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GRAIN-SIZE ANALYSIS OF LAKE SEDIMENTS: RESEARCH METHODS AND APPLICATIONS

Tallinn 2010

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GRAIN-SIZE ANALYSIS OF LAKE SEDIMENTS: RESEARCH METHODS AND APPLICATIONS

Institute of Mathematics and Natural Sciences, Tallinn University, Estonia.

The thesis is accepted for the commencement of the degree Doctor of Philosophy in Ecology on June 17, 2010 by the Doctoral Committee of Natural Sciences of Tallinn University.

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Author's contribution

Publications I, **II** and **V**: The author was responsible for grain-size analysis and contributed to interpretation of these data, participated in the fieldwork and preparation of the manuscript.

Publication III: The author was responsible for grain-size analysis and participated in the fieldwork.

Publication IV: The author has complete responsibility.

Publication VI: The author was responsible for grain-size analysis, participated in interpretations and preparation of the manuscript.

PREFACE

The grain-size distribution of sediment is an indicator of processes in the lake basin and changes in the water level, which enables to interpret lake conditions in the past. The grain-size distribution of large lakes and marine areas with mainly mineral and coarse-grained sediments has been quite intensively studied. The sediments of small Estonian lakes are fine-grained and contain large amounts of organic matter and carbonates. Therefore, it was not possible to just take over the necessary methods for grain-size study described in the literature. The main focus of this thesis is on developing grain-size analysis methods and selecting the most appropriate method for fine-grained (clay, silt) organic-rich cohesive sediments. Influences of different pre-treatment methods on sediment composition and grain size were analysed (**IV**). The laser diffraction method was used for studying cohesive lake sediment for the first time in Estonia. In addition, a significantly refined pre-treatment methodology was applied. During numerous repeated measurements and analyses, workflows of pre-treatment methods for sediments with different composition were developed.

The well established history of the water-level fluctuations in Lake Martiska during the last decades and its correlation with the lithological composition and grain-size parameters showed that the grain-size parameters of lacustrine sediments depend on the topography of the lake and its vicinity and reflect changes in the sedimentary processes, especially in lake-level fluctuations, adequately (**I, II, VII**).

In the large shallow Lake Peipsi a detailed surface sediment mapping showed high variability in the sediment composition (**V, VI**). On the basis of grain size the surface sediments in Lake Peipsi fall into three groups: sand (coarse-grained sediments in the southern part of the lake and on the near-coast areas), mixed sediments on till and varved clays (mainly in the northern part) and silt (in the central part). It is important to note that in an aquatic environment fine-grained sediments may form larger, porous aggregates. Organic matter from the water column absorbs on fine-grained particles, and the specific gravity of floating matter increases. As a result, the material settles on the bottom as flocculants (**III**). Fine-grained organic-rich sediments are very cohesive, playing the main role in the circulation of various inorganic and organic pollutants such as nutrients and xenobiotics. Because of the cohesive character of sediments their physical and chemical properties are diverse and in the case of suitable meteorological events, changes in the water level etc., the lake floor may be subjected to episodic erosion and resuspension. This may cause remobilisation of nutrients in muddy sediments and their return to the food chain.

1. INTRODUCTION

The development of lake ecosystems in the past can be reconstructed from stratigraphic analysis of sediment cores based on a range of sedimentary parameters – an approach that is widely used in landscape study (Berglund, 1986; Last & Smol, 2001). Sediments that accumulate in lake basins consist of numerous source materials and reflect changes that have occurred in the lake and in its catchment area. The amount of mineral matter and grain-size composition of sediment are indicators of processes in the lake basin (Boyle, 2001) and changes in water level (Digerfeldt, 1986; Dearing, 1997).

Sedimentological studies, especially on the texture of lake sediments, have been successful in reconstructing lake-level fluctuations in small temperate zone lakes (Digerfeldt, 1986; Saarse & Harrison, 1992; Dearing, 1997; Punning *et al*., 2005a,b). Changes in the hydrological regime and fluctuations of the lake level alter the lake morphometry and transform the characteristics of sedimentation zones of the lake floor, thereby directly influencing sedimentation and resuspension (Davis & Ford, 1982; Bloesch, 1995; Shteinman & Parparov, 1997). The mean grain size decreases with increasing distance from the shore at which the mineral matter can be supposed to originate. This is due to gravitational movement of the sediment, expressed as focusing, i.e. movement of sediment from shallower areas towards deeper ones, caused by water currents, especially during overturn (Davis & Ford, 1982). Focusing is more intensive in lake depressions with steeper slopes but it also occurs in lakes with gently sloping bottoms (Blais & Klaff, 1995). However, as the water level drops the accumulation area of coarse-grained sediment shifts towards the lake's profundal zone and the vegetation of the littoral also moves towards the profundal zone where it then starts to affect the fine-grained sediment. Because of the lowering water level, the erosion area and littoral zone are also shifting. Therefore the sediments can be relocated, which causes hiatus in sedimentation (Hilton *et al*., 1986; Dearing, 1997). The rising water level also brings about changes in sediment formation processes. As the water level rises, the accumulation area of fine-grained material expands, and that is why the fine-grained sediment accumulates on sediment layers that are more coarse-grained. At the same time, macrofossils of the former littoral vegetation are still left in the sediment of the deeper areas of the lake. Sedimentary signals of lake-level changes in small lakes are usually found in marginal sediments, which are sensitive to fluctuating lake levels in various ways, e.g. water depth may control the distribution of sediments and macrophytic vegetation.

It is important to know the distribution of grain sizes of sediment mineral matter to describe sediment composition (McCave & Syvitski, 1991), and therefore much attention is being paid to the methods of analysing the grain sizes of sediment mineral matter. To classify sediment particle size we have to consider the dimensions and the shape of the particles. For a spherical particle, the size is uniquely defined by its diameter.

However, most naturally occurring particles are irregular in shape. In most cases it is therefore necessary to measure more than one dimension. That is why there are many definitions of a particle size: volume diameter (diameter of a sphere having the same volume as the particle), surface diameter (diameter of a sphere having the same surface area as the particle), sieve diameter (defined as the length of the side of the minimum square aperture through which the particle will pass) (Last, 2001). Quite often the size of a particle is determined by the method, technique or equipment used to perform the measuring.

Depending on the aims of the research, different methods are used to describe sediment grain size: sieving, settling, visual estimation, laser diffraction analysis etc. One of the oldest methods is sieving. Electron microscopic research enables to fix the three-dimensional structure of particles or aggregates. Light microscopic research is used for primary estimation of sediment composition and selection of appropriate pre-treatment methods. Recent researches have shown that due to the fragile nature of aggregates, their properties have to be determined sometimes *in situ* (Mikkelsen & Pejrup, 2001; Thonon *et al.*, 2005).

Recently, the use of more precise laser particle sizers has become common. They are based on laser beam diffraction (Konert & Vandenberghe, 1997; Xu, 2000). These instruments use the principle of electromagnetic wave diffraction in order to determine the distribution of particle size.

Before adopting the laser diffraction method, sediment fraction analyses were time consuming and required intensive laboratory work. Traditional fraction analysis combines two or more methods. Firstly, in order to determine the distribution of clay and silt particles, the sedimentation principle (pipette method) is used. Then, sieving helps to measure sand content. Laser particle sizer is able to analyse everything considerably faster. Pre-treatment of sediment is the only time-consuming part of the process. The methods used for the pre-treatment of samples and grain-size analysis depend on the aim of the study. If the interest is in the distribution of allochthonous siliclastic matter in sedimentation processes, it is necessary to have purified material for analysis, i.e. disaggregate flocs, organics and secondary carbonates etc. have to be removed from the grains. The problem is quite easily solved in the case of coarse-grained particles by using the sieving method for grain-size analysis. Complicated problems arise in the case of fine-grained material where secondary side-effects (flocculation, damaged grains, etc.) in the sedimentation environment as well as during the pre-treatment process could seriously affect the reliability of the obtained grain-size spectrum.

Various methods are in use for removing organic matter. One of the widely used approaches is thermal combustion at 550°C (Boyle, 2001; Heiri *et al.*, 2001). Thermal combustion methods are certainly the easiest, but depending on sample lithology and mineral content, problems with aggregate formation of grain may occur (Murray, 2002).

To avoid damaging grains during pre-treatment, wet oxidation is often preferred. Hydrogen peroxide (H_2O_2) is a widely used reagent in the combustion for organic matter removal (Carver, 1971; Konert & Vandenberghe, 1997; Lu & An, 1997; Murray, 2002; Schumacher, 2002; Allen & Thornley, 2004; Mikutta *et al.*, 2005). In wet oxidation hydrochloric acid (HCl) is commonly cited for carbonate removal (Carver, 1971; Battarbee, 1986; Battarbee *et al.*, 2001; Schumacher, 2002).

It has also been shown that diatom valves, which consist mainly of biogenic silica, influence grain-size distribution. To remove biogenic silica KOH is used (Conley, 1998; Lyle & Lyle, 2002).

In an aquatic environment various compounds are absorbed on mineral matter depending on the physical, chemical and biological processes. This may change the sediment texture substantially. Many studies (Rodrigo *et al.*, 1988; Callieri, 1997; Georgian *et al.*, 2003) show that the composition and character of suspended particles – their capacity to dissolve, precipitate and coagulate – dictate the kinetics of particle accumulation. Extra difficulties arise in analysing fine-grained materials (clay and silt). Fine-grained sediments in an aquatic environment may form larger, porous aggregates, commonly called flocs (Van Rijn, 1993; Roberts *et al.*, 1998; Kim *et al.*, 2005). These sediments are cohesive by definition (Hayter & Pakala, 1989; Paterson, 1997) and their composition and structure are temporally changeable. Organic matter as well as various micro- and macrocomponents in the aquatic environment are closely associated with suspended mineral particles, e.g. are absorbed on single particles forming complexes with metal (usually iron) oxides, become aggregates and are deposited or transported in this form within the lake.

The majority of sediment grain-size studies are associated with marine, loess and fluvial sediments (Lu & An, 1997; Buurman *et al.*, 2001; McCave *et al.*, 2006), which are usually poor in organic matter. Also these researches commonly focus on coarse-grained (sand, gravel etc.) and generally rather well sorted sediments. The grain-size distribution in small Estonian lakes has not been studied widely; however, a number of researches have been carried out recently (e.g. Punning *et al.*, 2004; Terasmaa, 2004, 2005a,b; Vaasma, 2004, Punning *et al.*, 2005a,b; Terasmaa & Punning, 2006; Vaasma, 2006 etc.). For large lakes a comprehensive lithological approach was developed earlier by Raukas (1981, 1999).

2. OBJECTIVES

The objectives of the study were:

- to improve methods of grain-size analysis for studying sediments of different Estonian lakes;
- to develop pre-treatment methods for the grain-size analysis of fine-grained lacustrine sediments rich in organic matter;
- to use the sediment grain-size composition for determining the impact of short-term water level changes;
- to use modernised methods of grain-size analysis for mapping the spatial distribution of surface sediments of Lake Peipsi and to describe sedimentation dynamics.

3. STUDY AREAS

The lithological composition and grain-size parameters of surface samples and short cores were studied in different sedimentation environments: mainly in a small lake, Lake Martiska (**I, II**), and a large lake, Lake Peipsi (**III, V, VI**) (Figure 1, Table 1). Lake Tündre (Figure 1D) was selected to determine the influence of sediment pretreatment methods (**IV**) on the grain-size spectrum in the cohesive sediments.

Table 1. Characteristics of lakes Martiska, Peipsi *s.s.* and Tündre

Characteristic	Lake Martiska	Lake Peipsi	Lake Tündre
Coordinates	59°15′45′′ N, 27°34′13′′ E	58°41′53′′ N, 27°23′53′′ E	57°57′19′′ N, 25°36′32′′ E
Area, ha	3.5	261 100	71.2
Volume, m^3	80 000	21.8×10^9	3 143 000
Maximum depth, m	8.5	12.9	11.5
Average depth, m	2.3	8.3	4.4
Maximum length, m	370	81 000	2560
Maximum width, m	140	47 000	360
Average slope inclination, %	8	0.1	2.3
Dynamic ratio	0.08	6.16	0.19

3.1. Lake Martiska

Lake Martiska (hereafter L. Martiska) (Figure 1B) is located in north-eastern Estonia, in the central part of the Kurtna kame field. The kame field includes 40 lakes in glaciokarstic depressions forming the Kurtna Lake District (Saarse, 1987; Punning, 1994). The area lies in a transitional zone between a densely populated and heavily industrial oil shale mining and processing region and a sparsely inhabited territory with extensive forests and mires. Although previously oligotrophic (Mäemets, 1968), L. Martiska is now mesotrophic due to direct and indirect impacts of oil shale mining and processing (Punning, 1994; **I, II**).

Lake Martiska is a small (area 3.5 ha), closed, north-south elongated lake with a weakly indented shoreline. Its basin is bipartited (Figure 1B): the depth of its southern part is over 3 m, and the northern part is over 8 m deep (maximum depth of 8.5 m, Table 1). The lake lies in a deep glaciokarstic hollow. Its dynamic ratio of 0.08 means that sedimentation is very weakly influenced by wind/wave activities. The analysed sediments consisted mainly of unconsolidated dark brownish gyttja. The lake is strongly stratified in summertime with a thermocline at 3–4 m. The hypolimnion is oxygen deficient except during the spring and autumn turnover periods (Vaasma, 2006).

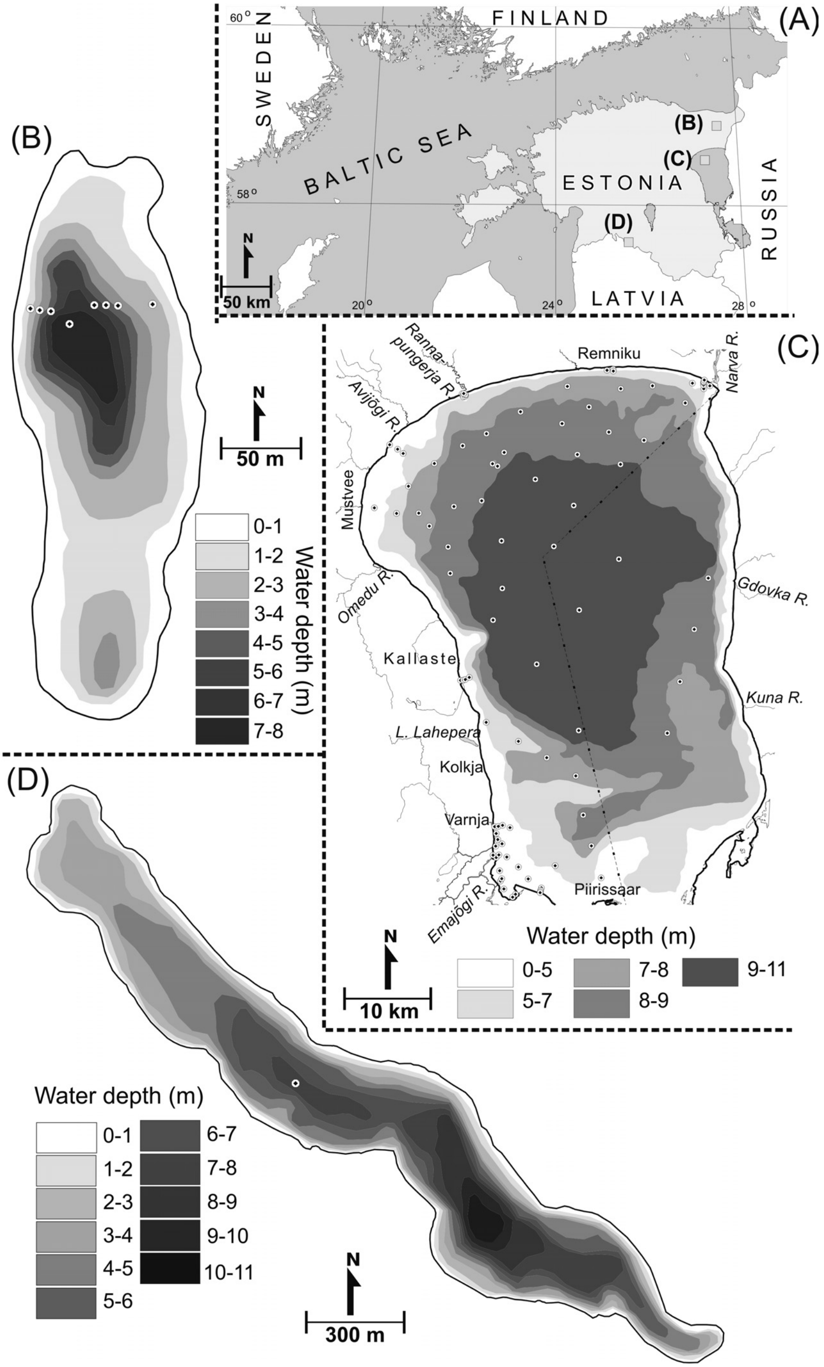

Figure 1. Location of the studied lakes (A) and bathymetric maps of Lake Martiska (B), Lake Peipsi (C) and Lake Tündre (D). Dots denote sampling sites.

