

Sedimentary record of heavy metals in Lake Rõuge Liinjärv, southern Estonia

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Abstract. Anthropogenic impact on Lake Liinjärv (Rõuge, southern Estonia) was studied back to the mid-19th century on the basis of heavy metals (Pb, Cu, Zn, Mn, and Hg) and geochemical parameters of a short sediment core dated by ²¹⁰Pb isotopes. The development of the lake and its sediment composition are heavily influenced by the inflow of saturated calcareous waters that cause precipitation of calcium carbonates. The concentrations of most of the metals started to increase at the end of the 1970s. This is most clearly observable for Zn, Cu, and Pb. At the same time the distribution pattern of Mn seems to be controlled mainly by the redox conditions in the hypolimnion. The main sources of pollutants in Lake Liinjärv, due to its large catchment area, are the influence of agricultural activity and atmospheric input. Organic matter is the main factor affecting heavy metal (Pb, Hg, Cu, and Zn) distribution in lake sediments.

Key words: heavy metals, ²¹⁰Pb dating, sediments, Lake Rõuge Liinjärv.

INTRODUCTION

Lake sediments are invaluable natural archives providing long-term records of past changes in climate and environment, related to processes taking place in catchments as well as to in-lake changes in biological communities. Moreover, lake sediments also register anthropogenic activities and man-induced environmental problems. Lake sediments are known to accumulate various compounds during their formation and adsorption processes, thus sediment investigations serve as an important tool in assessing the contamination of aquatic ecosystems (Boyle 2001), including accelerated supply of heavy metals into lakes.

Occurring in bedrock and soils, heavy metals are a natural part of the environment. They enter pristine lakes from a variety of sources, mostly by the weathering of bedrock in catchments and the following transport to lakes as part of the accumulating material in dissolved or particulate form through runoff, and as wind-blown soil dust particles. The anthropogenic contribution to heavy metal distribution depends on several factors, like airborne long-range transport of industrial contaminants, local point source effluents, rural land-use activities, etc. The observed metal distribution in lakes is thus a complex result of natural and human-induced inputs. Palaeolimnological studies based on sediment analysis permit the historical monitoring of the content of heavy metals in the environment and establishing the share

of their anthropogenic input (Durham & Joshi 1980; Nriagu & Pacyna 1988; Renberg et al. 1994; Von Gunten et al. 1997). However, post-deposition redox conditions, mobilization, and diagenesis (e.g. Boudreau 1999) complicate the heavy metal distribution in the sediment sequence and must be considered when past metal contamination trends are reconstructed from lake sediment profiles.

For environmental studies it is relevant to understand how the organic biomolecule transformation processes are affected by metal ions and which organic matter classes bind these metal ions. One of the reference lakes for this investigation is Lake Rõuge Tõugjärv in southern Estonia, where heavy metals and their organic complexes have been studied in lake water, sediment pore-water, and sediments.

In the present work heavy metals in the sediments of Lake Liinjärv lying upstream of Rõuge Tõugjärv were analysed as background information from the same key area. The down-core distribution of sediment composition and heavy metals (Pb, Cu, Zn, Mn, and Hg) in L. Liinjärv were determined by atomic absorption spectrometry (AAS), the method most commonly used in the study of the content of heavy metals in sediments (Hödrejäv & Ott 1988; Krumgalz & Fainshtein 1989). The principal objectives of this study were (1) to find out if any elevated heavy metal level trends existed in the recent sediments of L. Liinjärv and whether these could be related to industrial activity and geochemical back-

ground concentrations, and (2) to establish metal ion and organic matter interactions during natural transformation processes in aquatic environment.

MATERIAL AND METHODS

Study area

Lake Liinjärv is located in Võrumaa county, southern Estonia, in the ancient up to 75 m deep Rõuge Valley. It is a small (370 m long and 150 m wide) lake, with a surface area of 3.5 ha and maximum water depth of 11.5 m (Riikoja 1930). Liinjärv is the highest in the chain of seven lakes, which are connected by a stream flowing in the valley that cuts the western slope of the Haanja Uplands, the highest area in Estonia (Fig. 1).

The landscape around the lake is hilly hummocky with high slopes, especially to the northeast of the lake. The catchment area is 15 km² and it is characterized by clayey till and fluvioglacial sands. In land use arable land is predominating, with few forest patches and meadows in the near vicinity of the lake.

Liinjärv is a strongly through-flowing lake with stratified water and the water exchange period of a few months. Sediments are formed mainly of the allochthonous material, transported to the lake by two inflowing streams (Mäemets 1977) – one is from the Ööbikuorg Valley in the north and the other is from the Tindioru Valley in the east. These streams have strong falls and, passing numerous springs in their way, carry large amounts of calcareous sediments to the lake. This is why the mineral matter content in the lake water is

