a similar shift to less negative values in the $\delta^{13}C_{carb}$ profile compliant with increased carbonate content and low covariance between carbon and oxygen isotopes was described in a recent study of the eutrophic Lake Verevi (Mikomägi & Martma, 2009). In that lake such changes were apparently linked with eutrophication processes, which were detected from pigment analysis and confirmed by historical information (Ott et al., 2005). An increase in the carbonate content in the uppermost zone of the sediment was observed also in the eutrophic Lake Harku (Heinsalu & Alliksaar, 2005).

CONCLUSIONS

The uppermost sediment zone of Lake Nõmmejärv, which has accumulated since the beginning of the 1990s, has a more stable chemical composition than the underlying zone corresponding to the period of highest industrial and land use impacts. The chemical composition of the recent sediments has been most significantly influenced by two contributing processes – sedimentation of allochthonous siliciclastic mineral particles and accumulation of authigenic carbonates. High sedimentation of mineral matter is human induced and it has been caused by sedimentation of siliciclastic particles derived from mine water that has been directed from oil shale mines into the lake since the beginning of the 1970s. Although the carbonate content also began to increase during the early 1970s, according to the geochemical evidence ($\delta^{13}C_{carb}$ values and Sr/Ca ratio) clastic particle sedimentation is not a primary factor in the formation of $CaCO_3$. It is assumed that $CaCO_3$ is formed by authigenic precipitation mediated by lake photosynthetic processes. It is possible that sediment poorer in organic matter due to high mineral sedimentation also contributes to the development of suitable conditions for the preservation of carbonates.

To better understand possible links between carbonate precipitation and trophic processes in Lake Nõmmejärv and to be able to determine the role of human impact on the changing carbonate content, further studies of biological proxies would be beneficial. The results are important and applicable in the planning and management of land use and mine water inflow into the lake.

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Inimmõju jälg Nõmmejärve sette geokeemilisele koostisele

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Nõmmejärve on tugevalt mõjutanud kaevandusvete juhtimine läbi järve. Artiklis on uuritud Nõmmejärve setete keemilist koostist, mis on settinud viimase saja aasta jooksul. Keemilised elemendid on määratud XRF-spektroskoopiat kasutades. Karbonaatsest settefraktsioonist on mõõdetud stabiilsete isotoopide $\delta^{13}C$ ja $\delta^{18}O$ väärtused. Tulemused näitavad järsku muutust järvesette geokeemilises koostises, mis langeb kokku ajaga, mil järve suunati kaevandusveed ja kasvas inimmõju. Karbonaatide sisalduse suurenemine võib olla seotud eutrofeerumisega.