The shores in the west are steep and sandy, being gentler elsewhere. To the west of the lake is a sandy kame which is up to 20 m in relative height. To the east the kame field area is up to 6 m in relative height and with somewhat finer sand. The south-western shore is partly peaty, and there are old stumps and trunks of trees. The southern (shallow) end of the lake is rich in vegetation.

On the catchment area pine forests dominate on the poor soils on the well-sorted mostly fine-grain sands. A sandy area, which has become a popular resort beach, lies at the northern shore. There are also some smaller sandy swimming and fishing places along the waterline (mostly on the eastern shore). On the south-western and western shores there is burnt pine forest, which spreads over 10 to 20 m from the shore. The trees bear traces of burning up to the height of 1 m. Undergrowth has perished.

The main human impact on the Kurtna lakes is connected with emissions from the oil shale based industry, located 15–30 km from the lakes, and the lowering of the water level in L. Martiska due to groundwater exploitation. The Estonian oil shale deposits have been exploited since 1916. The abstraction of groundwater in this region started at the end of the 1950s, resulting in the lowering of water level by up to 3.0–3.5 m and consequent shore and slope erosion (Figure 2). Reorganisation of the local economy after Estonia regained its independence in 1991 has led to a continuous decline in the production of oil shale and a transfer to the use of more environmentally friendly technologies. As a consequence, the lake environments in the Kurtna area have been restored towards a more natural state. The water level in L. Martiska has risen by up to 3 m (by 2001), approaching almost its pre-disturbance level (Figure 2).

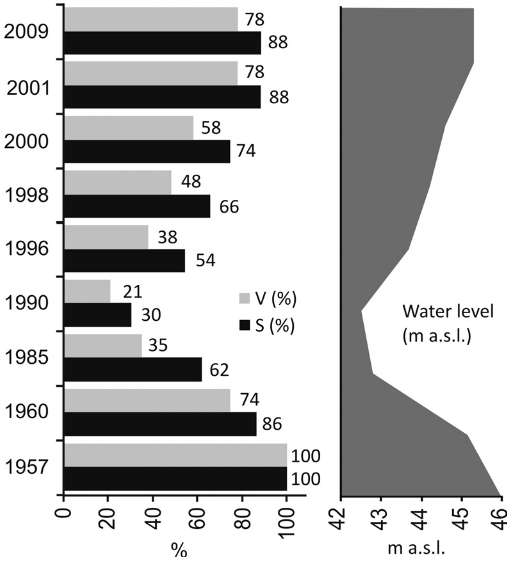

Figure 2. Changes in the surface area (S) and volume (V) according to water-level fluctuations in L. Martiska.

3.2. Lake Peipsi

Lake Peipsi (Figure 1C) is the fourth largest lake with respect to the surface area and the biggest transboundary lake in Europe (surface area 3555 km^2, maximum length 152 km and width 47 km) (Jaani & Raukas, 1999). It belongs to the Baltic Sea catchment and is located south of the Gulf of Finland into which it drains via the Narva River. The lake is submeridionally elongated on the border of Estonia and Russia. It consists of three parts: Lake Peipsi *sensu stricto*, Lake Lämmijärv and Lake Pskov. This study describes the largest part of the lake – L. Peipsi *s.s*. (Table 1; **III**, **V**, **VI**).

The present-day lake is shallow: its average depth at medium water level is 8.3 m (Jaani & Raukas, 1999; Table 1). The central part of the lake is 9–11 m deep; the coastal zone is shallow and descends to the rather monotonous floor in some kilometres in the eastern and western coasts. The area and depths of the lake are highly dependent on the water-level fluctuations. The capacity of its basin is more than 21 km^3 (Jaani & Raukas, 1999) of relatively clean water. However, eutrophication is today a major problem concerning L. Peipsi.

A flat lowland area 30–45 m a.s.l. with peculiar landforms rarely higher than 80 m surrounds L. Peipsi. The 50–60 m deep glacially eroded depression, which presently holds L. Peipsi, was formed in Ordovician and Devonian sedimentary bedrock. Till covers the bedrock over the entire lake bottom and is overlain by a ca 10 m thick bed of glaciolacustrine clay or silt. The distribution of lake marl and gyttja is limited to the deeper central part of the lake while the thickness of the calcareous layer varies from a few centimetres to 1.9 m. Gyttja deposits, up to 6 m thick, are greenish in their lower portion and change to dark black towards the top (Hang *et al*., 2001; Hang & Miidel, 2008).

Wind-drift and wind gradient (compensation, flow, seiche and internal pressure streams) exist in L. Peipsi (Kallejärv, 1973). Waves are steep and short, and with the wind speed of 8 m/s their height is 60–70 cm (Sokolov, 1983). Waves of such height are most common in L. Peipsi (57%). The highest waves 2.3–2.4 m in height were recorded in 1961 and 1962 with the wind speed of 20 m/s (Jaani, 2001).

The average velocity of the wind is 4–5 m/s. South-westerly and southerly (45–50%) winds predominate in the depression of the lake causing high rises in the water level in the northern part of the depression and intensive erosion of the coast (Tavast & Raukas, 2002). Longshore drift is there from west to east, and therefore the outflow of the Narva River, located in the north-eastern corner of the lake (Figure 1C), needs to be regularly scoured of sandy sediments, blocking the outflow. About 12 500 m^3 of sand accumulates here annually.

The catchment of L. Peipsi covers nearly 25% of Estonia's territory. The portion of L. Peipsi belonging to Estonia constitutes 89% of the total surface fresh water and yields 95% of the freshwater fish catch of the country (Nõges, 2001). Due to the intensive industrial activity within the lake's catchment, there are various human impacts on the lake. Lake Peipsi plays an important role in the fishery and transport, which both depend highly on bottom deposits, topography and coast types.

3.3. Lake Tündre

Lake Tündre (hereafter L. Tündre) is located in South Estonia (Figure 1D; **IV**) on the southern part of the Sakala heights. The catchment area is somewhat undulating and to the north-east of the lake are sandy and gravelly kames. On the catchment area pine and spruce forests dominate; except for the south-west where arable lands with some households are situated. The north-western part is swampy and covered with trees.

The lake lies presumably in an outflow hollow of glacier melting water. Lake Tündres (area 71.2 ha) is a north-west to south-east elongated 2560 m long lake with a winding shoreline (Table 1). The steep shores are sandy and in north-western part muddy. The relief of the bottom is variable. The deepest part (11.5 m) of the lake is located somewhat to the south-east of the central point (Figure 1D). In the central part of the lake is a stony shallower area (Mäemets, 1968). Close to the shoreline the sediments are sandy and clayey and in the deeper area dark black very cohesive and homogeneous organic matter rich (48.6%) gyttja occurs. That is why the typical south Estonian lake L. Tündre has a suitable sediment composition (almost 50% organic matter, large amount of diatoms, fine-grained) to analyse pre-treatment methods and to determine the grain-size spectrum by laser diffraction methods.

Lake Tündre has a weak in- and outflow. Reddish-brown bog water carried by streams into the lake and the water of the lake are yellowish-brown. Because of its colour the water warms considerably in the summertime.

4. METHODS

4.1. Fieldwork

In L. Martiska (Figure 1B, **I, II**) a detailed mapping of the lake bathymetry was undertaken in the wintertime of 2003 and 2005 from ice using a measuring disc of 10 cm in diameter. The sampling was performed with a modified Livingstone–Vallentyne piston corer and the lithology of the cores was recorded in the field. Eight short cores (0–24 cm) were collected on the cross-section through the deepest part of the lake. Sampling was continuous with intervals of 1 cm. The samples were saved in previously numbered and weighed plastic boxes. The site location was determined by GPS Garmin 12 (horizontal accuracy 3–5 m). To map the sample sites precisely, measurements were made in the winter from ice by using a measuring tape.

In L. Peipsi 97 samples with a thickness of 5 cm were taken from surface sediments from a research vessel during 2004–2009 (Figure 1C; **V, VI)**. For political reasons, most of the samples were taken from the Estonian side but during joint expeditions with researchers from the Estonian University of Life Sciences, some sediment samples were also collected from the part of the lake that belongs to Russia. Besides sites located all over L. Peipsi, there are more detailed data from profiles on the coastal zone. From the deeper area of the lake core sampling was performed with a modified Livingstone–Vallentyne piston corer from ice (**III, V, VI**). The lithology of the core was described in the field. On the coastal zone sediments were taken with a grab sampler. Samples were saved in previously numbered and weighed plastic boxes. The site location was determined with GPS Garmin 12, Garmin GPSMap 60 and Garmin Oregon (horizontal accuracy 3–5 m). Water depth was measured with a disc 10 cm in diameter and by sonar.

In L. Tündre samples with a thickness of 15 cm were taken from surface sediments in summer 2006. The sampling was performed with a modified Livingstone–Vallentyne piston corer from the deepest part of the lake and the samples were saved in a 10 l hermetic plastic box. The total amount of sediments taken was 5 l.

4.2. Laboratory analyses

The sediment samples were analysed in the laboratory immediately. Dry matter in sediments was determined by drying the samples at 105°C to constant weight. Organic matter was measured as loss-on-ignition (LOI) upon heating at 550°C for 3.5 h. The carbonate content was calculated as the loss of weight after burning the LOI residue at 950°C for 2.5 h (Heiri *et al*., 2001) (**I–VI**).

4.2.1. Development of pre-treatment methods for lacustrine sediments

In section 5.1 the results of an experimental investigation of five different pre-treatment methods (Figure 3) are presented for measuring grain-size distribution of allochthonous siliclastic matter in cohesive organic-rich sediments by laser diffraction method (**IV**). A total of 230 results of parallel measurements of grain-size distribution were obtained for analysis.

For the removal of organic matter thermal combustion (at 550°C) and wet oxidation with hydrogen peroxide (H_2O_2) were used and compared. Carbonates were removed with hydrogen chloride (HCl) or with heating at 950°C. To remove biogenic silicates (diatom valves and their fragments) potassium hydroxide (KOH) was used (Conley, 1998; Lyle & Lyle, 2002).

For thermal combustions the samples were placed in previously weighed crucibles, but chemical reactions were implemented in centrifuge tubes. To avoid flocculation of grains 1% solution of sodium hexametaphosphate $(NaPO_3)_6$ was used (Murray, 2002; Andreola *et al*., 2004) before measurements.

For estimating the efficiency of different pre-treatment methods a light microscopic study of the samples was conducted. Suspensions were mounted on glass slides using Naphrax® (R.I. ≥ 1.74) and examined under a compound light microscope. The general composition of each sample and sizes of particles were measured using an Olympus BX41 microscope with phase-contrast at 1000× magnification.

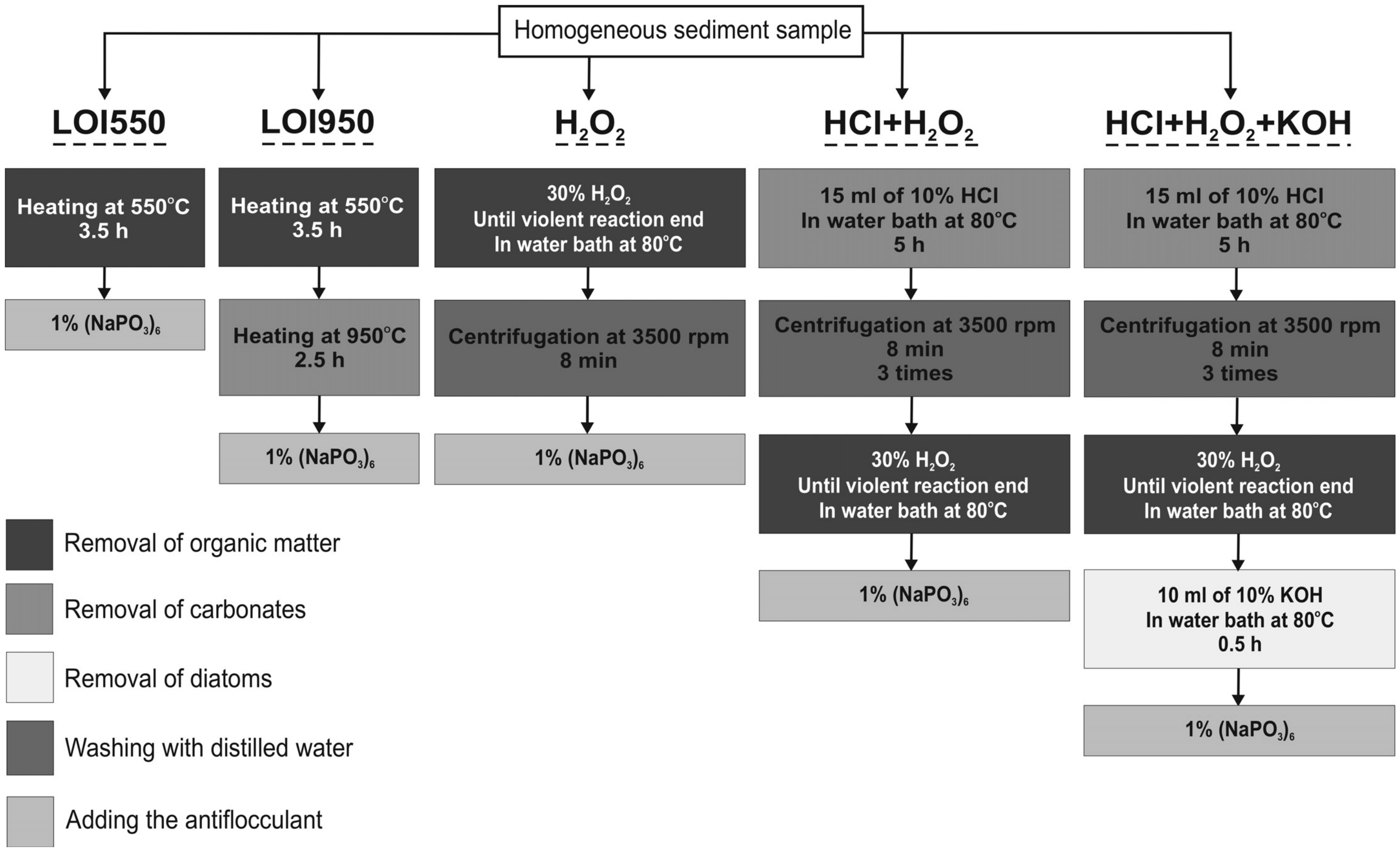

Figure 3. Pre-treatment workflows for grain-size analysis.

4.2.2. Grain-size measurements

Sediments in the erosion and transportation areas of the studied lakes usually vary significantly from silt to sand. Depositions in the accumulation areas are comparatively loose, with a high water and organic content, and are mainly fine grained. Therefore various grain-size measurement methods are required. For coastal samples where sand occurs grain size was determined by wet sieving. Sieving was carried out on five (1000, 500, 250, 63, 36 μm) metallic woven mesh sieves (if necessary gravel and shells were separated by a 2000 μm sieve) in a Vibratory Sieve Shaker "Analysette 3" PRO (**I, III, V, VI**).

Fritsch Laser Particle Sizer "Analysette 22" was used for measuring the grain-size spectra in fine-grained cohesive sediments (**I–VI**). The laser diffraction method for the analysis of sediment grain-size distribution is nowadays widely used (McCave & Syvitski, 1991; Konert & Vandenberghe, 1997; Buurman *et al.*, 2001; Bohling, 2004; Blott & Pye, 2006; McCave *et al.*, 2006). The used laser particle sizer can measure grain size in the range of 0.3–300 μm and to distinguish 62 fractions. The laser particle sizer's parallel laser-light is scattered to fixed spatial angles, which depend on the particle size and the optical properties of the particles. A lens focuses the scattered light concentric to the focal plane and the grain size is determined with special software of the device.

Previous experience has shown that to get statistically reliable results a minimum of three reproducible measurements have to be made whose standard deviations do not exceed precision. Precision is achieved by the laser particle sizer's own standard sample Fritsch Standard F500. The maximum standard deviation of the repeated measurements was 8%.

4.3. Data analysis

The results are given according to the Udden–Wentworth grain-size scale (Last, 2001; Table 2). In order to describe the surface sediment composition, fine-grained mineral sediment was used as the common nominator for the clay and silt fractions (<63 μm; >4 Φ units), and coarse-grained sediments were used as the common nominator for the sand fraction (63–2000 μm; from 4 to –1 Φ units) (Table 2).