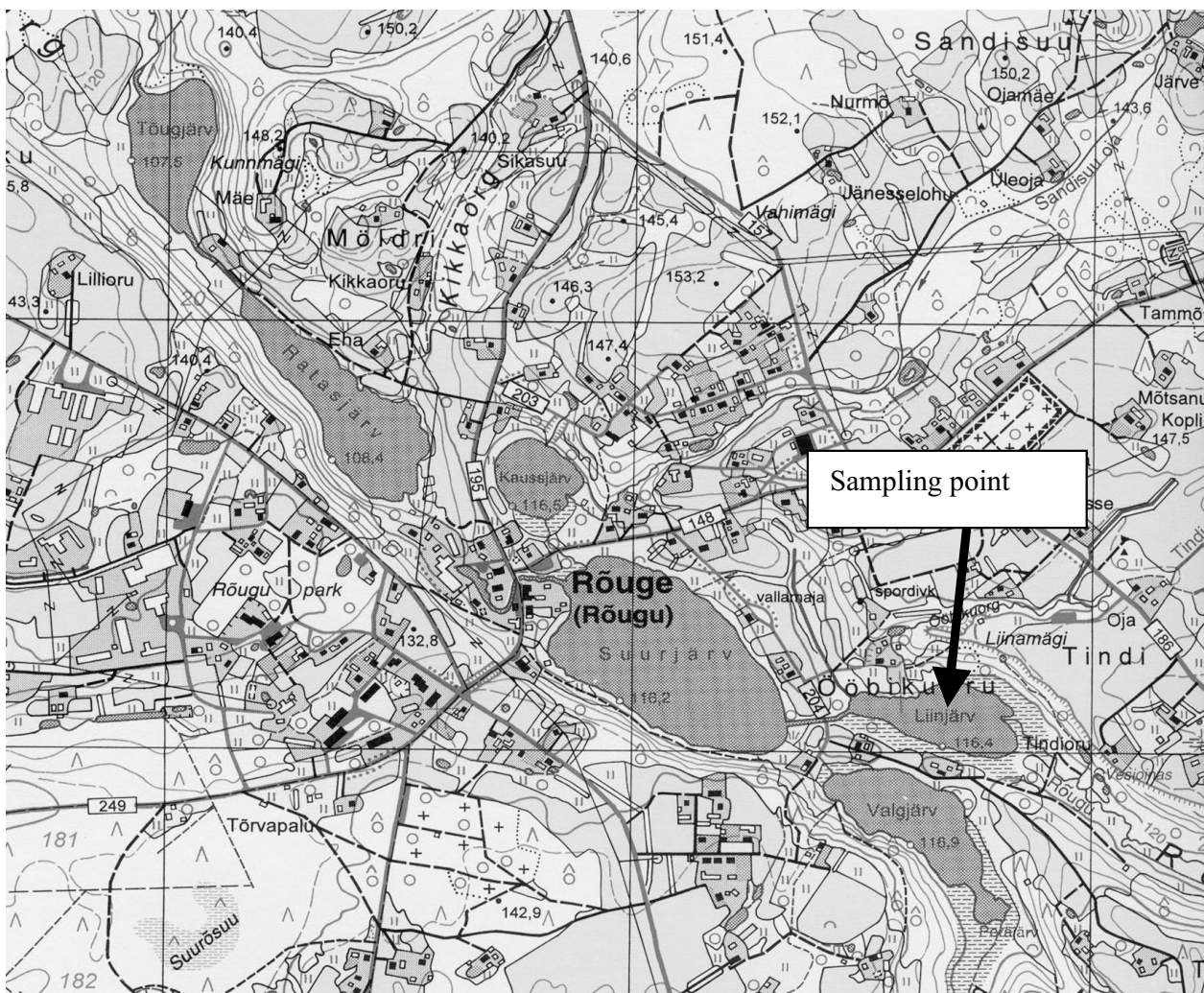


Fig. 1. Map of Lake Rõuge Liinjärv and its environment. The coring site is indicated by an arrow.

one of the highest in Estonia, with HCO_3^- reaching 300 mg L^{-1} (Mäemets 1977). This hardwater lake has outflow to Lake Suurjärv (Fig. 1). Liinjärv is a meso-eutrophic lake.

The lake is of glacial thermokarst origin, and its evolution correlates with that of Lake Rõuge Tõugjärv, a small-sized lake located 2 km to the northwest down the valley (Fig. 1) (Veski et al. 2005). The complete melting of the buried dead ice block and formation of the kettle-hole lake depression took place in the Early Holocene ca 11 400 calendar BP (Heinsalu & Veski 2007). The sediment sequence in L. Liinjärv reaches as much as 21 m in thickness (Rõuk 1992), which is so far the maximum observed thickness of lake sediments in Estonia.

Sampling

Samples of bottom sediments were taken from the deepest part of the lake (coring site $57^\circ 43' 35'' \text{N}$; $26^\circ 55' 56'' \text{E}$, water depth 11 m; Fig. 1). Initially sediment was cored with a Russian sampler (Glew et al. 2001) for visual examination of the sediments. Then the upper 62 cm long core of unconsolidated sediments was extracted using a modified Livingstone–Vallentyne piston corer equipped with extension rods (Glew et al. 2001). The samples were cut into 1–2 cm thick subsamples in the field, packed into plastic bags, transported to the laboratory, dried, and then ground to fine powder.

Dating

Sediment layers were dated using the ^{210}Pb method. For age calculations the Constant Rate of Supply (CRS) model (Appleby & Oldfield 1978) was used. The model is based on the assumption that the atmospheric or unsupported ^{210}Pb flux has been constant throughout the last 100–150 years. ^{210}Pb was detected α -spectrometrically via its granddaughter isotope ^{210}Po using ^{208}Po as a yield tracer, assuming radioactive equilibrium between these radionuclides in the entire sediment profile. After the spiking of each sample with a certain amount of ^{208}Po , ^{210}Po was extracted with concentrated HNO_3 . Polonium isotopes were then self-deposited into a silver disc from the solution of 1M HCl, following the procedure of Eakins & Morrison (1978), and counted using a semiconductor detector and pulse-height multi-channel analyser (AI-1024). In order to get the values

of unsupported ^{210}Pb , the fraction of supported ^{210}Pb , produced in situ by radioactive decay of ^{226}Ra , was subtracted from detected, or total ^{210}Pb values. The value of supported ^{210}Pb has been estimated from values of total ^{210}Pb in the deeper part of the core where ^{210}Pb and ^{226}Ra are assumed to be in equilibrium. The uniform distribution of ^{226}Ra (and supported ^{210}Pb) activity was assumed throughout the sediment profile.

Analyses

In order to calculate the water content of the sediment samples, they were dried at 110°C to a constant weight. The content of organic matter was determined as loss on ignition (LOI) at 550°C for 4 h and carbonate content at 950°C for 2 h (Heiri et al. 2001). Terrigenous matter was calculated as the remaining material after this step-wise thermal treatment of samples. The density of bulk sediment necessary to determine dry matter accumulation rates was also calculated for every subsample (Håkansson & Jansson 1983).

Atomic absorption spectrometry was used for determination of heavy metals. For the digestion of the samples a modified procedure from Hödrejärvi et al. (1989) was employed. For Pb, Cu, Zn, and Mn measurements samples were digested in high pressure teflon vessels with 20 mL of concentrated nitric acid for 6 h at 140°C . After cooling, 2 mL of 30% hydrogen peroxide was added and the solution was heated for another 6 h. Thereafter the solution was diluted to 25 mL with MilliQ water and analysed with a flame AAS SP 9-700 (Pye Unicam). The exact conditions of analysis are presented in Table 1.

For Hg, a cold vapour AAS was used after the digestion of the samples with the nitric acid–sulphuric acid mixture (1 : 1) according to Ott (1986).