Table 2. Grain-size scale by Udden–Wentworth (Last, 2001)

	Particle diameter		Descriptive terms		
(Φ units)	(mm)	(µm)			
0 to –1	1.0–2.0	1000–2000	Very coarse	Sand	Coarse-grained sediment
1	0.5	500.00	Coarse		
2	0.25	250.00	Medium		
3	0.125	125.00	Fine		
4	0.0625	62.50	Very fine		
5	0.03125	31.25	Very coarse	Silt	Fine-grained sediment
6	0.01563	15.63	Coarse		
7	0.00781	7.63	Medium		
8	0.00391	3.91	Fine		
9	0.00195	1.95	Very fine		
>9	<0.00195	<1.95		Clay	

For general classification of sediments and separation of sediment groups in L. Peipsi, the thesis uses Shepard's (1954) scale, which takes the share of different grain-size fractions in the sediment composition into account while grouping the sediments. In this thesis the sediment group "mixed sediments" includes different grain-size groups (silty sand, sandy silt and clayey silt).

Statistical analyses were made with the laser particle sizer control program (*Analysette 22_32BIT Fritsch GmbH (C) 2000)* and *MS Excel*. Some results are given according to the terminology of Folk (1980) in terms of median grain size ($\Phi_{50} = -\log_2 D$ (mm)). In this scale coarser fractions have smaller Φ_{50} values and Φ_{50} for silt and clay fractions is >4 (Table 2).

Cartographic analysis was made with *MapInfo Professional 9.0* and *VerticalMapper 2.5* (**I**–**VI**). Statistical analysis was made with *XLSTAT2008*. Stratigraphic zones for the L. Martiska cores were determined with *CONISS* (constrained incremental sum of square cluster analysis) in the *TILIA* program (Grimm, 1990).

5. RESULTS AND DISCUSSION

Grain-size distribution is one of the most fundamental physical properties in sedimentology. Determination of the sediment grain size is not a trivial task because of the heterogeneity of the shape and density of particles and absorbed materials (organics, carbonates etc.). Therefore, special attention is paid to methods of grain-size analysis (**IV**). Depending on the sediment particle structure and minerals' physical and chemical composition as well as the sedimentation environment (electric conductivity, temperature, cycling of substances etc.) varied structures may occur. Thermal or chemical treatment is accompanied by different transformations reflected in the grain-size spectra and in the statistical data. It is especially difficult to choose the right pre-treatment method of cohesive sediments for the analysis of the grain-size distribution of allochthonous mineral matter.

5.1. Development of pre-treatment methods

As fine-grained material tends to dominate in the sediment composition of the accumulation areas of small lakes of Estonia, sieving is not the best method for grain-size analysis. Undoubtedly, this method will still be used in studies of sandy shores (**V**, **VI**). By using the sieving method, mainly the coastal areas of L. Peipsi and of some small lakes have been mapped. It is reasonable to use sieving in the case of additive-free sediments. In other words, in the cases where no organic and carbonate matter is present. As the sieving method requires a rather large amount of sample, pre-treatment would be extremely time consuming and troublesome. Sieving the material that contains organic matter, which will later be separated, might not be right. In this case, conglomerations of particles of unknown size may form or break into pieces when vibrating on the sieves. As the two-dimensional sieve diameter is used for measuring, the third dimension of particles cannot be determined (Last, 2001). Moreover, a particle whose one dimension does not correspond to the eye diameter of the sieve can go through the sieve. For example, a particle with dimensions 0.6 mm × 0.6 mm × 10 mm might pass a 0.63 mm sieve. As the Institute of Ecology at Tallinn University studies mainly cohesive lake sediments, analysis methods need to be changed and new ones developed. That is why the institute started to use and the author of the thesis to develop a new laser diffraction method and a Fritsch Laser Particle Sizer "Analysette 22" was obtained. This device enables detailed analysis of grain-size distribution in the fine-grained sediments.

To determine the influence of sediment pre-treatment methods (**IV**) on the grain-size spectrum of lacustrine sediments, two different types of sediments were selected: organic-rich (from L. Tündre, a typical South Estonian lake) and mineral matter rich sediment (L. Peipsi). Sediments from L. Tündre are dark black very cohesive and homogeneous organic matter rich (48.6%) gyttja (Table 3). The surface sediment of the L. Peipsi sample consisted of dark grey gyttja with a small (3.3%) content of organic matter (Table 3).

Table 3. Sediment lithology of lakes Tündre and Peipsi

	Lake Tündre	Lake Peipsi
Water content, %	91.7	50.5
Dry matter, %	8.3	49.5
Organic matter, %	48.6	3.3
$CaCO_3$, %	4.1	3.1
Mineral matter, %	47.3	93.6
Biogenic silica, valves/g	133×10^6	20×10^6

The results show that the pre-treatment methods influence substantially the grain-size spectra measured by the laser particle sizer (**IV**). It can be clearly seen that after thermal combustion the median value of grain size is shifting more to the coarser-grained (very coarse silt) fraction than in the chemically treated samples. This may show the effect of aggregate formation (Murray, 2002). The intensity of aggregation depends on the pore-water content and sediment texture and composition.

This aggregation effect can be avoided by chemical pre-treatment. Combustion for the removal of organic matter by the widely used H_2O_2 method is very time consuming and the amount of H_2O_2 exceeds essentially the stoichiometrically needed amount. The content of Fe plays an important role in standardising the procedures. It is an inhibitor of H_2O_2 disintegration, and therefore the demand for H_2O_2 increases. Because of a large amount of Fe and its compounds in the sediments it was very hard to get reproducible results (Figure 4A) (standard deviation larger than 10%). After the H_2O_2 treatment part of the samples were treated applying the LOI550 method. In the course of this treatment 12% of the analysed matter was eliminated. This suggests that wet oxidation with H_2O_2 leaves the oxidation reaction of organic matter incomplete.

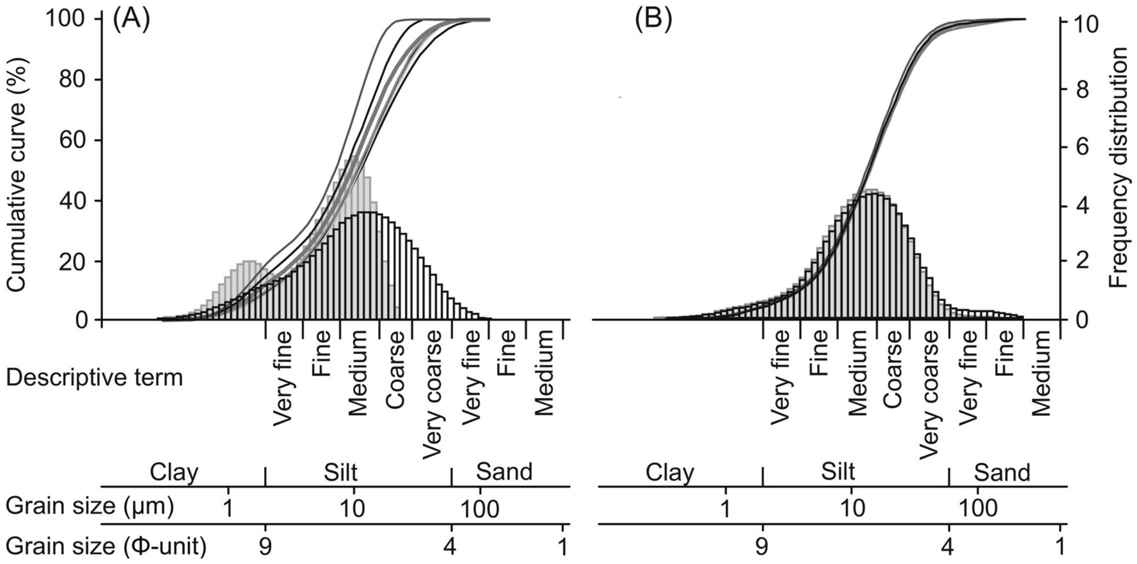

Figure 4. The most contrasting results of repeated measurements with some cumulative curves and two grain-size distributions in L. Tündre: (A) pre-treatment method H_2O_2; (B) pre-treatment method $HCl+H_2O_2$ (**IV**).

The specific surface area of sediment in L. Tündre was the largest (13729.0 cm²/g) in the case of treatment with H_2O_2, which means that the percentage of fine-grained matter (clay, very fine silt) was the greatest. This may be due to the carbonate content.

As an additional method for checking the completeness of the removal of non-siliclastic material light microscopic analysis was used. This analysis enables to see the sample content, monitor the pre-treatment process and make primary estimations of the grain-size distribution. In addition, it proves the correctness of distribution and gives the best descriptive characterisation. Also the presence of absorbed matter can be followed. Light microscopic analysis also helps to make the decision which pre-treatment method to use. Microscopic analysis showed that the samples were red-coloured after H_2O_2 treatment, which means that they were coated with Fe oxide. To remove carbonates and Fe oxide, the samples were extracted with HCl as suggested by Dominik & Kaupenjohann (2000). In that case the needed H_2O_2 amount and the treatment time decreased substantially. Treatment with HCl decreased significantly the specific surface area of the samples of L. Tündre and repeated measurements were very similar (Figure 4B).

As the size of diatom valves is mainly from 5 to 200 µm (Round *et al.*, 1990), their presence might essentially distort the grain-size spectra. The most effective elimination method of diatoms, which are composed mainly of biogenic SiO_2, is treatment with alkali (Conley, 1998; Lyle & Lyle, 2002). Microscopic analysis allows monitoring changes in sediment samples after removing diatoms by using the $HCl+H_2O_2+KOH$ method. After treatment with $HCl+H_2O_2+KOH$ the samples were white and individual grains were clearly distinguishable (Figure 5B). The median value of grain-size distribution of the sediment samples from L. Tündre shifted towards a finer grain-size median (Figure 5B). This is analogous to the results of Reynolds *et al*. (2004) and is also confirmed by the increase in the specific surface area of sediment from 8282.0 to 12310.6 cm²/g. The grain-size distribution of samples treated by this method shows an increase in the percentage of clay and very fine silt (10.8% and 13.5%, respectively) compared to $HCl+H_2O_2$ treatment (4.7% and 7.1%, respectively). However, the content of medium silt was smaller (18.6%). In samples from L. Peipsi treated with $HCl+H_2O_2+KOH$ changes occurred in the same fraction classes and their trend was the same as in L. Tündre. The decrease in the percentages of fine, medium and coarse silt after using KOH indicates a certain amount of diatoms in those samples.

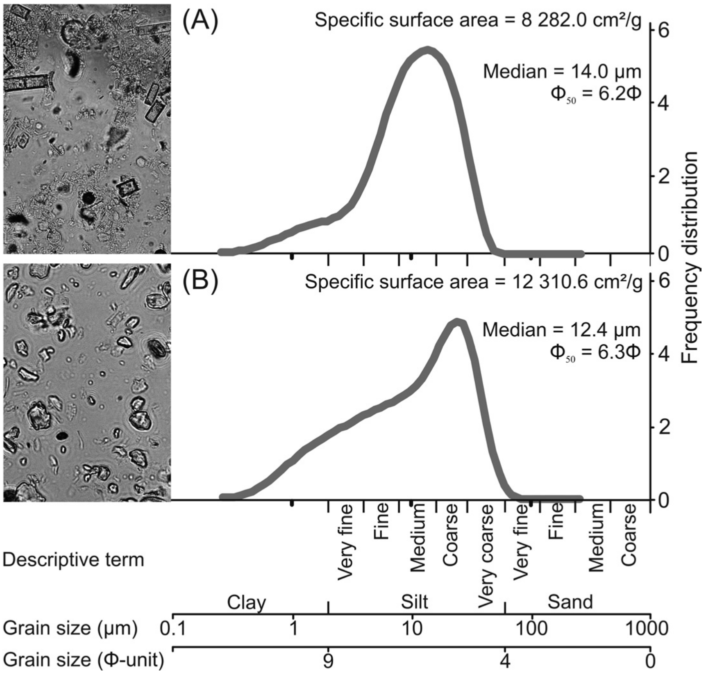

Figure 5. Grain-size distributions and microscopic observations after treatment with $HCl+H_2O_2$ (A) and $HCl+H_2O_2+KOH$ (B) (**IV**).

So treatment with $HCl+H_2O_2+KOH$ proved to be the most effective. Now the method has been developed further and all chemical reactions are carried out in a standard 1 l beaker and on a heating plate. This ensures that the process runs faster and there is no need for sample centrifugation. The development of the present method took place in consultations with the sedimentology laboratory of Vrije University in the Netherlands.

The treatment of samples is performed on a heating plate. The workflow is the following:

1. Place the sample in a 1 l beaker, remove carbonates with 5 ml of 10% HCl. Heat the sample to the boiling point and boil no more than 1 min. If there is a violent reaction, add more acid. Avoid too large excess of HCl. After boiling fill up the beaker with distilled water and leave it to stand for 24 h.
2. Decant the solution and oxidize organic matter with 10 ml of 30% H_2O_2. Avoid boiling to dryness by using distilled water. Too active reaction can be controlled by spraying the sample with distilled water. If violent reaction continues, add more H_2O_2.

3. After the end of the active reaction add distilled water up to 100 ml, and then boil until all the H_2O_2 is removed.
4. Clean the wall of the beaker with distilled water. Avoid reaching a volume of more than 100 ml.
5. Add 2.5 ml of 10% KOH to remove diatoms. Heat the sample to the boiling point. After that fill up the beaker with distilled water and leave it to stand for 24 h.
6. Decant the solution down to approximately 75 ml. Add 300 mg of the antiflocculant $(NaPO_3)_6$ and heat the sample to the boiling point.
7. After cooling the sample is ready for measuring the grain-size spectra by a laser particle sizer. It is very important to measure the whole sample. The amount of the sample depends on the sediment properties and settings of the device.

The elaboration and inculcation of a scientific methodology is a long process. The methods described above have been implemented in works focused on palaeolimnology. These have provided experience for developing the pre-treatment method to such a level that we can be certain about the validity of the obtained results.

5.2. Temporal changes in the sedimentation pattern

Lake Martiska is a very good site for grain-size distribution research (**I, II**). According to monitoring data (Punning, 1994), a very specific phenomenon has influenced the development of L. Martiska: the water level fluctuated by 3–3.5 m due to groundwater abstraction (Figures 2 and 6). Therefore two phases could be distinguished in the sedimentation process in the lake: (1) regression phase since the beginning of the 1960s; (2) transgression phase since 1992 up to nowadays, during which the water level recovered in response to a decrease in water use. Our earlier studies on the impact of water-level fluctuations in small Estonian lakes (Punning *et al.*, 2004) showed that sediment erosion, redistribution and accumulation are linked to changes in bottom topography caused by fluctuations in the lake level. The firmest evidence for this is recorded in the marginal areas. The amount and origin of the reworked matter associated with this sediment redistribution varies both spatially and temporally, as the changes in sedimentation mechanisms have a significant impact on the accumulation dynamics.

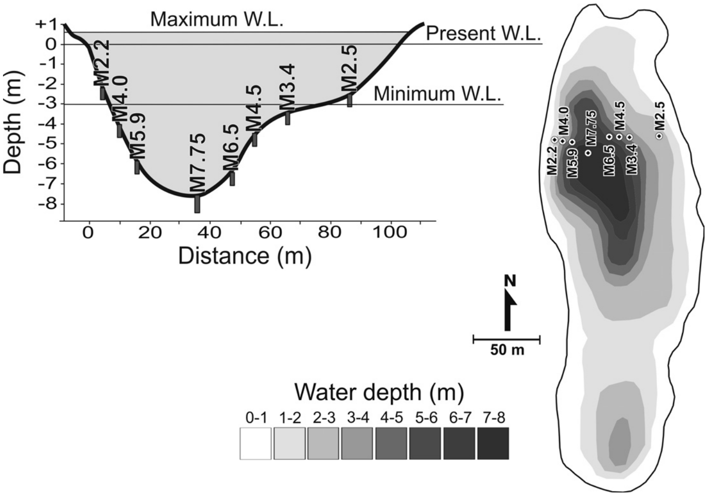

Figure 6. Water levels (W.L.) in L. Martiska and the locations of the sampling sites. The codes of the sampling points also show the water depth at the site.

The water-level fluctuations are reflected in the mineral matter concentration of the sediment (Figure 7) and in grain-size variations (Figure 8) (**I, II**). The values of eight studied short cores show that in the lowermost part the concentration of mineral matter varies very little. This means that the main sources of mineral matter were well-sorted sediments accumulated before the water-level fall. Also the relatively stable values of mineral content in cores deeper than 14 cm (Figure 7) suggested homogeneity of the source material and depositional environment. Above ca 14 cm the concentration of mineral matter increases steadily in almost all cores. When the water level decreases, the mineral matter content of the cores in the deeper area of the lake increases because these areas become close to the coastal zone. From this zone the eroding material may be carried deeper down due to gravity compared to the period when the water level is higher.