Table 1. The instrumental parameters of atomic absorption spectrometry

Parameter	Pb	Cu	Zn	Mn
Wavelength, nm	217.0	324.8	213.9	279.5
Bandpass, μm	0.5	0.5	0.5	0.5
Lamp current, mA	5	4	9	12
Background- Deuterium lamp	+	–	+	+
Detection limit, $\mu\text{g mL}^{-1}$	0.2	0.06	0.04	0.03

RESULTS AND DISCUSSION

Sediment characteristics, composition, and age

The lithological examination of the core shows that sediments of L. Liinjärv consist of distinctly visible laminated dark-coloured unconsolidated calcareous gyttja. Regular laminations occur as ca 2 mm thick light–dark laminae couplets. A lighter layer consists primarily of clastic materials and CaCO_3 , while a darker layer contains more organic-rich material. Most probably such a cyclic structural element constitutes an annual unit, i.e. varved lake sediment (e.g. Saarnisto 1986). The lighter lamina is likely formed in early spring during the snowmelt period as well as in spring and early summer due to biochemical precipitation of carbonates, and the darker lamina is deposited in other seasons from autochthonous organic material produced in the lake. However, annual lamination in L. Liinjärv does not provide an accurate calendar year time-scale, because massive and more compact calcareous interlayers identified as re-sedimented spring tufa (travertine) beds irregularly interrupt varves. Coarse-grained and relatively cemented tufas are continuously deposited along the foot of the Rõuge Valley slope nearby the lake (on the steep northeastern shore), reaching a thickness of 5–6 m at groundwater spring outflows

(Lõökene 1968). Extreme rainfall events likely lead to erosion of tufas and the inflowing stream carries suspended material into the lake.

Sediment composition of L. Liinjärv (Fig. 2) correlates well with the lithological description of sediment. The dry bulk density of the sediments is about $0.3\text{--}0.4\text{ g cm}^{-3}$ in the uppermost part of the core where sediments are not compacted yet and have a high water content. Dry bulk density is increasing downwards, but is very variable due to changing sediment composition. The values of organic matter in sediments are generally low and vary considerably, from 8.6 to 22.9%. Carbonate and terrigenous matter contents also fluctuate in a wide range and usually their rise causes lower organic matter values in these sediment layers. Changing sediment composition is a result of strong inflow and periodically heavy catchment erosion with deposition of material rich in calcium carbonate and minerals.

The results of radioisotope dating are given in Table 2 and shown graphically in Fig. 3. In the case of undisturbed and monotonous sedimentation the total ^{210}Pb activity should demonstrate an almost linear decreasing trend down the core, showing the decay of the radioisotope. Instead of that, the ^{210}Pb concentration in L. Liinjärv has distinctive gradients where decrease in activity is followed by increase and vice versa.

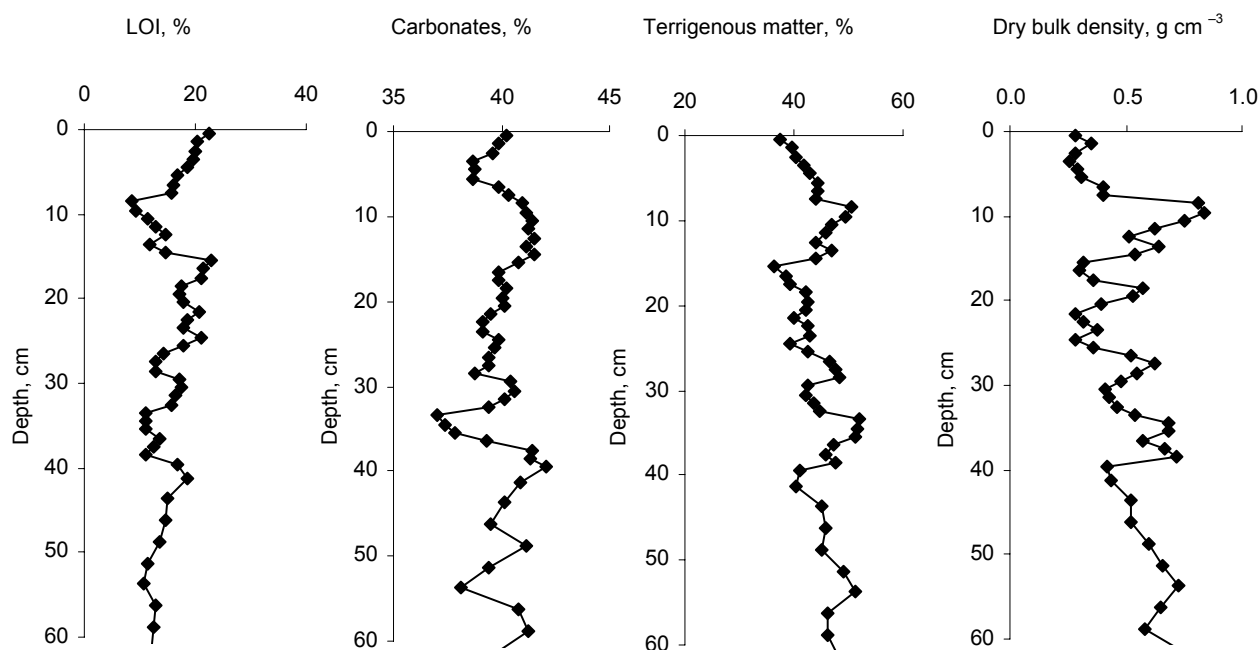


Fig. 2. Sediment composition: organic matter (LOI, %, dry weight), carbonates (as CO_2 , %, dry weight), terrigenous matter (% dry weight), and temporal changes in sediment dry bulk density (g cm^{-3}).

Table 2. Summary of ^{210}Pb analyses of Lake Rõuge Liinjärv sediments. Supported ^{210}Pb activity is 49.95 mBq g^{-1}

Depth, cm	Total ^{210}Pb , mBq g^{-1}	Total ^{210}Pb error, $\pm \text{mBq g}^{-1}$	Unsupported ^{210}Pb , mBq g^{-1}	Years by CRS model
0–1	62.9	3.7	12.95	1989–1990
1–2	92.5	3.7	42.55	1987–1989
2–3	103.6	7.4	53.65	1985–1987
3–4	118.4	3.7	68.45	1982–1985
4–5	107.3	3.7	57.35	1979–1982
5–6	70.3	3.7	20.35	1978–1979
6–7	74.0	3.7	24.05	1977–1978
7–8	51.43	2.96	1.48	1977
8–9	23.31	2.22	0.00	1977
9–10	23.68	1.48	0.00	1977
10–11	45.14	2.96	0.00	1977
11–12	59.2	3.7	9.25	1976–1977
12–13	62.9	3.7	12.95	1975–1976
13–14	70.3	3.7	20.35	1972–1975
14–15	40.33	1.85	0.00	1972
15–16	96.2	3.7	46.25	1968–1972
16–17	114.7	7.4	64.75	1963–1968
17–18	70.3	3.7	20.35	1960–1963
18–19	48.1	2.96	0.00	1960
19–20	59.2	3.7	9.25	1959–1960
20–21	70.3	3.7	20.35	1956–1959
21–22	92.5	3.7	42.55	1951–1956
22–23	77.7	3.7	27.75	1947–1951
24–25	85.1	3.7	35.15	1935–1941
26–27	52.91	2.96	2.96	1928–1930
28–29	50.69	2.96	0.74	1927
30–31	70.3	3.7	20.35	1905–1917
32–33	70.3	3.7	20.35	1863–1884
34–35	40.33	1.85	0.00	nd
36–37	51.8	3.7	0.00	nd
38–39	58.83	2.22	0.00	nd
40–42.5	57.72	3.7	0.00	nd
45–47.5	52.54	2.59	0.00	nd
50–52.5	54.76	3.7	0.00	nd
57.5–60	44.4	0.74	0.00	nd
60–62.5	40.33	1.85	0.00	nd

nd, not determined.