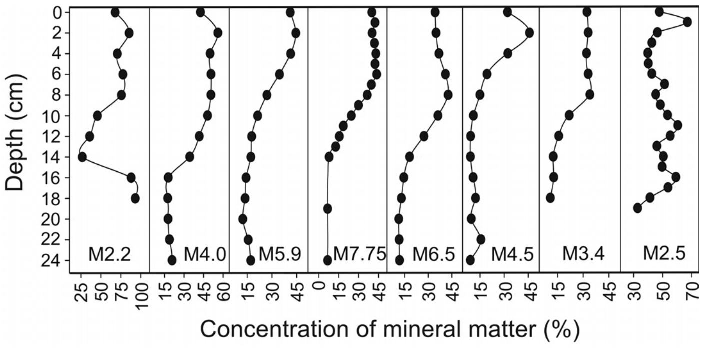

Figure 7. Concentrations of mineral matter in short cores from L. Martiska. For locations see Figure 6. The codes of the sampling points also show the water depth at the site.

The regression of the water level has resulted in extensive erosion and redeposition of sediments, changes in the distance to the shore and displacement of the erosion–transport–accumulation zones (**I, II**). The sediments accumulated during this period originate from two principally different sources: in-lake concurrently accumulated sediments (mainly atmospheric input, influx from the catchment, autochthonous organic matter) and matter eroded from the nearshore area from where water retreated in the course of regression. The eroded matter consists of fine-grained sands (limnoglacial sands surrounding the lake) and of previously accumulated lacustrine sediments. In sites deeper than 3 m lacustrine sedimentation took place during the whole regression phase. When the regressive lake level reached –2.5 m the surface of sites M2.2 and M2.5 were higher than the lake level. In these cores the grain size of sediment is close to sands around the lake. In sites that have remained dry during regression periods, hiatus has formed and therefore the information contained in settled material in sites M2.2 and M2.5 cannot be viewed as a linear time-line. After the transgressive water level reached the surface of sites M2.2 and M2.5 sediment accumulation began there again.

The grain-size distribution of mineral matter in sediment samples (Figure 8) shows links with the fluctuation of the water level. When previous studies (Punning *et al.*, 2004) confirmed that more short-term and sharp changes in the water level occur in the sediment of the transition area, then in the case of L. Martiska the signal was even stronger in the deepest part of the lake. This might be also strongly influenced by the bottom configuration: in this lake the deepest part has steep slopes, therefore sediments are exposed to several influences and the signal showing the impact of water-level change reaches the bottom faster. The data suggest that during the regression medium silt sediments from depths of 14–15 cm up to 6–7 cm accumulated. Besides the lake morphometry the lateral transport of sedimentary material was influenced by the change in the littoral vegetation.

The grain-size distribution shows that at sites M5.9, M7.75 and M6.5 the sediment became coarser (Figure 8) when the water level started to fall. In the deeper part of core M7.75 the Φ_{50} values vary from 6.6 to 7.0, corresponding to medium silt. Above 14 cm the content of the coarser fraction increases, reaching a sharp maximum at 7 cm (Φ_{50} value 6.0; coarse silt). Upwards the proportion of silt increases but the mean grain size remains greater like in the deeper layers.

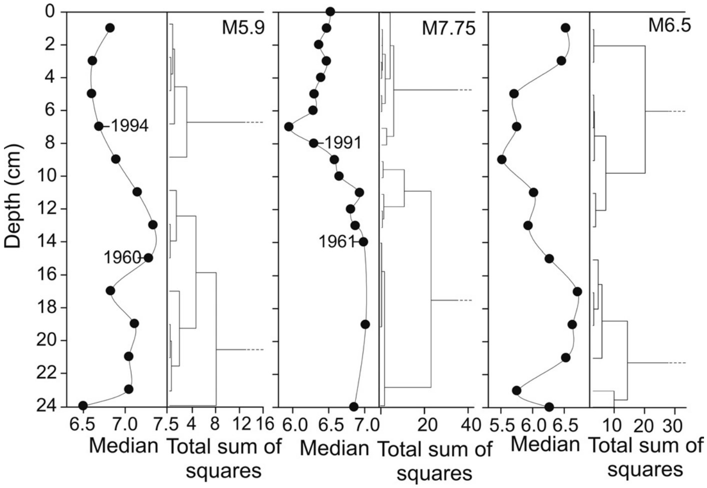

Figure 8. Median values (Φ units) of short cores M5.9, M7.75 and M6.5 and results of cluster analysis (mineral, organic and dry matter, grain size).

The mineral matter carried into the lake from the catchment area by surface water and wind starts to focus and fraction in a way that leaves the coarse-grained material accumulated in the shallower areas of the lake and finer-grained material in the deeper areas (Dearing, 1997; Terasmaa, 2005a,b). The reason for the decrease of the Φ_{50} value (Figure 8) that took place at site M5.9 from the 13-cm-deep sediment layer to the 4-cm-deep layer was the increasing domination of coarse-grained silt at this depth. An increase in the share of coarse-grained silt can also be observed at site M7.75 from the 14-cm-deep layer to the 7-cm-deep layer. The reason for the increase of the share of very coarse-grained silt in the 7-cm-deep layer might be the regression period and the subsequent approach of its shores to the deeper areas, where coarser mineral matter has been carried down along the steep slope. Therefore, as the water level gradually decreased, coarse-grained material moved towards the deeper areas.

In core M7.75 an up-core increase in the coarse fraction begins at a depth of about 14 cm, reaching a maximum value at 7 cm. This layer probably accumulated in 1992–1994 when the water level was the lowest. It can be expected that during the rapid subsequent transgression in the second half of the 1990s shoreline erosion reduced, while normal lake sediment accumulation increased. Correlations between mineral matter and Φ_{50} values show a positive link ($R = 0.65$). This suggests that as the sediment becomes coarser, its mineral matter content increases; therefore more coarse-grained mineral matter was carried into the sampling point during this period. During the regression period, the mineral matter content reached the maximum value, which reflects the addition of eroded material. The large mineral contents of site M2.2 (Figure 7) are caused by the location of the sample site both in the erosion area (slope inclination 36.30%) and close to the shore. Håkanson & Jansson (1983) demonstrated that in deep large lakes the mineral matter content is considerably higher in shallow areas of the lake with precipitous slopes than in deeper areas that are further away from the shore. The same links were also proved in the case of small lakes of Estonia (Terasmaa, 2005a). While comparing sites M2.2 and M2.5, the impact of differences of slope inclination and distance from the shore (6 and 20 m respectively) on the sediment can clearly be seen. Having gentler slopes (slope inclination 11.30%) and being further away from the shore, site M2.5 shows somewhat smaller mineral matter content in the sediment than site M2.2.

Cluster analysis was performed using the results of grain-size analysis and other lithological characteristics (mineral, organic, dry matter). Three time periods (Figure 8) corresponding exactly to monitoring data are clearly distinguishable. Also some shorter periods can be distinguished but the most important are stable sedimentation before regression (up to17–14 cm), regression (up to 7 cm), and transgression. Thus statistical processing confirmed the influence of water-level fluctuation on grain-size distribution.

In the course of the water-level rise the sedimentation regime stabilised and sediments became better sorted and finer in the direction of sediment transport. The reason might be that during the earlier regression, the top layer of the sediment became conformed (certain fraction intervals were carried away), and the subsequent material transport was balanced, even if the material was transported to the deepest area. The water line had no direct contact with the shore from where new coarse-grained mineral source material could be transported. Instead, as water level decreased, the material that had already been processed once was processed again. Thus, lake-level fluctuations were responsible for essential changes in the composition and structure of sediments and consequently in the biogeochemical matter cycling in the lake.

One can claim, relying on all the collected data and relevant analysis, that the regression and transgression periods (1960–2005) in L. Martiska have significant impacts on mineral matter carried into the sediment and its grain-size composition (Figures 7 and 8). It was proved that the extensive changes in the water level that have lasted for 50 years have left their mark in the sediment grain-size composition.

As the pre-treatment method has changed after the analysis of L. Martiska sediments, it is important to keep in mind that those results are directly comparable with each other, but only to certain level with the results of the later studies. The newly developed method (**IV**) will probably give slightly different results. However, as the sediments of L. Martiska do not contain much carbonates (maximum up to 2%) and diatoms (meaning that treatment with KOH is not necessary), the differences cannot be very significant. The changes could appear only by removing the absorbed matter with HCl and subsequently the grain size may be slightly coarser.

5.3. Spatial variation in the composition of surface sediments

To describe and analyse the role of sediments in the matter cycling in the large shallow L. Peipsi, detailed surface sediment mapping was conducted (**III, V, VI**). The studies of surface sediments of L. Peipsi are of great scientific and practical value, because the understanding of sediment processes helps to interpret palaeoinformation correctly and also to understand the lake's internal matter cycles. The granulometric composition of deposits determines greatly the physical and chemical properties of particles like cohesiveness, sorption ability, redeposition etc. (Van Rijn, 1993). After all, the sediments include various components that affect the natural environment and can return to the water environment.

The bottom of the central area in L. Peipsi is extensively covered with gyttja and the content of organic matter reaches up to 27.0% (Figure 9A; **III, V**). The colour of the sediment in the middle of the lake varies from black to dark grey. The rather low C/N values (8.0–8.8) of organic matter point to its autochthonous origin (the proportion of planktonic matter may be up to 90%; Punning & Leeben, 2003). Organic matter from the water column absorbs on silt and clay particles, causing the specific gravity of floating matter to increase, and the material settles on the bottom as flocculants (**III**). This was also proved by the study of polycyclic aromatic hydrocarbons (PAHs; **III**), which concluded that the content of PAHs is much larger in gyttja (0.01–0.08 mg/kg) than on coastal coarse-grained sediments and till (0.001–0.01 mg/kg).

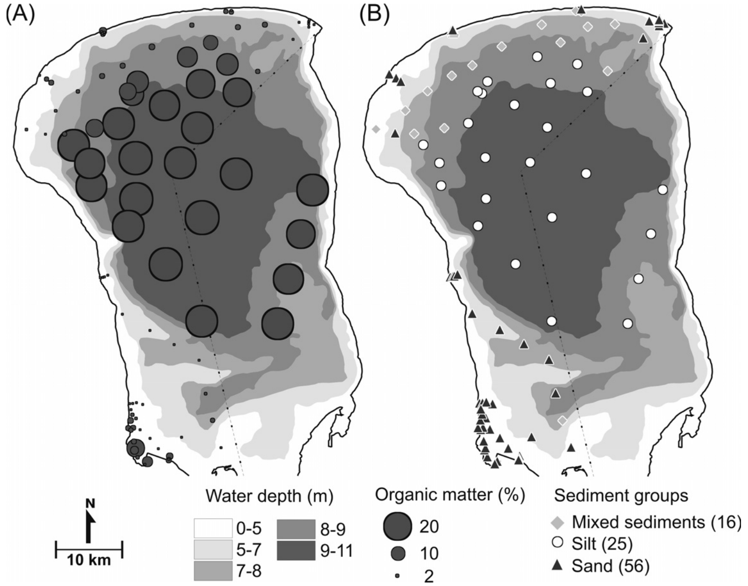

Figure 9. Organic matter content (A) and sediment groups (B) according to cluster analysis (**VI**) (number of samples in parentheses).

A database was compiled using the results of grain-size analysis of surface sediments taken from all over L. Peipsi. Cluster analysis made (**VI**) on the basis of this database enabled to divide sediments into three groups: mixed sediments, silt and sand (Figure 9B). Besides lithological characteristics of sediment, cluster analysis included also the distance of sampling locations from the coast and water depths.

In the central area of L. Peipsi it is possible to clearly distinguish the area of silt sediments (Figure 9B). The deposit consists mainly of fine-grained sediments (>87.4%) with median values of grain size ranging between 5.5 and 6.3 Φ units (Table 4, Figure 9B). Water is also the deepest there with depths ranging from 6.4 to 11.8 m. Measured from the west coast of the lake, the fine-grained mineral sediment zone begins from about 4.3 km from the coastline. In the northern part, it begins from 6.7 km (including the internal creek of 13 km in the north-western part), and on the eastern coast it begins from 3.3 km into the lake. The organic and fine-grained mineral factions have reached the deeper area of the lake basin due to the co-effect of several factors. However, it is still rather unclear how exactly the material has reached that location because such sediments are not abraded anywhere. Theoretically this material might originate from till and varved clay (Raukas, 2008).

Table 4. Lithological characteristics of sediment samples and bathymetrical parameters of sampling sites in L. Peipsi by sediment groups

		Depth (m)	Distance from shore (m)	Coarse-grained sediments (%)	Fine-grained sediments (%)	Median (Φ units)	Organic matter (%)
Mixed sediments (n = 16)	Minimum	4.4	250.0	3.9	46.5	3.5	1.5
	Maximum	8.8	8700.0	53.5	96.1	7.6	12.9
	Mean	7.5	4160.0	28.2	71.8	5.6	4.0
	Median	7.8	4650.0	28.5	71.5	5.7	3.0
	Standard deviation	1.2	2761.0	17.3	17.3	1.3	3.1
Silt (n = 25)	Minimum	6.4	3300.0	0.0	87.4	5.5	12.5
	Maximum	11.8	17700.0	12.6	100.0	6.3	24.2
	Mean	9.4	10028.0	1.5	98.5	6.0	21.1
	Median	9.4	9900.0	0.4	99.6	6.0	22.6
	Standard deviation	1.1	4001.0	2.7	2.7	0.2	3.3
Sand (n = 56)	Minimum	0.7	10.0	68.2	0.0	-0.3	0.0
	Maximum	9.3	11500.0	100.0	31.8	3.7	12.9
	Mean	3.8	1507.0	96.4	3.6	2.5	1.7
	Median	3.5	590.0	99.1	0.9	2.7	0.7
	Standard deviation	2.3	2484.0	7.0	7.0	0.7	2.2

Microscopic observations also showed silt particles to be coated with inorganic (oxides, carbonates, clay minerals etc.) and organic (mainly plant and animal detritus and bacteria) substances absorbed on the surface. Thus those sediments are cohesive by definition (Hayter & Pakala, 1989; Paterson, 1997) and their deposition and redeposition depend on many external and internal conditions. Corresponding sediments are characterised by an extremely high diversity because due to their dependence on physical-chemical and biological processes the cohesive sediments are rather unstable: they can change their composition very easily (Hayter & Pakala, 1989; Paterson, 1997).

The bottom of coastal areas of L. Peipsi is mainly covered with coarse-grained sediments, originating probably from coast abrasion. Close to the coast in the southern area of L. Peipsi the Quaternary deposits are mainly represented by well sorted coarse-grained sediments with a small content of organic matter (<12.9%, on average 1.7%) (Table 4, Figure 9A). This shallow (only 0.7 m in some places) area (from Kolkja to the central axis of the lake and from there to Piirissaar, continuing on the Russian side) is located within the influence of less active waves. The material near Piirissaar is probably of glaciofluvial delta origin (Raukas, 2008), with the median value of 2.7 Φ units (Table 4). Sieving is the best way to analyse such coarse-grained sediments. For example, our laser particle sizer leaves most of the material outside the device's measurement range. In the south-western part of L. Peipsi, sands spread extensively also in deeper parts (Figure 9B), in one location at a maximum depth of 9.3 m. However, usually sandy sediments dominate in shallower areas (Table 4). As more locations fall into the sand group, including the locations of coastal profiles, the mean value of depth can be somewhat lower.

In this study, the surface sediments of the northern and north-western parts of the lake with depths up to 8.8 m and distances from the coast up to 8.7 km were defined as mixed sediments that include till and varved clay. Till in the north-western part of the lake consists of unsorted particles, which have two peaks in the grain-size distribution corresponding to clay and sand fractions. The median grain-size values are 3.5–7.6 Φ units. The deposits also contain a large amount of coarse fraction (>200 µm) gravels and conglomerates. Very often, the bottom in this part of the lake is covered with zebra mussel (*Dreissena polymorpha*) that adhere to stones on till. The sediments vary most in the northern part of the lake and in the mouths of rivers. In the north-western part of the lake, near Lake Lahepera and also in some other places (in Russia) there is till, and in the mouth of the Emajõgi River there is peat (Raukas, 2008). The northern part of the lake has quite sporadic sediments, and small abysses and basins between underwater barriers by the coast. There organic matter might settle for a limited amount of time, depending on the season and dominant winds; however, during unfavourable conditions, organic matter might be absent from there.

The conducted analysis enables to claim that the slopes of L. Peipsi are very gentle (on average only 0.1% in the analysed sampling locations), and therefore irrelevant as far as sediment transport is concerned. As the lake environment is influenced by the shape of its bottom, it means that it also has an impact on the sedimentation rate in the lake (Jonasson, 1984). The peculiarities of the lake bottom also determine the location of erosion, transport and accumulation areas and the characteristics of settled material (Terasmaa, 2005a,b).

It was demonstrated that in the case of small lakes the slopes play an important role in the formation of the content of sediment (Terasmaa, 2005a,b). But in L. Peipsi – thanks to its high dynamic ratio (DR = 6.16, calculated according to Hakanson & Jansson, 1983; Lindström *et al*., 1999) – sedimentation is influenced by the movement of waves, and also by currents and rivers flowing into the lake. The composition and distribution of the surface deposits of L. Peipsi show that the general process of sediment formation consists of many processes: erosion of sandy coasts and primary surface sediment – mainly glaciofluvial deposits and till; river input; sediment transport towards the Narva River outflow; resedimentation due to the shear stress at the bottom with an important role of autigeneous material. The wind (and waves) is also crucial. Luettich *et al.* (1990) carried out a field investigation in Lake Balaton and showed that episodic increases in the suspended sediment concentration are forced by wind-generated surface waves. In addition, also precipitation, hummock ice and biota, plus human activity have started to play an important role.

Raudsepp *et al.* (2006) modelled the resuspension of gyttja in the north-eastern part of L. Peipsi. They found that with the wind speed of 15 m/s the wave height reaches 1.6 m and the near-bed current speed is up to 20 cm/s in the central area of the lake and 55 cm/s on the near-coast area. This is an extremely high speed: according to Kuhrts *et al.* (2004), the critical velocity for resuspension of cohesive organic-rich sediments is 1.4 cm/s. Sediment particles transported as a suspended load are moving at or very close to the velocity of fluid. It clearly follows from our core studies that when the near-bottom shear stress increases (extreme meteorological events, changes in the water level etc.) the sediment bed may be subjected to episodic resuspension. This phenomenon together with water-level fluctuation has a significant impact on resedimentation and thus on the distribution of pollutants within the lake and makes it possible to return deposited impurities to the food chain.

The map of the surface sediments of L. Peipsi shows three areas in the lake. Their lithological characteristics reflect clearly the impact of the current systems of the lake: on the near-coast area erosion of sandy coast sediments with clear longshore transportation exists and in the central deeper area deposition of fine-grained particles, transported due to the complicated current systems from near-coast areas and mixed with autochthonous organic material, plays the most important role. These sediments are clearly of cohesive character as proven by their texture and attached organic matter. The origin and dynamics of particulate matter and surface sediments give valuable information for understanding the dependence of the matter cycling and ecological state of the lake on the external and internal environmental factors. The detailed surface sediment map will open possibilities for understanding the matter exchange on the water–sediment interface and making budget calculations for the nutrients in L. Peipsi.

During the years of the surface sediment studies of L. Peipsi (2004–2009), the grain-size pre-treatment methodology changed. At the beginning diatom cells were not removed before measuring. Because of that the proportion of clay and very fine silt may be lower than without diatoms. In the situation where about 20×10^6 diatom valves/g are present the clay concentration may increase approximately by 6% and very fine silt by 2.5%. At the same time the concentration of medium silt may decrease by 4% and coarse silt by 3.5% (**IV**). If so, these differences between measurements would not cause changes in the grouping of L. Peipsi sediments. But it has to be considered that results at every site depend on its amount of diatoms.

6. CONCLUSIONS

The aim of the thesis was to develop pre-treatment methods for grain-size analysis of organic-rich cohesive lake sediments and to use them in paleolimnological studies. In analysing the distribution of allochthonous siliclastic matter in lake sediments, it is necessary to remove additional materials (organic, absorbed matter), which can affect the results. Complicated problems arise in the case of fine-grained material where secondary side-effects in the sedimentation environment as well as during the pre-treatment process could seriously affect the reliability of the obtained grain-size spectrum.

The main results of the study are:

- The most appropriate pre-treatment method to get reproducible results of grain-size distribution in studies of allochthonous siliclastic matter from organic-rich cohesive lake sediments was selected. It was established that the fastest and most reliable method for removal of organic matter from cohesive sediments was the combined method of oxidation on the heating plate with the use of 10% HCl followed by 30% H_2O_2 and after that 10% KOH. As an additional method for checking the completeness of the removal of non-siliclastic particles light microscopic analysis was used. This analysis enables to see the sample content, monitor the pre-treatment process and make primary estimations of the grain-size distribution. In addition, it proves the correctness of the distribution and the presence of absorbed matter can be followed.
- A workflow of the pre-treatment methods was developed. Different analysed methods were tested and applied to studies focusing on palaeolimnology in L. Martiska and L. Peipsi. One can claim, relying on all the collected data and their analyses, that the used methods of grain-size analysis are correct, and the obtained results are trustworthy and applicable.
- Detailed comparison of the well documented history of lake-level fluctuations in L. Martiska during the last decades with the lithological composition and grain-size parameters of its sediments showed that the grain-size parameters of lacustrine sediment varied according to the lake bathymetry and consequently were responsive to lake-level fluctuations.
- A new, improved and more trustworthy map of the surface sediments of L. Peipsi was compiled. On this map three distinct areas of surface sediments could be separated in L. Peipsi: mixed sediments, silt and sand. Their lithological characteristics reflect clearly the impact of the current systems of the lake: on the near-coast area the erosion of sandy coast sediments with clear transportation exists and in the central, deeper area deposition of fine-grained particles, transported due to complicated current systems from near-coast areas and mixed with autochthonous organic material, plays the most important role. The detailed surface sediment map improves the understanding of the matter exchange on the water–sediment interface and nutrients cycling in the L. Peipsi.

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JÄRVESETETE LÕIMISANALÜÜS: UURIMISMEETODID JA RAKENDAMINE

KOKKUVÕTE

Dissertatsiooni peamine eesmärk oli arendada lõimisanalüüsi eeltöötlusmetoodikat sobivaks orgaanikarikaste kohhesiivsete järvesetete uuringuteks paleolimnoloogias. Allohtoonse mineraalaine uurimisel on oluline eemaldada lisandid (orgaanika ning mineraalaine terakestele absorbeerunud ained), mis võivad mõjutada terasuuruse jaotuse tulemusi. Lõimise uuringud on komplitseeritud just peenterise mineraalaine korral, kuid lisaks looduslikele mõjuritele võivad tulemust ning selle korratavust mõjutada ka eeltöötlusmeetodid.

Doktoritöö peamisteks tulemusteks on:

- Töötati välja sobivaim lõimisanalüüsi eeltöötlusmeetod orgaanikarikaste kohhesiivsete setete analüüsimiseks. Tehti kindlaks, et kiireim ja usaldusväärseim oksüdeerimise meetod tuleb läbi viia kuumutusplaadil, töödeldes proovi järjestikku 10% HCl-ga, seejärel 30% H_2O_2 lahuses ning siis 10% KOH lahuses. Valitud meetodi puhul andsid kordusmõõtmised kõige parema reprodutseeritavuse. Lisameetodina tuleb kasutada mikroskoopilist analüüsi, mis võimaldab monitoorida eeltöötluse käiku ja selle toimet proovile. Samuti võimaldab see teha esmaseid järeldusi terasuuruse jaotuse kohta ja valida sobivat töötlusmetoodikat.
- Töötati välja eeltöötluse töövood. Erinevaid analüüsitud meetodeid kasutati paleolimnoloogilise suunitlusega uurimustes Martiska ja Peipsi järves. Tulemuste tõlgendamisel ning võrdlemisel teiste uuringutega tuleb arvestada eeltöötluses kasutatud meetodite eripäradega.
- Detailne võrdlus hästi dokumenteeritud Martiska järve veetaseme kõikumise andmete ja järvesette mineraalaine ja terasuuruste sisalduse vahel näitas, et terasuuruse jaotus varieerub sõltuvalt järve batümeetriast, veetasemest ning kaldajoone asendist proovivõtukoha suhtes. Veetaseme kõikumised on tihti kõige põhilisemaks mõjuriks järve aineringetele ja eriti just troofsustasemele. Veetaseme muutused muudavad järve põhja topograafiat ja settimisalade jaotust ning seetõttu mõjutavad otseselt settimisprotsesse, resuspensiooni ja sellega kaasnevalt ka akumuleerunud ainete veekeskkonda sattumist.
- Peipsi järve pindmiste põhjasetete uuringute tulemusi on korduvalt publitseeritud, kuid arvestades Peipsi järve tähtsust nii looduslikust kui ka majanduslikust aspektist, on selle teemalisi uuringuid olnud liialt vähe. Aastate lõikes on setete kaardistamine üha täiustunud ja koostise määramise täpsus tõusnud. Dissertatsioonis koostati uus ja usaldusväärsem Peipsi Suurjärve pindmiste setete kaart. Selle põhjal saab pindmised setted jagada kolme gruppi: liiv, segasetted, aleuriit.

Peipsi Suurjärve kohta saab üldistatuna öelda, et rannalähedaste erosiooni- ja transpordialade setete koostis varieerub suuresti – leidub liiva- ja mudapõhja, paiguti avaneb moreen. Akumulatsioonialadel, kus veesügavus ja kaugus rannast suur, kuhjub peamiselt peenterine materjal segatuna autohtoonse orgaanilise ainega. Kuna antud materjal allub kergemini sette transporti mõjutavatele teguritele (hoovused, lainetus, bioturbatsioon), siis kandub seda suuremates kogustes rannast kaugematele aladele. Detailne põhjasetete kaardistamine ning sette päritolu ja dünaamika mõistmine annab olulist informatsiooni mõistmaks järve arengulugu ja ökoloogilist seisundit. Settesse on ladestunud mitmeid looduskeskkonnale kahjulikke ühendeid, mis teatud tingimuste kokkulangemisel võivad uuesti veekeskkonda tagasi pääseda.

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PUBLICATIONS

I

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THE IMPACT OF LAKE-LEVEL FLUCTUATIONS ON THE SEDIMENT COMPOSITION

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Abstract. Lithological and granulometric investigations of the surface and short core sediments in L. Martiska (northeastern Estonia) showed that variations in the grain-size parameters and LOI content were influenced by the changes in deposition conditions during the regression and transgression phases monitored in the lake since the 1960s. During the regression and transgression phases displacement of the erosion-transport-accumulation zones in the lake took place depending on the bottom topography. The water level fluctuations are especially clearly reflected in grain-size variations in cores from peripherial area.

Keywords: lake-level fluctuations, palaeolimnology, resedimentation, sediment grain size

1. Introduction

Numerous sediment studies are focused on describing direct responses of various bioindicators, geochemical records and hydrological changes to the trophic state of a lake (Dearing, 1983; Engstrom, Swain, & Kingston, 1985). Less attention has been paid to sedimentary processes, especially to the grain size of lake sediments; however, these studies have been promising in investigating lake-level variations in small temperate lakes (Digerfeldt, 1986; Punning, Alliksaar, Terasmaa, & Jevrejeva, 2004).

The fluctuations of water level alter the lake morphometry and transform the characteristics of the sedimentation zones (erosion, transportation, accumulation; Håkanson, 1977) of the lake bed, thereby directly influencing sedimentation, resuspension as well as biogeochemical dynamics in the lake. Several studies have been successful in investigating water level variations in small temperate lakes (Dearing, 1997; Digerfeldt, 1986). Recent studies in palaeolimnology (Beierle, Lamoreux, Cockburn, & Spooner, 2002) have shown that the quantitative and qualitative analyses enable to describe sedimentological processes and distinguish the changes of the past environment. The main aim of this research was to study the lithological composition and grain-size parameters of sediments accumulated in a small lake and to compare the data with the historical evidences about its water level fluctuations.

2. Materials and Methods

The lithological composition and grain-size parameters of surface samples and short cores were studied in Lake Martiska (area 3.5 ha, maximum depth of 8.5 m) situated in northeastern Estonia (57°38′07″ N, 27°05′06″ E) in the area of the Kurtna Kame Field (Figure 1a, Table I). The lake lies in a deep glaciokarstic hollow, and its dynamic ratio (Håkanson & Jansson, 1983) is 0.08, which mean that sedimentation is very weakly influenced by wind/wave activities. Kurtna area lies in a transitional zone between densely populated and heavily industrialised oil shale mining and processing region and a sparsely inhabited territory with large

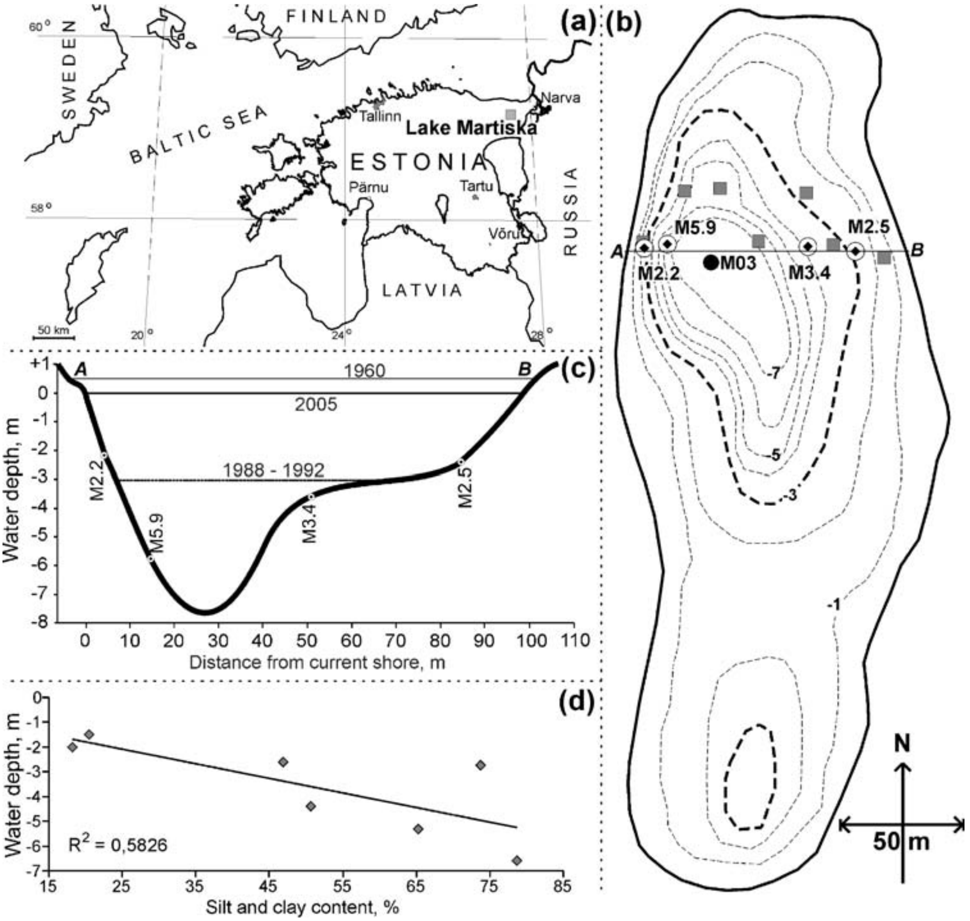

Figure 1. Location of L. Martiska in northeastern Estonia (**a**). The bathymetry of the lake and study sites: squares-surface samples from the northern part of the lake; M2.2., M2.5, M3.4 and M5.9 short cores, the number denotes water depth; M03 core dated by ^{210}Pb (**b**). Lake levels in 1960, 1988–1992 and 2005 and the studied sites along profile AB (**c**). Water depth and silt and clay content in the surface samples along profile AB (**d**).

TABLE I

Characteristics of the Lake Martiska

Characteristic	Value
Volume (V), m^3	80,000
Area (S), ha	3.5
Maximum depth, m	8.5
Average depth, m	2.3
Maximum length, m	370
Maximum width, m	140
Perimeter, m	870
Average slope inclination, %	8.0
Dynamic ratio	0.08
Shape factor	1.24
Water retention time, yr	1.6
Catchment area, ha	30

forests and mires. Pine forests with some other species are dominant on the poor sandy soils on the well sorted mostly fine-grain sands. Lake is closed and fed by groundwater and atmospheric precipitation, its yearly water level displacement is 20–30 cm. The lake is clearly stratified in summertime and the thermocline lies at a depth of 3–4 m. Strong oxygen deficiency occurs in the water deeper than 3–4 m practically all over the year, except during the spring and autumn overturn periods. The area is severely affected by oil shale mining and processing (Punning, 1994). The pumping out of groundwater in the area began in the 1960s resulting in a 3.0–3.5 m drop of the lake water level (Figure 1c). Since 1991 the production of oil shale has continuously declined, and the use of environmentally friendlier technologies has led to the restoration of the natural state of the lake environments.

Detailed mapping of the contemporary lake and mineral bottom topography was done in the wintertime of 1987 and 2003 from ice using a measuring disc of 10 cm diameter and a Belarus type corer (2003 data see on Figure 1b). Ten surface sediment samples (0–10 cm) and five short cores (0–30 cm) were collected in 2003 using a modified Livingstone–Vallentyne piston corer. The cores were taken from different depths and are nominated in Figure 1b and c according the water depth at the coring site in metres.