These features indicate dilution of radioisotope and record changes in the sediment accumulation rate, suggesting sharp acceleration of sedimentation in these parts of the sequence. Higher accumulation rates were registered at sediment depths of 7–15, 17–19, and 25–29 cm, most probably due to inflow of eroded tufas to the lake. Below the sediment depth of 34 cm, the values reach the background level, which is supposed to be the supported ^{210}Pb concentration with equilibrium

between ^{210}Pb and ^{226}Ra , and which corresponds to approximately 150 years of sediment accumulation. Radiometric dates calculated using the CRS model are shown in Fig. 4.

According to radioisotope dating, the sedimentation rate has been fairly uniform (about 0.2 cm y^{-1} , Fig. 5), except for these travertine inflow occasions when it reaches up to 10 cm y^{-1} . The sedimentation rate is extremely high at the depth interval of 7–11 cm. As this

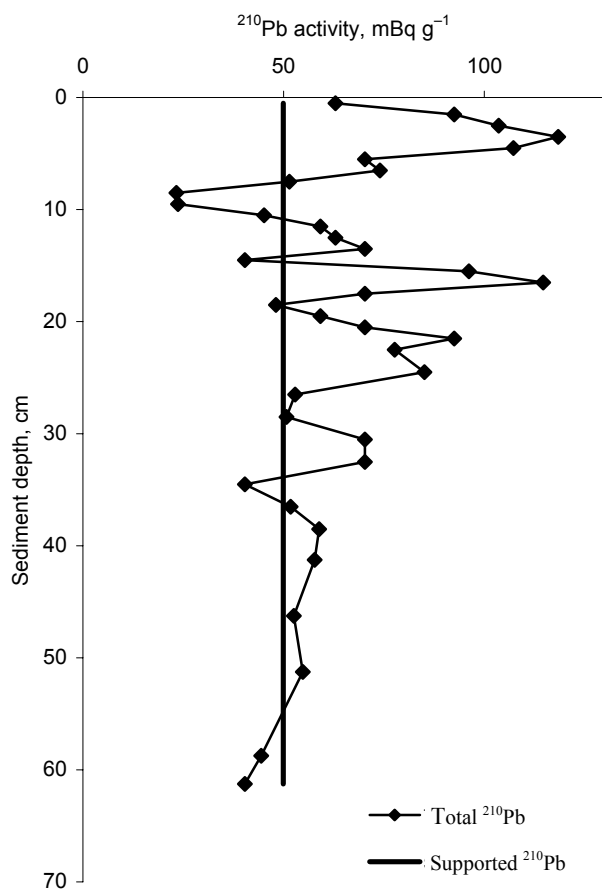


Fig. 3. Radioisotope dating of the sediment core of Lake Rõuge Liinjärv.

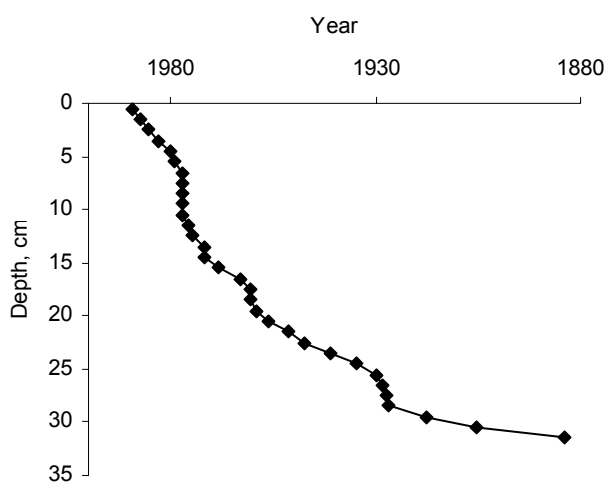


Fig. 4. Radiometric dates of the sediment core of Lake Rõuge Liinjärv by the CRS model.

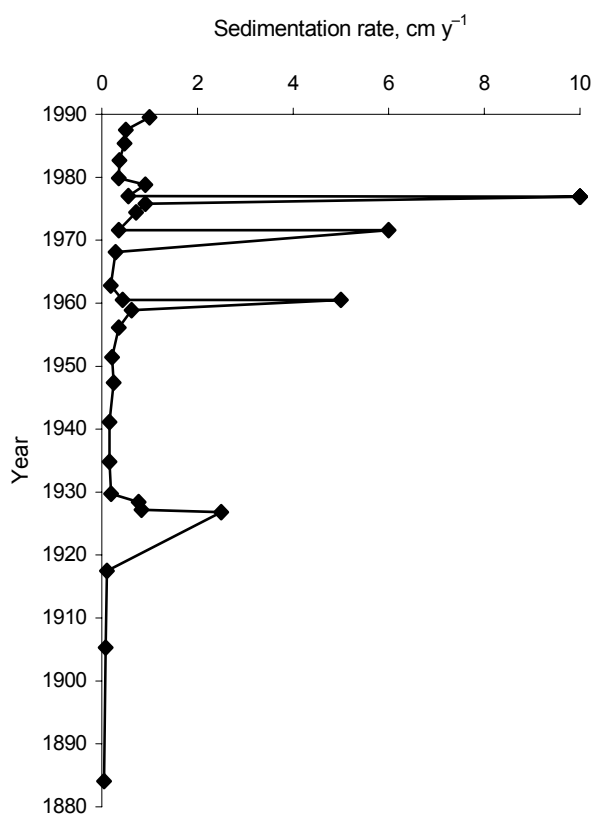


Fig. 5. Temporal changes in the sedimentation rate (cm y^{-1}) of Lake Rõuge Liinjärv.

interval is dated to the year 1978, it coincides very well with this unusually wet year, causing floods in many places in southern Estonia. Some increase occurs also in the upper part of the core, where the estimated rate of accumulation is $0.4\text{--}1.0 \text{ cm y}^{-1}$, however, to a certain extent it is due to uncompacted nature of the surface sediment layers.

Trends of heavy metals in the sediment core

Many chemical processes where heavy metals can participate take place in an aquatic environment. The most important of these are (1) complexation with inorganic ligands and formation of inorganic complexes; (2) complexation with organic ligands and formation of organic complexes, most likely with humic substances; (3) formation of colloid complexes; (4) participation in redox reactions; and (5) biological reactions in several organisms. When heavy metals enter the aquatic system

they associate with particulate (sediment) phases. Sediments contain residues of weathering and erosion (clays, other aluminosilicates, Fe and Al oxyhydroxides and sulphides), substances produced by biological activity (microorganisms, detritus, humic substances), and inorganic substances (carbonates, phosphates, and silica). This complex sediment mixture allows a wide range of mechanisms of metal–sediment interactions, such as incorporation into crystal lattices of clays, adsorption or ion-exchange in Fe–Mn oxyhydroxides and humic substances, coprecipitation with Fe–Mn oxyhydroxides and carbonates, and organometallic bonding with humic substances (Tessier 1992). Metals association with insoluble sulphide precipitates, which are formed by bacterial sulphate reduction in connection with decomposition of organic matter, have been reported by several authors (Di Toro et al. 1996; Huerta-Diaz et al. 1998; Canavan et al. 2007).

In Fig. 1 the location of the sampling point is indicated together with the close surroundings of L. Liinjärv. As there is no direct industrial activity in this region, the metal input to the lake is mainly from the agricultural activity and atmosphere. The measured concentrations of metals in the lake sediment core are shown in Fig. 6. The concentration intervals of heavy

metals were as follows (in mg kg^{-1}): Pb, 0.5–34.6; Cu, 6.4–64.0; Zn, 23–100; Mn, 241–748; Hg, 0.08–0.24. Mean values with confidence limits are shown in Table 3. Cu, Zn, and Pb in the environment usually result from industrial activities. The increase in metal concentrations in sediments began at the end of the 1970s and was most clearly observable for Zn, Cu, and Pb. The year 1970 is estimated to separate the natural or background concentrations from anthropogenic ones. The major sources of Pb are anthropogenic emissions (Yin et al. 2006). The Pb concentrations in sediments decreased after 1985 likely due to the ban of leaded gasoline usage. As L. Liinjärv has strong throughflow and its watershed is quite large compared to the lake area, the watershed may have notable influence on the formation of heavy metal profiles in lake sediments through the fixation of metals on soils and later leaching. The decrease in metal concentrations in sediments in the 1920s, 1950s, 1960s, and 1970s may also have been caused by changes in the sedimentation rates, resulting in the increase in the particulate phase and thus dilution. To estimate the natural background, sediment samples from the deepest parts of the core were analysed. The background concentration of Pb in the studied lake sediments is estimated not to exceed 5 mg kg^{-1} , which is close to the

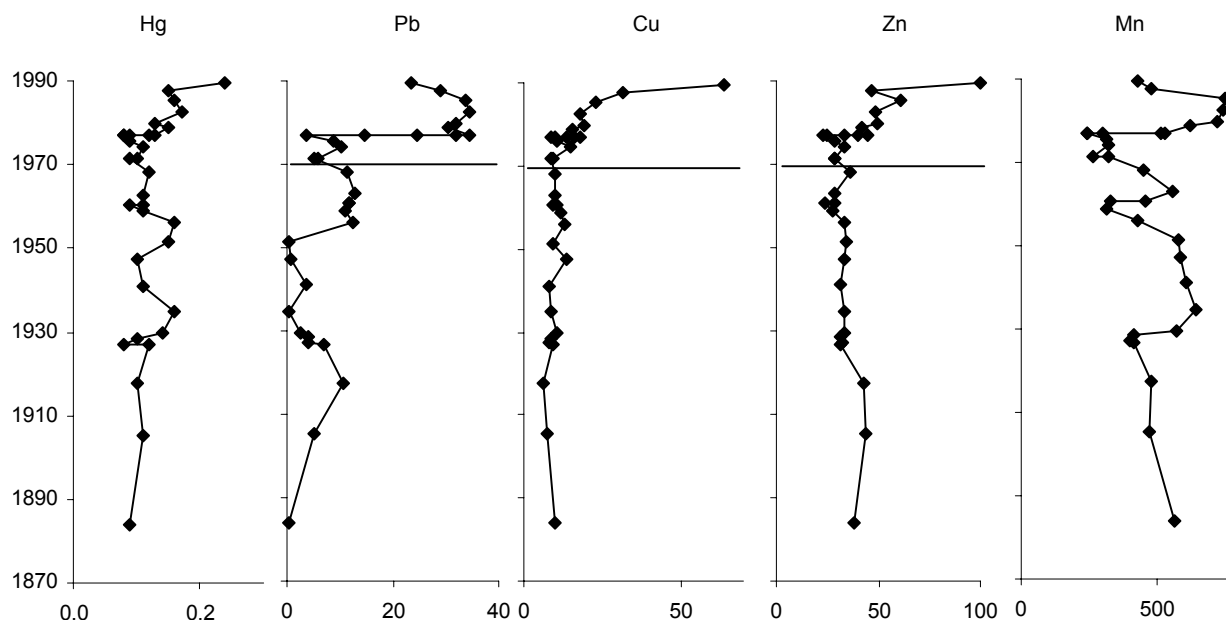


Fig. 6. Distribution of heavy metals (mg kg^{-1}) in the sediment core. Natural background concentrations for Pb, Cu, and Zn are separated from the anthropogenically impacted time period by horizontal lines.

Table 3. Analytical results of heavy metals for Lake Liinjärvi sediments (mean value, ± confidence interval, mg kg⁻¹, 95% confidence level)

Metal	1970–1990	1930–1970	1880–1930	All data
Pb	21.5±6.7	7.66±4.00	4.89±3.02	13.6±4.2
Cu	18.7±7.7	10.4±1.3	8.57±1.37	13.9±3.8
Zn	42.1±10.6	31.2±2.7	36.2±5.0	37.4±5.1
Mn	452±103	495±82.5	472±66	470±52.1
Hg	0.13±0.024	0.12±0.018	0.11±0.018	0.12±0.012

natural background level for L. Peipsi, <2 mg kg⁻¹, and to the general freshwater lake background of <20 mg kg⁻¹ (Lepane 1992).

The very similar concentration profiles of Cu and Zn point to related sources. The concentrations of those metals in sediments remained relatively constant up to the 1970s. Zn is reported to enter the sediments mainly from wet and dry atmospheric fallout (Von Gunten et al. 1997). Cu and Zn concentrations in sediments of natural background non-polluted areas are below 20 and 50 mg kg⁻¹, respectively (Bowen & Moule 1979). The present study estimates the local background concentrations in L. Liinjärvi to be <40 mg kg⁻¹ for Zn and <10 mg kg⁻¹, for Cu, which is in accordance with the generally reported values.