The concentration of dry matter in sediment was determined by drying the samples at 105°C to constant weight. Organic matter was measured as loss-on-ignition (LOI) after the heating samples at 550°C for 120 min. One core (Figure 1b, core M03) was radiometrically dated. Direct gamma assay was used to measure ^{210}Pb activity in samples and CRS ^{210}Pb model was used to determine dates (Appleby et al., 1986). The surface samples were analysed using wet sieving through four metallic woven mesh sieves (36, 63, 100 and 315 μm), which were stacked vertically and placed in a Fritsch Vibratory Sieve Shaker ‘Analysette 3’

PRO. Mineral particle size partitioning was determined from the amount of sediment remaining in each specific sieve (Last, 2001). In the current study the grain-size fractions were amalgamated into two main groups: sand (>63 μm) and silt and clay (<63 μm) (Terasmaa, 2005). The short-core samples were treated by the hydrogen peroxide and then the grain size was analysed using a Fritsch Laser Particle Size 'Analysette 22'. Results are given following the terminology of Folk (1980) in terms of median grain size (Φ_{50}=–log$_2$D (mm)). In this scale coarser fractions have smaller Φ_{50} values and Φ_{50} for silt and clay fractions is >5.

3. Results

The lithological composition of the seven samples taken from surface layers on profile AB (Figure 1 b,d) of L. Martiska varied largely due to the different depths and slope inclinations. The analysed sediments consisted mainly of unconsolidated dark brownish gyttja (mud like lake sediment) of the water content from 86.6 to 95.6% and LOI values from 24 to 74.2%. In the deeper northernmost area the correlation between the proportion of silt and clay and water depth is 0.5826 (Figure 1d). In the cores taken from deeper areas (M3.4 and M5.9) the dominating fraction is medium-size silt in all the studied samples (median diameter 6–10 μm) (Figure 2). In the cores from shallower areas (M2.2 and M2.5) the median diameter of particles in the samples from a depth of 14–16 cm increases up to 120 μm and the dominating fraction is very fine sand. The LOI values in cores M2.2, M3.4 and M5.9 are higher (60–80%) in the lower part decreasing upwards (in surface samples 30–60%). In core M2.5 several cycles can be distinguished vertically in the distribution LOI values (Figure 3).

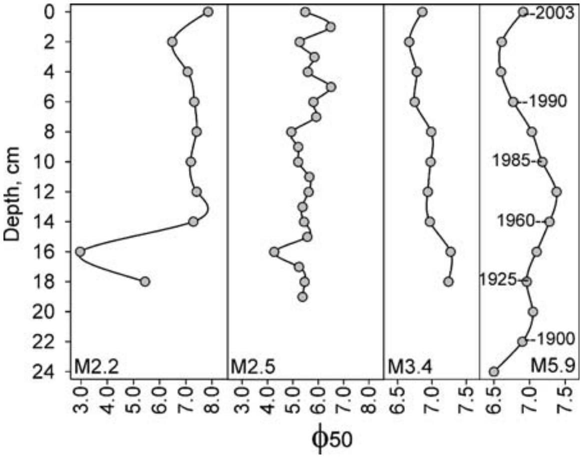

Figure 2. Grain-size in short cores in phi units (see Figure 1). Note that the Φ_{50} scale values for different cores are different.

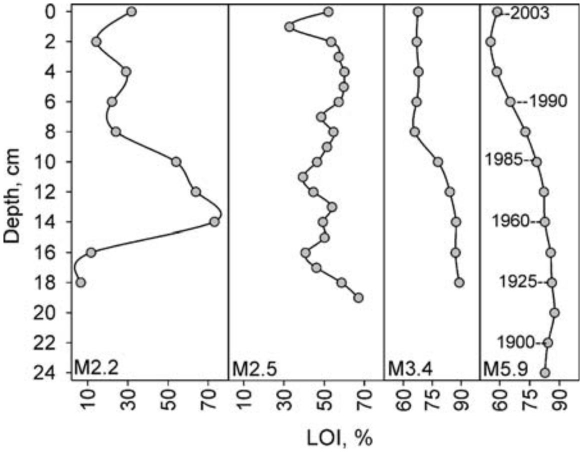

Figure 3. LOI values in short cores (see Figure 1).

4. Discussion

The LOI values and grain-size parameters in the surface sediment samples in the studied profile showed that the distribution of grain-size fractions depends on water depth at the sampling site (Figure 1d). As the topography of the lake basin is quite variable essential changes in the bottom topography took place in the course of lake-level fluctuations.

According to the monitoring data, three phases could be distinguished in the sedimentation process (see Figure 1c): (1) regression phase since the beginning of the 1960s; (2) minimum lake level in 1988–1992; (3) transgression phase since 1992 up to now.

The regression of the lake has resulted in extensive erosion and redeposition of sediments, changes in the distance to the shore and displacement of the erosion-transport-accumulation zones. During this period accumulated sediments originate in principal from two different sources: in-lake concurrently accumulated sediments (mainly atmospheric input, influx from the catchment, autochthonous organic matter) and matter eroded in the nearshore area from where water has retreated in the course of regression. The eroded matter consists of fine grain sands (limnoglacial sands embracing the lake), as well as of previously accumulated lacustrine sediments. In sites M3.4 and M5.9 lacustrine sedimentation took place during the whole regression phase. The ^{210}Pb chronology shows that during regression medium silt sediments from depths 14–16 cm up to 6–7 cm accumulated. Besides lake morphometry the lateral transport of sedimentary material was influenced by the change in the littoral vegetation. Although the water depth of site M3.4 was smaller than of M5.9, the Φ_{50} values are rather similar which might be explained by the gentler slope of the eastern shore (Figures 1c, 2). When the regressive lake level reached levels of –2.2 and –2.5 m the surface of sites M2.2 and M2.5 became above the lake level and erosion and accumulation of organic matter took place mainly as humic substance. As Figure 2 shows there is a very sharp short-lived increase in the coarser component of mineral matter (decline in the Φ_{50} values) in cores M2.2 and M2.5 at a depth of 16 cm from the sediment surface. In these cores the Φ_{50} values (2.3–2.5) are close to the values of bulk limnoglacial sands around the lake.

When the transgressive water level reached the surface of sites M2.2 and M2.5 sediment accumulation began there again. On the relatively badly sorted (average deviation 90.78 μm) and sandy sediments (Φ_{50}=2.9) well-sorted (average deviation 7–9 μm) mainly medium-grained silt accumulated (Figure 2). This means that the main source of mineral matter was well-sorted sediments accumulated before the water-level fall. Also the relatively stabile LOI values in core M2.2 (Figure 3) suggested homogeneity of the source material and depositional environment. The grain-size parameters of the deposits accumulated during this phase in sites M3.4 and M5.9 are relatively similar. At the beginning of transgression the flooding of the shores caused degradation of the vegetation and increasing shore erosion. Later, in course of the water-level rise the sedimentation regime stabilised and sediments became better sorted and finer in the direction of sediment transport. That regularity in the successive deposition during lake-level changes was pointed out also by McLaren and Bowles (1985). Thus, lake-level fluctuations were responsible for essential changes in the composition and structure of sediments and consequently in the biogeochemical matter cycling in the lake. The oil shale mining and processing nearby was responsible for emitting huge amounts of alkaline fly ash, characterised by a high concentration of several heavy metals and harmful organic compounds, into the atmosphere in 1960–1990 (Punning, 1994). In process of the erosion of older sediments, their resuspension, lateral transport and resedimentation, the pollutants were returned in the biogeochemical matter cycling in the lake.

Comparison of the fluctuations in the water level in some Estonian lakes with the lithological composition of the sediment, P content, carbon and nitrogen ratio, fossil pigments and diatom communities showed that in medium-term time scale (10^3 years) the decisive factor in the trophy of the lake was the depth of the water column above the sediment (Punning et al., 2004).

5. Conclusions

Well established history of the water-level fluctuations in L. Martiska during the last decades and its correlation with the lithological composition and grain-size parameters showed that: (1) the grain-size parameters of lacustrine sediments depend on the topography and reflect adequately changes in the sedimentary processes, first of all lake-level fluctuations; (2) the newly accumulated sediments during the regressive -transgressive period originate from two main sources: in-lake concurrently accumulated sediments and from the limnoglacial nearshore sands.

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II

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Changes in lake-sediment structure and composition caused by human impact: repeated studies of Lake Martiska, Estonia

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Abstract: This research uses a comparison of the sediment record of Lake Martiska (NE Estonia) with well-documented historical changes in human impact to identify the factors dominantly affecting the sediment lithological composition, and the accumulation of heavy metals and other microelements into the sediments. To this end, comprehensive lithological-geochemical studies of the upper sediment were undertaken in 1986 and repeated in 2003 and 2005. Oil shale mining and processing heavily impacted the area via atmospheric pollution and groundwater extraction. As a result of the fly-ash deposition clear marker horizons of chemical compounds were formed. Historical water-level fluctuations are clearly reflected in the lithological composition and grain-size variations of the studied sediment cores. During regression and transgression phases displacement of the erosion–transport–accumulation limits caused redistribution of previously accumulated sediments and their return into the biogeochemical matter cycling of the lake. The ^{210}Pb chronology of the sediment records is in contradiction with the historical records of fly-ash emissions, suggesting that changes in ^{210}Pb flux and focusing of sediments caused by lake-level change have invalidated the dating models.

Key words: Sediment chemistry, lake sediments, water-level fluctuation, grain-size, 210Pb, fly-ash emissions, repeated studies, human impact, Estonia.

Introduction

Changing natural conditions and human impacts that influence landscape development fundamentally alter ecosystem biogeochemical cycles. Ecosystems reach new states which then determine the direction of their further development. Understanding the mechanisms controlling these processes has fundamental importance for reconstruction of past ecosystem status, estimation of human impact on the environment and predicting the future trends of ecosystems caused by changes in the physical environment or altered land use.

Water-level fluctuations greatly impact the development of a lake's ecosystem and especially its trophic status. Even small changes of water-level may result in a large shift in aquatic vegetation assemblages and may shift macrophyte zones (Tarras-Wahlberg *et al.*, 2002; Coops *et al.*, 2003; Punning *et al.*, 2004). Madsen *et al.* (2001) demonstrate that water movement affects sediment dynamics in and around submerged macrophytes beds, altering the composition and particle size of the freshwater sediment. Water-level fluctuations also have a great impact on erosion and matter fluxes in a lake. With so many affected processes, investigation of the impacts of a single factor is often very complicated by their simultaneous action.

Objective information about the development of lake ecosystems in the past can be obtained from the stratigraphic analysis of sediment cores based on a range of sedimentary parameters, an approach that is widely used in landscape study (Berglund, 1986; Last and Smol, 2001). Owing to the diverse origins of the studied sediment components as well as the great number of external and internal factors influencing their state, it is not possible to determine universal causal–consequence relationships. Therefore, from a practical perspective it is necessary to analyse different ecosystem components separately and then identify general rules governing their dynamics. These difficulties are aggravated by the temporal and spatial variability of the ecosystems and by variations in their tolerance and inertia (Punning *et al.*, 1997).

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To calibrate palaeorecords reliably in relation to specific human impacts, repeated observations are required. The aim of this work is to compare the rich historical archive documenting drastic changes in human impact with geochemical and lithological sediment records, and from this to determine the factors dominantly affecting the sediment lithological composition and accumulation of heavy metals and other microelements into the sediments. Special attention is paid to the uppermost 25–30 cm of the sediment sequence, which formed under the influence of the oil shale mining and processing industry, which grew rapidly after *c.* 1950 and started to decline during the 1990s.

Study area

Lake Martiska (Figure 1) is situated in northeastern Estonia in the central part of the Kurtna Kame Field, where 39 lakes of different shape, size, drainage area, hydrological regime and trophic status formed during the Preboreal (*c.* 10 000–9500 years ago). The Kurtna Kame Field area lies in a transitional zone between a densely populated and heavily industrialized oil shale mining and processing region, and a sparsely inhabited territory with extensive forests and mires. Though previously oligotrophic (Riikoja, 1940), Lake Martiska is now mesotrophic because of the direct and indirect impacts of oil shale mining and processing (Punning, 1994).

Lake Martiska is a small closed lake with an area of *c.* 3.5 ha, and a maximum depth of 8.0 m (in 2005), and is fed by groundwater and atmospheric precipitation. Mineralization of the lake water is rather low and the concentration of HCO_3^- in water is below 25 mg/L. A substantial increase has occurred in the aqueous SO_4^{2-} concentration since the end of the 1930s (3–5 fold). The lake is strongly stratified in summertime with a thermocline at 3–4 m. The hypolimnion is oxygen deficient except during the spring and autumn turnover periods.

Investigation of the Kurtna Kame Field area has been carried out over several years and many scientific papers have been published about various study sites (Tolonen *et al.*, 1992; Varvas and Punning, 1993; Koff, 1994; Punning, 1994), and the land-use history has been studied in detail. The main human impact on the Kurtna lakes is connected with emissions from the oil shale based industry located 15–30 km from the lakes and the lowering of the water-level in Lake Martiska because of groundwater exploitation. The Estonian oil shale fields are the world's largest oil shale deposits of commercial significance, and have been exploited since 1916. The abstraction of groundwater started at the end of the 1950s, resulting in a lake water-level lowering of up to 3.0–3.5 m and consequent shore and slope erosion (Figure 1b, c). Evidence of the impact of oil shale processing occurs in the lake sediment record, where the distribution curves of heavy metals that are characteristic of thermal combustion of oil shale have been used earlier for rough estimation of age-scales of lacustrine sediments of these headwater lakes (Varvas and Punning, 1993).

Following Estonian independence in 1991 a reorganization of the local economy has led to a continuous decline in the production of oil shale and the use of more environmentally friendly technologies. As a consequence there has been a restoration of the lake environments in the Kurtna area towards a more natural state. The water-level in Lake Martiska has risen by up to 3 m (by 2003, Figure 1c, 2) approaching its pre-disturbance level, and by 2002 fly-ash emissions from the surrounding power plants had decreased more than tenfold compared with maximum rates during the late 1970s (Figure 2).

Methods

Detailed mapping of the lake bathymetry was undertaken in the winter of 1986 and 2003 from ice, using a measuring disc of 10 cm diameter and a Russian corer (2003 data on Figure 1b). The coring sites in all study years (1986, core M86; 2003, core M03; and 2005, core M05) were selected in the deepest area of the lake (6.2 m in 1986 and 7.9 m in 2003 and 2005 owing to the water-level rise during this interval). The sampling was performed with a modified Livingstone-Vallentyne piston corer and the lithology of the cores was recorded in the field. Sampling was continuous with intervals of 1 cm (top layers) and 2 cm (below, covering the last few centuries).

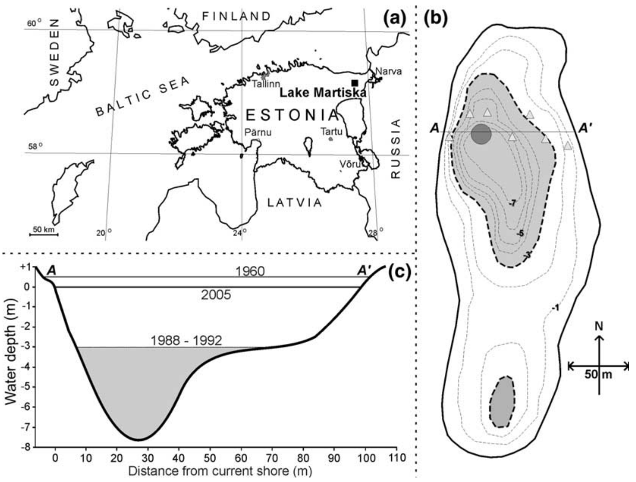

Figure 1 Study area and studied lake (a), depth contours (shaded area shows the contour of lake during minimal water-level) and area of sampling of cores M86, M03, M05 (shaded circle), grey triangles denote locations of the upper sediment samples (b); water level at different times (c)

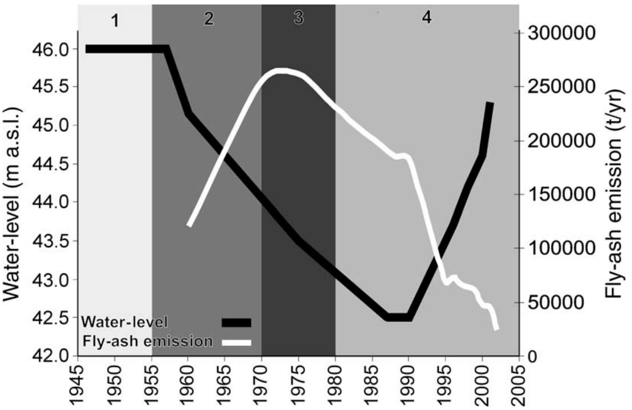

Figure 2 Water-level fluctuations in Lake Martiska and fly-ash emissions from the surrounding thermal power plants 1950–2003. Zones 1–4 represent periods in the emission history as estimated by CRS ^{210}Pb chronology

The M86, M03 and M05 cores were analysed for lithological composition (water, organic and mineral matter content) using the same technique. The concentration of dry matter (DM) in the sediment was determined by drying the samples at 105°C to constant weight. Organic matter was measured as loss-on-ignition (LOI) after heating samples at 550°C for 210 minutes. $CaCO_3$ content was calculated as the loss of weight after ignition of the LOI residue at 950°C for 150 minutes (Heiri *et al.*, 2001).