The anthropogenic load has not induced elevated concentrations of Mn. The distribution of this element in the sediment core seems to be controlled by redox conditions and/or by the organic matter content. The variability of Mn concentrations is probably the result of changes in the redox potential at the bottom of the lake, because that determines the solubility of manganese compounds. The changes in redox potential are caused mainly by varying weather and temperature conditions that influence bioproductivity and related biogeochemical processes, for example the oxidation of organic matter.

The predominant source of Hg in lake sediments is atmospheric deposition. The residence time of Hg in the atmosphere is close to a year, thus enabling the distribution of this metal over quite long distances (Perry et al. 2005). It has been found that atmospheric Hg is distributed evenly and its concentrations are constant, but deposition rates of wet Hg can depend locally on precipitation patterns (Meili 1995). The results of the present study show that Hg concentrations are constant in the L. Liinjärvi sediment core. A slight increase however, was detected starting from the 1980s. We conclude that Hg concentrations are on the background level, which is estimated to be 0.12 mg kg⁻¹.

Factors affecting heavy metal distribution

For the reconstruction of the metal pollution history as well as for the accurate ²¹⁰Pb dating, the sediments should be perfectly protected against any processes which may change the original records. The main factor potentially affecting the initial distribution of heavy metals is bioturbation (Robbins et al. 1977). However, on the basis of the metals and ²¹⁰Pb curves rather sharp changes in concentrations can be noticed in L. Liinjärvi, which speak against smoothing of the values in the course of sediment mixing. Therefore, as the lake water is stratified nearly all the year round and the water in the epilimnion is oxygen-depleted, it seems that the conditions in the deeper water layers are unfavourable for the bottom fauna and their role in the early diagenesis is modest. The formation of varves bears information about environmental conditions in the water column, i.e. suggests that temporary or permanent anoxia has developed in the hypolimnion of the lake, which effectively minimizes bioturbation and is a prerequisite for the preservation of features of seasonal sedimentation. In addition, preservation of these laminations provides evidence for anoxic conditions in the sediment–water interface. Thus, the accumulation of redox active metals in the sediment can change, whereas the hypolimnion is temporarily anoxic. Postsedimentary mobility of several chemical elements, caused by the changing redox conditions, has been concluded from the data of several studies (Gobeil & Silverberg 1989; Santschi et al. 1990).

In the present study it is assumed that most of Ca is in the form of CaCO₃. Although CaCO₃ is a major component of sediments, it seems to have no correlation with the heavy metals studied, especially in older sediments. Only a small and constant fraction of Hg, Pb, Cu, Zn, and Mn may be associated with carbonates. Interestingly, in younger sediments, dated after 1970, all metals show a similar behaviour – the increase in carbonates causes a decrease in metals. This trend is more pronounced in case of Pb and Mn (correlation coefficients –0.85 and –0.93, respectively). A similar finding has been made in UK lake sediments where negative correlation between Pb and Ca has been explained by the dilution of metals at a high concentration of CaCO₃ (Yang & Rose 2005). To conclude, carbonates and other inorganic (terrigenous) matter seem not to be the main factor affecting heavy metal distribution in L. Liinjärvi sediments.

The other factor considered in the present study was organic matter. Sedimentary organic matter in lake sediments is derived from the catchment area but is also produced in the lake water column. Differences in the composition of organic matter originate from the transformation and alteration processes. To reveal possible heavy metal associations with organic matter, the correlation coefficients were calculated for the entire dataset and separately for three time periods: 1970–1990, 1930–1970, and 1880–1930. The results show that generally most of the metals are weakly correlated with organic matter (correlation coefficients in the range 0.4–0.6, Table 4). However, temporal differences were observed (Fig. 7). Significant differences of metal–organic

matter associations were established for surface (1970–1990) and older sediments. Strong correlations of Hg, Pb, Cu, and Zn with organic matter confirm that metals form organic complexes with humic substances in surface sediments. Those complexes or organic matter in deeper sediment layers are transformed by different geochemical or biological processes, as seen from different trendline slopes and respective low correlations presented in Fig. 7 and Table 4. A different behaviour was detected for Pb in surface sediments. Two distinct groups could be separated, characterized as low organic and Pb and high organic and Pb. A substantial change in Pb concentrations in sediments occurred around 1977.

Table 4. Correlation coefficients for the indicated variables in sediments of Lake Liinjärv

All data					
	Hg	Pb	Cu	Zn	Mn
Hg	1				
Pb	0.4280	1			
Cu	0.7524	<i>0.5099</i>	1		
Zn	0.7863	<i>0.5020</i>	0.8933	1	
Mn	<i>0.5094</i>	0.3463	0.1411	0.3915	1
LOI	0.6374	0.1241	0.3540	0.4493	0.6392
1970–1990					
	Hg	Pb	Cu	Zn	Mn
Hg	1				
Pb	<i>0.5728</i>	1			
Cu	0.8804	0.3560	1		
Zn	0.9384	<i>0.5023</i>	0.9446	1	
Mn	<i>0.5923</i>	0.8512	0.2514	<i>0.4876</i>	1
LOI	0.8844	<i>0.5870</i>	0.7189	0.8075	0.7370
1930–1970					
	Hg	Pb	Cu	Zn	Mn
Hg	1				
Pb	–0.2935	1			
Cu	–0.0214	0.1820	1		
Zn	<i>0.5947</i>	<i>–0.5150</i>	0.1169	1	
Mn	0.3529	–0.7568	–0.2789	<i>0.5823</i>	1
LOI	0.2197	–0.0124	–0.3336	0.4178	0.3812
1880–1930					
	Hg	Pb	Cu	Zn	Mn
Hg	1				
Pb	0.0297	1			
Cu	0.4531	–0.7394	1		
Zn	–0.1001	0.3137	<i>–0.6083</i>	1	
Mn	0.3915	–0.4100	0.4607	0.3768	1
LOI	0.3986	–0.0261	–0.0347	0.7196	0.8116

95% confidence level in italic; 99% confidence level in bold.