Total carbon (TC) and nitrogen (N) from cores M03 and M05 were measured at Tallinn Technical University with an Elementar Analysersystem GmbH VarioEL and calculated as percentage of DM. The organic carbon (OC) content was calculated as the difference between TC and inorganic carbon as described by Dean (1999).

The concentrations of several microelements in core M86 were measured at the Institute of Physics of the Latvian Academy of Sciences using neutron activation (Punning, 1994) and in the cores M03 and M05 at the University of Liverpool where elements determined by x-ray fluorescence spectrometry (XRF) using a Metorex Xmet920 x-ray fluorescence spectrometer, with ^{55}Fe and ^{109}Cd isotope sources. Deconvolution of the spectra, mass attenuation correction and calibration were achieved using the program DECONV (Boyle, 2000). The M86 core was dated in the Institute of Geology Estonian Academy of Sciences via ^{210}Po using an isotope dilution technique (Varvas and Punning, 1993). The core M03 was dated by the ^{210}Pb method at the Centre for Environmental Monitoring and Technology, Ukrainian Hydrometeorological Research Institute in Kiev. The CRS and CIC ^{210}Pb models were applied following the approach of Appleby *et al.* (1986) and Appleby (2001).

For determination of grain-size, samples from core M05 were treated with hydrogen peroxide and measured using a Fritsch Laser Particle Size 'Analysette 22'. Results are given following the terminology of Folk (1980) in terms of median grain size ($\Phi_{50} = -\log_2 D$ (mm)). In this scale coarser fractions have smaller Φ_{50} values and Φ_{50} for silt and clay fractions is > 5.

Cartographic analysis and visualisation used *MapInfo Professional 5.5* and *VerticalMapper 2.5*.

Results

Lithology

The upper layers of sediment in Lake Martiska consist mainly of homogeneous porous light-brown gyttja. The water content of the surface layers is 98–99% and decreases downward to values of 94–95% at 10–15 cm. The LOI in all studied cores (M86, M03, M05) is 60–70% in surface layers, and increases with depth to near constant values of 80–90% at 15–20 cm. OC/N ratios (analysed and calculated for cores M03 and M05) are lowest in topmost layers (above *c.* 12 cm) and increasing almost continuously with depth to a maximum of 15–16 at 20–50 cm (Figures 3, 4).

In all analysed samples the clay-silt fraction dominates the sediment (the < 63 μm fraction is 50–60 wt.%). More detailed grain size analysis is performed for core M05 (Figure 3c). In the deeper part of the core the Φ_{50} values vary from 6.6 to 7.0, corresponding with medium silt. Above 12 cm the coarser fraction content increases reaching a sharp maximum at 7.5 cm (Φ_{50} value 6.0; coarse silt). Upwards the proportion of silt increases but the medium grain size remains coarser as in the deeper layers.

Sediment element concentration zones

The concentrations of some metals (Na, K, Al, Sc, Cr, Co, Fe, Mn, Zn, Br, As, Th, La, Eu, Hf, Yb, Sm, Cs) from core M86 have been published earlier (Varvas and Punning, 1993). The element concentrations in that core started to increase from 24 cm, peaked at 8–10 cm and then slightly decreased to the surface.

From cores M03 and M05, Si, Ti, Ca, K, Fe, S, Zn, Br, Zr, Rb, Sr were analysed (not all presented) (Figures 3, 4). From concentration variations it is possible to distinguish four zones characterized by similar trends (described in detail below, Zones I–IV on Figures 3, 4). By assuming that these changing concentrations can be attributed to specific events in the emission history of nearby power plants, independent dates can be obtained to compare with the ^{210}Pb dates (Punning *et al.*, 1997).

^{210}Pb chronology

Unsupported ^{210}Pb activity curves versus depth for cores M86 and M03 differ (Figure 5) showing a somewhat greater apparent mean sedimentation rate in core M03 than in core M86 (respectively, *c.* 9 and 6 mg/cm^2 per yr since AD 1900). The ^{210}Pb activity curves for both cores show typical disturbed profiles in the upper part probably influenced by erosion or resedimentation. Consequently, the use of the CIC model for age calculations is inappropriate. ^{210}Pb total inventories for cores M86 and M03 are 4280 and 3540 Bq/m^2.

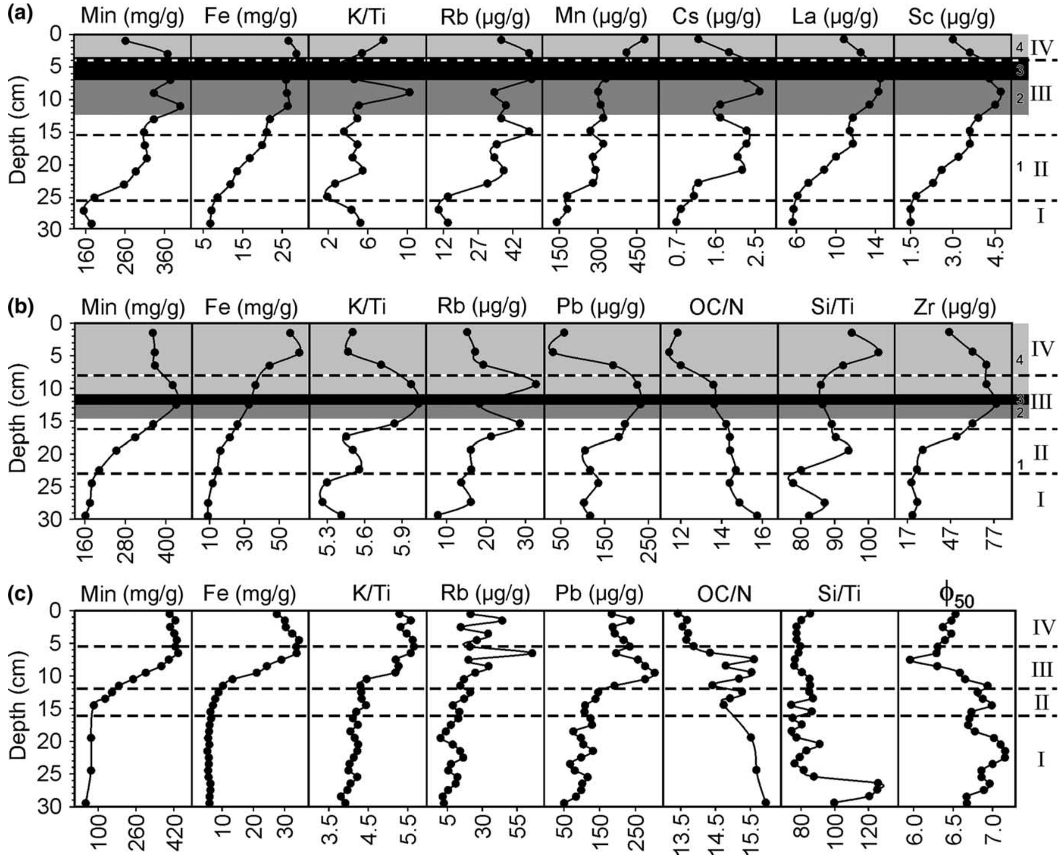

Figure 3 Lithological and chemical records for cores M86 (a), M03 (b) and M05 (c). Zones I–IV are distinguished by the distribution of pollutants in the cores. Zones labelled 1–4 represent the same periods in the emission history for cores M86 and M03 (Figure 2) but with ages estimated by CRS ^{210}Pb chronology

In core M86 the ^{137}Cs activity decrease is rather smoothed and it is not possible to separate any peaks (Varvas and Punning, 1993). In core M03 the ^{137}Cs/^{241}Am peak is sharply represented in 1986 on ^{210}Pb scale.

Synthesis and conclusions

Geochemical zonation and human impact history

In the radiometrically dated cores M86 and M03, most elements increase in concentration above *c*. 25 cm, reaching a subsurface maximum at *c*. 15–5 cm. Zone I (see Figure 3a, b, 4) corresponds with the environmental situation in the lake prior to atmospheric pollution. The sediment chemical content shows minimal mineral matter supply, likely due to high lake level and minimal catchment erosion. It is characterized by a low Si/Ti ratio (clay-rich) and high OC/N values, indicating an oligotrophic status for the lake ecosystem with macrophytes supplying most of the organic sediment.

The start of Zone II is characterized by a steadily increasing concentration of mineral matter, particularly Ca (Figure 4). There is a distinct increase in a number of elements (K, La, Rb, Sc, Zr) characteristic of emissions from oil shale fired power plants (Punning, 1994). A decrease

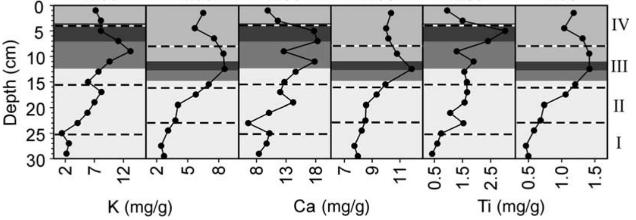

Figure 4 Chemical records of some dominating elements of fly ash emitted to the atmosphere for cores M86 and M03. Geochemical dated emission zones as defined in Figures 2 and 3 and CRS ^{210}Pb dated emission zones (labelled 1–4) are as defined in Figure 2

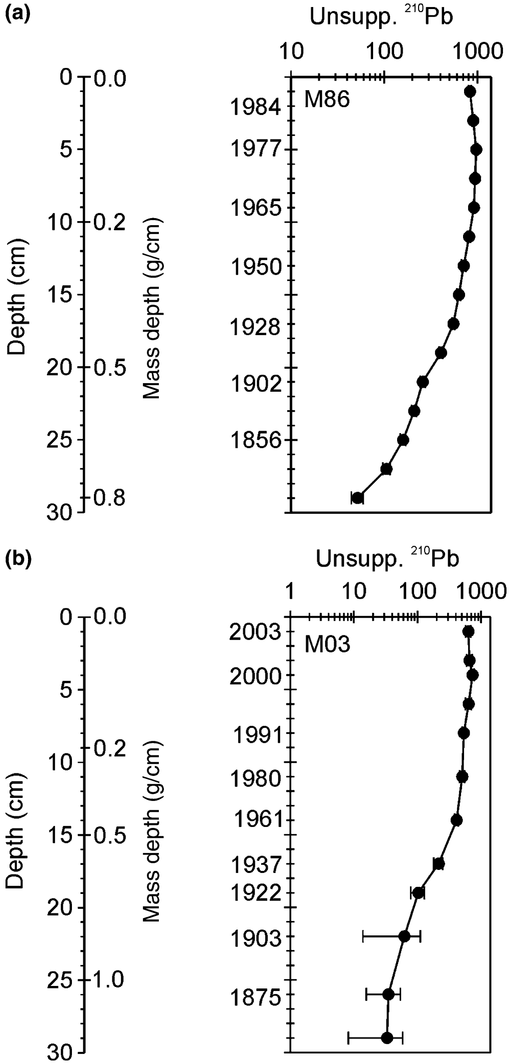

Figure 5 Unsupported ^{210}Pb (Bq/kg) in cores M86 and M03 and mass-depth in g/cm

in OC/N ratio points to an increasing importance of primary production in the lake.

Zone III starts with a steepened rise in the concentration of elements associated with oil shale use in power plants. Subsequently, the concentrations level off before declining slightly.

Zone IV is characterized by a steady decrease in the concentration of metals associated with oil shale emissions. Coincident with these decreases is an abrupt increase in the Fe and Mn concentrations, pointing to a dramatic shift in the lake system towards reduced material influxes, and decrease in OC/N ratio indicating a shift of the lake ecosystem towards higher trophy and a increased contribution of plankton to the organic matter.

The zones identified agree well with the emission records of nearby oil shale power plants, and also with the results of previous studies of recent lake biogeochemical cycling within the Kurtna Kame Field. Zone I reflects low-level human impact in the region, which was minimal prior to the beginning of the 1930s, before increasing slightly with the first small-scale oil shale use during the 1940s. The start of Zone II can be attributed to the inception of significant regional exploitation of oil shale in the 1950s. The rapid changes of Zone III are attributed to an expansion of oil shale power generation after 1960, emissions from which peaked in 1975–1980. The Zone IV changes are attributed to decline in the use of oil shale after 1980, and to later improved emission control after 1991. These dates are summarized on Figure 2 as emission periods (1–4), marking changes in the intensity of oil shale use and application of purification technology to fly ash emissions from power plants in the region. The emission data are in good correspondence with data obtained by modelling of fly ash dispersal through the atmospheric boundary layer (Punning *et al.*, 1997).

The CRS ^{210}Pb dates for these sedimentation events (especially in core M03) are incompatible with the historical dates. This is demonstrated on Figure 3a, b, which compares the emission periods (1–4, different shading) determined using historical data (Figure 2) with emission periods dated using CRS ^{210}Pb ages. The substantial temporal difference between the first appearance of elevated concentrations in palaeorecords dated by ^{210}Pb of elements and their emissions as pollutants, points to additional factors influencing their distribution. Varvas and Punning (1993) described this discordance and proposed that it might be caused by bioturbation or erosion resulting from the rapid water-level fluctuations in the period 1957–2003 (Figure 2). A comprehensive analysis of previous data, combined with new information from cores M03 and M05 to cover the full cycle of the regression–transgression, provides better insights into the reasons for the discrepancy in the CRS ^{210}Pb dates.

Water-level fluctuations and their impact on the sediment composition

One very specific phenomenon influencing the development of Lake Martiska but not other lakes in the Kurtna Kame Field (Punning, 1994) is the lake-level drop of 3–3.5 m due to groundwater abstraction via a nearby intake. Since 1990 the water-level has partially recovered in response to a decrease in water use (see Figure 2). The water-level fluctuations are clearly reflected in the lithological composition of the sediment and in grain-size variations (Figure 3). In the lowermost part of the cores the mineral matter concentration varies very little. Above *c*. 25 cm in cores M86 and M03, and above 15 cm in core M05, the mineral matter concentration increases steadily. These concentrations show well-developed subsurface peaks. Our earlier studies of the impact of water-level fluctuations in Estonian small lakes (Punning *et al.*, 2004) showed that sediment erosion, redistribution and accumulation are linked to changes in bottom topography caused by fluctuations in lake level. The firmest evidence for this is recorded in the marginal areas. In areas with steep underwater slopes, lake-level fluctuations are reflected mainly by changes in mineral matter concentration, while in areas with flat topography the fluctuations are shown by the development of littoral vegetation. The amount and origin of the reworked matter associated with this sediment redistribution varies both spatially and temporally, as the changes in sedimentation mechanisms have a significant impact on the accumulation dynamics. A statistical analysis of mineral and organic matter concentration data from 14 surface cores within Lake Viitna in northern Estonia, and its association with bottom topography, allowed identification of lake areas that were more sensitive to the

Table 1 Differences between the historically dated events and CRS ^{210}Pb dated signals in the sediment cores M86 and M03

Event	Age by historical documents (AD)	M86				M03			
		^{210}Pb depth (cm)	Indicated depth on the geochemical record (cm)	Difference (cm)	Difference in accumulation (g\cm^2)	^{210}Pb depth (cm)	Indicated depth on the geochemical record (cm)	Difference (cm)	Difference in accumulation (g\cm^2)
Water-level started to drop	1958	12	25	13	0.4	14	23	9	0.7
Increase in element concentration	1960	11	25	14	0.4	14	23	9	0.7
Maximum element concentration	1980	4	10	6	0.26	11	12	1	0.12

water-level changes (Punning *et al.*, 2004). The results showed that a water-level fluctuation of 1 m or greater causes changes in the sedimentation in the steep-sloped areas and in the littoral zone where the water depth is less than 3 m.

These general associations between sediment composition and both lake water depth and lake bed topography are clearly seen at Lake Martiska. Grain size analysis of seven surface (0–10 cm) samples (Figure 1b) show that the < 36 μm fraction is dominant, reaching up to 55–60% in areas deeper than 3 m. Only in nearshore areas (water depth less than 1.5 m) does the sand fraction reach 70%. The lithological composition varies greatly because of the different depths and slope inclinations. The correlations of silt and clay proportion with water depth is 0.86 ($p < 0.001$) and with slope inclinations is -0.54 ($p > 0.05$).