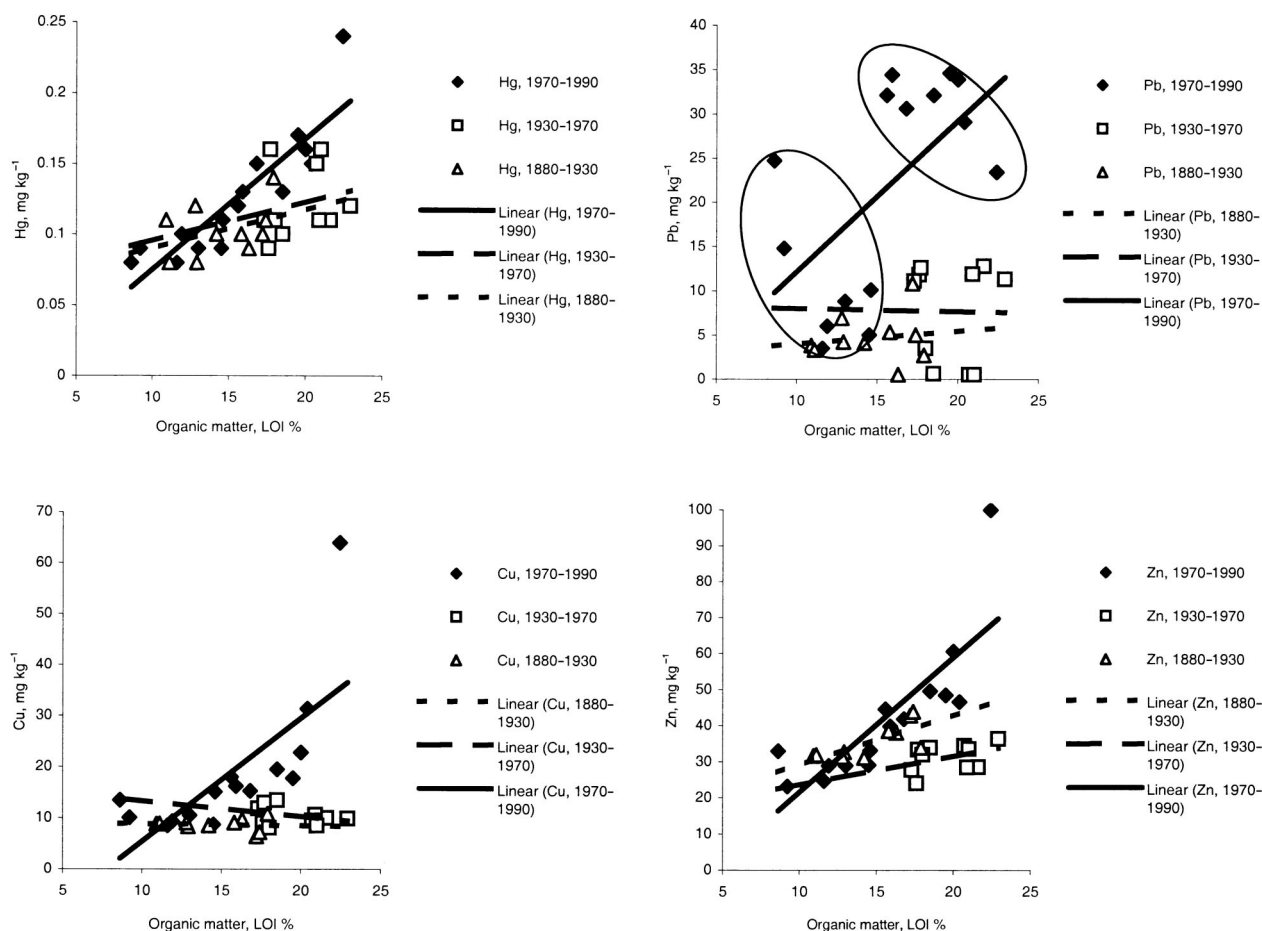


Fig. 7. Temporal differences in heavy metal–organic matter relationships with linear trendlines. Metals: Hg, Pb, Cu, Zn (mg kg^{-1} , dry weight); organic matter (LOI, %, dry weight).

CONCLUSIONS

In L. Liinjärv in South Estonia, where the anthropogenic load is not too high and is expressed mainly through the agricultural activity, high surficial metal concentrations were observed in the sediment core, reflecting the influence of man-induced pollution. Heavy metal concentrations began to increase after the 1970s. The main sources of pollutants in L. Liinjärv sediments, due to the large catchment area, are the agricultural activity and atmospheric input. The main factor affecting heavy metal (Pb, Hg, Cu, and Zn) distribution in L. Liinjärv sediments is organic matter. The estimated natural background concentrations for heavy metals were: $<5 \text{ mg kg}^{-1}$ for Pb, $<40 \text{ mg kg}^{-1}$ for Zn, $<10 \text{ mg kg}^{-1}$ for Cu, and $<0.12 \text{ mg kg}^{-1}$ for Hg.

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REFERENCES

- Appleby, P. G. & Oldfield, F. 1978. The concentration of ^{210}Pb dates assuming a constant rate of supply of unsupported ^{210}Pb to the sediment. *Catena*, **5**, 1–8.
- Boudreau, B. P. 1999. Metals and models: diagenetic modelling in freshwater lacustrine sediments. *Journal of Paleolimnology*, **22**, 227–251.

- Bowen, H. & Moule, J. 1979. *Environmental Chemistry of the Elements*. Academic Press, London, 333 pp.
- Boyle, J. F. 2001. Inorganic geochemical methods in paleolimnology. In *Tracking Environmental Change Using Lake Sediments, Volume 2: Physical and Geochemical Methods* (Last, W. M. & Smol, J. P., eds), pp. 83–142. Kluwer Academic Publishers, Dordrecht.
- Canavan, R. W., Van Cappellen, P., Zwolsman, J. J. G., van den Berg, G. A. & Slomp, C. P. 2007. Geochemistry of trace metals in a fresh water sediment: field results and diagenetic modelling. *Science of Total Environment*, **381**, 263–279.
- Di Toro, D. M., Mahony, J. D., Hansen, D. J. & Berry, W. J. 1996. A model of the oxidation of iron and cadmium sulfide in sediments. *Environmental Toxicology and Chemistry*, **15**, 2168–2186.
- Durham, R. W. & Joshi, S. R. 1980. Recent sedimentation rates, ²¹⁰Pb fluxes and particle setting velocities in Lake Huron, Laurentian Great Lakes. *Chemical Geology*, **31**, 53–66.
- Eakins, J. D. & Morrison, R. T. 1978. A new procedure for the determination of lead-210 in lake and marine sediments. *International Journal of Applied Radiation and Isotopes*, **29**, 531–536.
- Glew, J. R., Smol, J. P. & Last, W. M. 2001. Sediment core collection and extrusion. In *Tracking Environmental Change Using Lake Sediments, Volume 1: Basin Analysis, Coring, and Chronological Techniques* (Last, W. M. & Smol, J. P., eds), pp. 73–106. Kluwer Academic Publishers, Dordrecht.
- Gobeil, C. & Silverberg, N. 1989. Early diagenesis of lead in Laurentian Tough sediments. *Geochimica et Cosmochimica Acta*, **53**, 1889–1895.
- Håkansson, L. & Jansson, M. 1983. *Principles of Lake Sedimentology*. Springer-Verlag, Berlin, 318 pp.
- Heinsalu, A. & Veski, S. 2007. Lõuna-Eesti väikejärvede pärajääajast arenguloost Rõuge Tõugjärve näitel [Post-glacial development of small lakes in South Estonia on the example of Lake Rõuge Tõugjärv]. In *Eesti Loodusuurijate Seltsi järvekommisjon 100 aastat. Tähtpäevaettekannete kogumik* (Timm, H., Paju, M.-M. & Sammul, M., eds), pp. 43–48. Sulemees, Tartu [in Estonian].
- Heiri, O., Lotter, A. F. & Lemcke, G. 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. *Journal of Paleolimnology*, **25**, 101–110.
- Hödrejärv, H. & Ott, R. 1988. Heavy metals in the environment of Estonia. *Transactions of Tallinn Technical University*, 73–83.
- Hödrejärv, H., Ott, R., Lepane, V. & Vaarmann, A. 1989. Heavy metals in Lake Peipsi. *Proceedings of the Academy of Sciences of the Estonian SSR, Biology*, **38**, 137–144.
- Huerta-Diaz, M. A., Tessier, A. & Carignan, R. 1998. Geochemistry of trace metals associated with reduced sulfur in freshwater sediments. *Applied Geochemistry*, **13**, 213–233.
- Krumgalz, B. S. & Fainshtein, G. 1989. Trace metal contents in certified reference sediments determined by nitric acid digestion and atomic absorption spectrometry. *Analytica Chimica Acta*, **218**, 335–340.
- Lepane, V. 1992. *Physico-chemical Methods of the Determination of Heavy Metals in Natural Waters and Sediments*. Master Thesis. Tallinn University of Technology, Tallinn, 99 pp.
- Lõokene, E. 1968. Allikalubja levik ja iseloom Haanja kõrgustikul [Distribution and character of travertine on the Haanja Heights]. *Tartu Ülikooli Toimetised*, 213, 3–33 [in Estonian].
- Mäemets, A. 1977. *Eesti NSV järved ja nende kaitse [Estonian lakes and their protection]*. Valgus, Tallinn, 263 pp. [in Estonian].
- Meili, M. 1995. Pre-industrial atmospheric deposition of mercury: uncertain rates from sediment and peat cores. *Water, Air and Soil Pollution*, **80**, 637–640.
- Nriagu, J. O. & Pacyna, J. M. 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature*, **333**, 134–139.
- Ott, R. 1986. Heavy metals in Baltic Sea sediments. *Transactions of Tallinn Technical University*, 619, 57–63.
- Perry, E., Norton, S. A., Kamman, N. C., Lorey, P. M. & Driscoll, C. T. 2005. Deconstruction of historic mercury accumulation in lake sediments, Northeastern United States. *Ecotoxicology*, **14**, 85–99.
- Renberg, I., Wik-Persson, M. & Emteryd, O. 1994. Pre-industrial atmospheric lead contamination detected in Swedish lake sediments. *Nature*, **386**, 323–326.
- Riikojä, H. 1930. *Zur Morphometrie einiger Seen Eestis*. Tartu Ülikooli Eesti veekogude uurimise komisjoni väljaanne Nr. 13, Tartu.
- Robbins, J. A., Krezoski, J. R. & Mozley, S. C. 1977. Radioactivity in the sediments of Great Lakes: post-depositional redistribution by deposit-feeding organisms. *Earth and Planetary Science Letters*, **36**, 325–333.
- Rõuk, M. 1992. Laminated sediments in Estonian lakes – preliminary data. In *Laminated Sediments. Proceedings of the Workshop at Lammi Biological Station, 4–6 June, 1990* (Saarnisto, M. & Kahra, A., eds), *Geological Survey of Finland, Special Paper*, **14**, 105–107.
- Saarnisto, M. 1986. Annually laminated lake sediments. In *Handbook of Holocene Palaeoecology and Palaeohydrology* (Berghlund, B. E., ed.), pp. 343–370. John Wiley and Sons, Chichester.
- Santschi, P., Höhener, P., Benoit, G. & Brink, M. 1990. Chemical processes at the sediment–water interface. *Marine Chemistry*, **30**, 269–315.

- Tessier, A. 1992. Sorption of trace elements on natural particles in oxic environments. In *Environmental Particles* (Buffle, J. & van Leeuwen, H. P., eds), pp. 425–453. Lewis Publishers, Chelsea.
- Veski, S., Koppel, K. & Poska, A. 2005. Integrated palaeo-ecological and historical data in the service of fine-resolution land use and ecological change assessment during the last 1000 years in Rõuge, S Estonia. *Journal of Biogeography*, **32**, 1473–1488.
- Von Gunten, H. R., Sturm, M. & Moser, R. N. 1997. 200-year record of metals in lake sediments and natural background concentrations. *Environmental Science and Technology*, **31**, 2193–2197.
- Yang, H. & Rose, N. 2005. Trace element pollution records in some UK lake sediments, their history, influence factors and regional differences. *Environment International*, **31**, 63–75.
- Yin, X., Liu, X., Sun, L., Zhu, R., Xie, Z. & Wang, Y. 2006. A 1500-year record of lead, copper, arsenic, cadmium, zinc level in Antarctic seal hairs and sediments. *Science of Total Environment*, **371**, 252–257.

Raskmetallide jaotus Rõuge Liinjärve (Lõuna-Eesti) settes

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On uuritud inimtegevuse mõju keskkonnale alates 19. sajandi keskpaigast, kasutades raskmetallide (Pb, Cu, Zn, Mn ja Hg) ning geokeemiliste parameetrite jaotust Rõuge Liinjärve (Lõuna-Eesti) setetes. Setted on dateeritud ^{210}Pb isotoopide alusel. Järve arengut ja setete koostist mõjutab suur valgala ning kaltsiumirikka vee sissevool, mis põhjustab kaltsiumkarbonaadi sadenemise settesse. Enamiku metallide kontsentratsioonide suurenemist täheldati alates 1970. aastate lõpust ja eriti märgatav oli see tendents Zn, Cu ja Pb puhul. Peamiseks teguriks, mis määrab raskmetallide (Pb, Hg, Cu ja Zn) jaotuse settes, on orgaaniline aine, mitte sissekantav karbonaatne materjal. Samal ajal mõjutavad Mn jaotust settes põhjalähedase veekihi redokstingimused. Looduslikule foonile vastavad metallide sisaldused Rõuge Liinjärve settes on madalamad kui 5 mg kg^{-1} Pb, 40 mg kg^{-1} Zn, 10 mg kg^{-1} Cu ja $0,12 \text{ mg kg}^{-1}$ Hg puhul.