The patterns seen in the surface sediment at Lake Martiska are also seen in the sediment column. In the core M05 an up-core increase in the coarse fraction begins at a depth of about 12 cm, reaching a maximum value at 7.5 cm. This pattern is compatible with regression of the lake margin caused by falling lake level, resulting in extensive erosion and redeposition of sediments, and changes in the distance to the shore and displacement of the erosion–transport–accumulation zones. These layers probably accumulated in 1992–1994 when the water-level was lowest. During the rapid subsequent transgression in the second half of the 1990s, it can be expected that shoreline erosion would reduce, while normal lake sediment accumulation would increase.

Such a pattern suggests that the particulate matter accumulated during water-level change comes in principal from two different sources: in-lake concurrently accumulated sediments (mainly atmospheric input, autochthonous organic matter and reworked mineral matter) and from the mineral matter eroded from the shoreline. The proportions of these materials in newly accumulated sediments will determine the composition and ^{210}Pb content of specific layers. Two principal situations might occur: the resuspension of sediment will lead to enrichment by previously accumulated pollutants (heavy metals principally) and dilution of the ^{210}Pb activity. In contrast, during transgression and lateral transport of the sand from nearshore erosion, dilution is likely for both the content of heavy metals from oil shale processing and the ^{210}Pb activity. The ^{210}Pb flux to the profundal lake sediment is enhanced by both sources, though focusing related to resuspension will have the greater impact on the ^{210}Pb inventory. It is rather complicated to model the impact of both scenarios; probably they naturally occurred simultaneously during the both phases, having different extent because of the bottom and slope characteristics at any particular time.

Comparison of the CRS ^{210}Pb chronology with the historically inferred dates (derived from correspondence of the geochemical zonation with the emission period, Figure 2) allows inferences to be made about the source of redistributed sediment in Lake Martiska. The fundamental disagreement between geochemical zones and dated horizons in cores M86 and M03, whereby the CRS ^{210}Pb dated changes in the geochemical records are always older than the corresponding historical ages (Table 1), can be explained by enhanced focusing of ^{210}Pb leading to an elevated local inventory in deep sediment cores. Though marginal sediment reworking does not alter the total ^{210}Pb flux, it does alter the apparent flux at individual sites, invalidating the CRS model for specific profundal cores. Furthermore, the magnitude of deviations in apparent flux will vary greatly within the lake depending upon local bottom topography. This can be seen in the distinctly different dating discrepancies for the M86 and M03 cores. It can also be seen in the differences in sedimentation rate enhancement. The additional accumulation in the M86 core is approximately 0.4 g/cm^2 in the interval from 1958 to 1986, while in the M03 core the enhancement exceeds 0.7 g/cm^2 in the interval from 1960 up to 2003 (Table 1). In the latter core the accumulation also reflects the transgressive phase and therefore the proportion of the eroded sands is greater than in the M86 core.

Conclusions

A detailed comparison of the well-documented history of lake-level fluctuations in Lake Martiska during the last decades with the lithological composition and grain-size parameters of its sediments showed that: (1) the lacustrine sediment grain-size parameters vary with bathymetry and consequently are responsive to changes in lake-level fluctuations; (2) the newly accumulated sediments during regressive–transgressive periods originate from two main sources: in-lake concurrently accumulated sediments and from the limnoglacial nearshore sands; (3) changes in sediment dynamics resulting from lake-level fluctuation strongly impact the apparent ^{210}Pb flux, leading to a serious mismatch between CRS ^{210}Pb chronologies and independently dated marker horizons.

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Historical changes in the concentrations of polycyclic aromatic hydrocarbons (PAHs) in Lake Peipsi sediments

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Tiit Vaasma · Galina Kapanen

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Abstract The distribution of 11 individual polycyclic aromatic hydrocarbons (PAHs) was analysed in a ^{210}Pb dated sediment core from the deepest area of Lake Peipsi and in four surface sediment samples taken from littoral areas. According to the concentrations in the core three groups of PAHs may be distinguished: (1) relatively stable concentrations of PAHs within the whole studied time interval; (2) very low concentrations in sediments accumulated before intensive anthropogenic impact (from 19th century up to the 1920s) following a slight increase and (3) an overall increase in PAH concentrations since the 1920s up to the present. Comprehensive analysis of PAHs in the core and monitoring data obtained in the 1980s together with the lithology of sediments show that an increase of anthropogenically induced PAHs correlates well with the history of fuel consumption in Estonia and speaks about atmospheric long-distance transport of PAHs. The continuous increase of PAH concentrations since the 1920s do not support the earlier hypothesis about the dominating impact of the oil shale fired power plants near the lake, because their emissions decreased significantly in the 1990s. The concentration of PAHs in the deep lake core sample correlates well with the content of organic matter, indicating absorption and co-precipitation with plankton in the sediment.

Keywords PAH · Lake sediment · Sediment lithology · ^{210}Pb · Lake Peipsi

Introduction

The generation, deposition and redeposition of polycyclic aromatic hydrocarbons (PAHs) as widely distributed pollutants and relatively persistent compounds in water and sediments have been extensively studied during the last decades (Suess 1976; Behymer and Hites 1988; Cripps 1989; Zhang et al. 1993; Trapido and Veldre 1996; Pikkarainen 2004; Quiroz et al. 2005; Fragoso et al. 2006; Vaine et al. 2007). As many PAHs are carcinogenic the origin and pathways of PAHs in the environment have been the focus of numerous studies.

PAHs find their way into the aquatic environment through atmospheric deposition directly on water surfaces or indirectly via land runoff and wastewater disposal. If emitted to the atmosphere PAHs are associated with aerosols, soot and other airborne particulate matter. Because of their hydrophobic property, in aquatic environments PAHs rapidly become deposited and persist in bottom sediments for long periods.

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PAH concentration and distribution studies in the atmosphere, water and surface sediment samples have made it possible to identify their common patterns and possible sources. Taking into account the chemical composition and persistence of PAHs, there is evidence that two- and three-ring compounds indicate relatively stronger petrogenic origin and four- to six-ring compounds pyrogenic origin (Dahle et al. 2003). Though PAHs are quite persistent, long-range atmospheric transport would selectively degrade compounds such as anthracene and pyrene through photo-oxidation (Zhang et al. 1993). On the surface of water bodies, PAHs rapidly become associated with seston. Sediment–water partitioning coefficients vary according to specific PAHs (Johnson et al. 2001). When resedimentation occurs, PAHs will be released back into the water and can re-enter the aquatic ecosystem through the food chain. This is especially prevalent in the case of large and shallow lakes. Several studies reveal that historical records of PAH distribution in age-dated sediment cores reflect the elevated anthropogenic inputs of pyrolytic compounds caused by the increased use of fossil fuels during the last century (Ke et al. 2005; Quiroz et al. 2005; Heath et al. 2006). This finding makes it possible to monitor surface water and air quality trends in the longer time scale than from the use of instrumental data alone.

The detailed studies on the PAH content in Lake Peipsi (northeastern Europe) and its catchment conducted in 1979–1987 (Paalme et al. 1988; Trapido and Veldre 1996; Veldre et al. 2001) indicated that the regional atmospheric and riverside load can contribute a significant part of the total pollution of this lake. It was concluded that the main source of benzo(*a*)pyrene (BaP) is atmospheric emissions from the nearby power plants operating on a fossil fuel (oil shale).

The aim of this study is to examine the temporal distribution PAHs in dated Lake Peipsi sediment samples by applying a number of paleolimnological methods. Lake Peipsi as a large lake acts as a regional sink for atmospherically transported particles and chemical compounds as well as those originating from the catchment and so its sediments can provide valuable information on temporal changes in these inputs. For interpretation of such environmental records an understanding of the processes of sedimentation and resulting distribution is necessary. The objectives of the present study are (a) to study the temporal distribution of different PAHs and their concentrations in sediment profile, (b) to estimate the temporal trends in the influx of PAHs and compare these with earlier data, (c) to investigate the degree of correlation between PAHs and total organic matter and grain size composition of sediments, and (d) draw conclusions about the origin and pathways of PAHs.

Study area

Research was carried out in Lake Peipsi (thereafter L. Peipsi). L. Peipsi belongs to the Baltic Sea catchment and is located south of the Gulf of Finland. The catchment basin of L. Peipsi (47 800 km^2 including the 3555 km^2 lake surface) extends from 59°13′ to 56°08′ N and from 25°36′ to 30°16′ E (Fig. 1). This is the fourth largest lake with respect to the surface area and the biggest transboundary lake in Europe. Nowadays its catchment is shared between Russia (27 917 km^2), Estonia (16 323 km^2) and Latvia (3 560 km^2) (Nõges 2001).

The average depth of L. Peipsi is 7.1 m, maximum depth 15.1 m and the residence time of water is about two years. Its basin capacity is more than 25 cubic kilometres of still relatively clean water. About 240 rivers, brooks and channels enter the lake; it is drained to the Gulf of Finland via the Narva River. The lake is submeridionally elongated and consists of three limnologically different parts called (from north to south): the largest and deepest northern part L. Peipsi *sensu stricto*, the middle strait-like part Lake Lämmijärv, and the southern part Lake Pskovskoye (also L. Pihkva) (Fig. 1). The drainage area of the lake is characterized by a Boreal climate. The lake is covered with ice usually from December to May. According to Kullus (1976), precipitation and influx account respectively for 20% and 80% of the average long-term water balance.

L. Peipsi is of especially high importance for Estonia, because its catchment covers nearly 25% of Estonia's territory. The portion of L. Peipsi belonging to Estonia constitutes 89% of the total surface freshwater and yields 95% of the freshwater fish catch of the country (Nõges 2001). Due to the intensive industrial activity within the lake's catchment, there are various human impacts on the lake. The rivers and lake itself are very intensively used for water transport, recreation and fishing, which cause

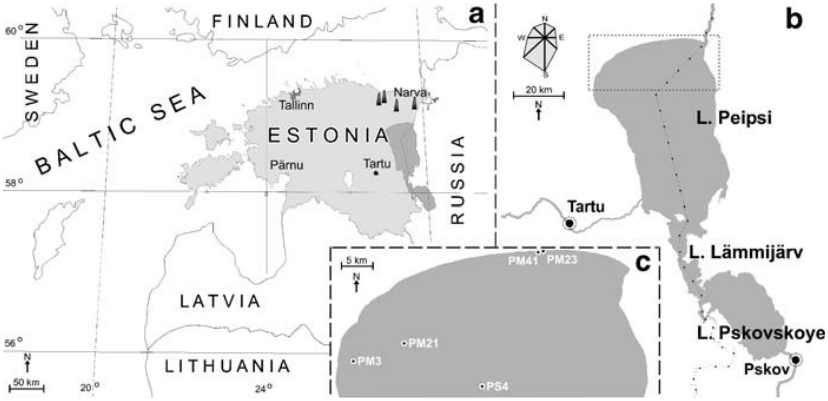

Fig. 1 Location of Lake Peipsi (**a**), and studied area (**b**). Locations of studied sites (**c**); see also Fig. 4. Scale and dominating wind rose are also given

oil spillage and fuel exhausts from boats and ships. Near the northern shore of the lake there are large power plants operating on oil shale. After World War II, in 1949–1969, several oil shale fired power plants were erected there and at the end of the 1970s about 27 million tonnes of oil shale was burned in the power plants annually. Total fly ash emission to the atmosphere from the power plants reached annually more than 300 kilotonnes in the end of the 1970s (Punning et al. 1997), among this more than 100 kg PAHs. Therefore, in the 1970s–1980s much attention was paid to power plant emissions as a potential source of the pollution to L. Peipsi and its catchment. Since that time serious measures to decrease emissions have been implemented and by 2002 fly-ash emissions from the power plants had decreased more than 10–fold compared with maximum rates during the late 1970s.

The surface water in L. Peipsi moves in the direction of the wind. Near the bottom of the compensation streams form; in the shallow southern part, the surface currents reach the bottom. As L. Peipsi is shallow and has a large surface area, waves may be as high as 2.3–2.4 m (Jaani 2001) reaching the bottom, mixing waters of the lake and resuspending accumulated sediments. This phenomenon has a significant impact on the distribution of pollutants within the lake and makes it possible to return deposited impurities back to the food chain.

Methods

The 46–cm long sediment core (PS4) was taken from the northern part of Lake Peipsi at monitoring station number 4 where the water depth is 9.3 m. (Fig. 1). The sampling was performed with a modified Livingstone-Vallentyne piston corer from the ice in winter 2006 and the lithology of the core was recorded in the field. Sampling was continuous over the core with intervals of 2–3 cm. In addition, four surface sediment samples 3–4 cm thick (PM4, PM21, PM23, and PM41) were taken from different near-shore areas of the northern part of the lake. The content of dry matter in sediments was determined by drying the samples at 105°C to constant weight. Organic matter was measured as loss-of-ignition (LOI) upon heating at 550°C for 120 min. The contents of C, N and S were measured in Tallinn University of Technology with a Perkin-Elmer Elemental Analyser, type PE 2400/2 and the results were expressed as percentage of dry weight at 105°C. On the basis of these data C/N ratios were calculated (Punning and Leeben 2003).

For the determination of grain–size, the samples were treated with HCl and H_2O_2 and measured using a Fritsch Laser Particle Size "Analysette 22". Results are given as medium diameter of particles following the Udden-Wentworth grain–size scale (Last 2001). The grain size of surface sediments was estimated using wet sieving carried out on four metallic woven mesh sieves in a Vibratory Sieve Shaker "Analysette 3" PRO. Particle size was determined from the amount of the sediment that remained on each sieve partitioning of the fractions >1000 μm; 1000–500 μm; 500–250 μm; 250–63 μm; 63–36 μm and <36 μm.

The radiometric dating of the core was performed in the Centre for Environmental Monitoring and Technology, Ukrainian Hydrometeorological Research Institute by direct gamma assay using an

EG&G Ortec HPGe GWL series well-type coaxial low background germanium detector (Appleby et al. 1986).

The PAH analyses were made in the Estonian Agricultural Research Centre. Eleven individual PAHs were extracted from dried samples using hexane/acetone (1:1 v/v) in an accelerated solvent extraction system (Dionex ASE 300) at the pressure of 2000 PSI at 100°C in accordance with the EPA method 3545. The recovery of different PAH compounds during the extraction were between 82.8–102.8%. Extracts were analysed on a gas chromatograph coupled with a mass spectrometry detector (Agilent 6890/5973) the GC was fitted with a 30 cm×250 mm×0.25 μm HP-5MS capillary column. The detection limit of analyses for single PAHs is 0.002 mg/kg.

Results

Lithology and chronology

The analysed sediments in sequence PS4 (Fig. 1) consisted of green-grey gyttja. The water content in the deeper layers of the sediment core (from 46 up to 20 cm) is 89–90% and increases up to 95% in the surface layers (Fig. 2). The concentration of organic matter expressed as LOI decreases from the layers at 44–40 cm from 26.5% to 24% at a depth of 28 cm and then increases up to 27% in surface layers. Organic carbon concentration in the bottom layers is 12.5%, decreases up to 11% at a depth of 17 cm and increases upward reaching 13% near the surface (Fig. 2). The C/N values exhibit a slight decreasing trend from the bottom to the surface (from 8.8 to 8.0) indicating an increase in the proportion of planktonic matter in sediments. Sediments are fine grained – the medium diameter of the mineral particles in the profile varies from 14 μm to 18 μm, which corresponds mainly to the class of coarse silt by Udden-Wentworth grain-size scale. The differences in grain size throughout the profile are within the determination limit. Some characteristics of surface sediments (see Fig. 1 and 4) are given in Table 1.

The surface sediment samples from PM3 and PM21 represent erosional areas and in locations PM23 and PM41 nearshore accumulation areas, dominated by transport from the sandy sediments from old coastal dunes or by rivers.

The sediment core was dated and the radionuclide analysis data are given in Table 2. Though the average ^{210}Pb flux of 108 Bq m^{-2} y^{-1} and mean sedimentation rate of 0.026–0.028 g m^{-2} y^{-1} are comparable to earlier ^{210}Pb data for Lake Peipsi (Nõges et al. 2006) and Lake Pskovskoye (Kangur et al. 2007) the distribution of ^{210}Pb in surface high porosity layers and elevated sedimentation rate (up to 0.07 g cm^{-2} y^{-1}) during the last decades indicate certain mixing of sediments. In the case of large shallow lakes mixing might essentially disturb the paleolimnological records as also seen from fly-ash particles distribution in sediments (Nõges et al. 2006).

PAHs concentration

Vertical distributions of the concentrations of 11 individual PAHs differ sharply. According to the concentrations measured, three groups variations of PAHs may be distinguished (Table 3, Fig. 3). The first (I) group consists of PAHs that are present in all samples throughout the core, and their concentrations increase insignificantly in the upper layers. This group includes phenanthrene (PHE) (highest back-

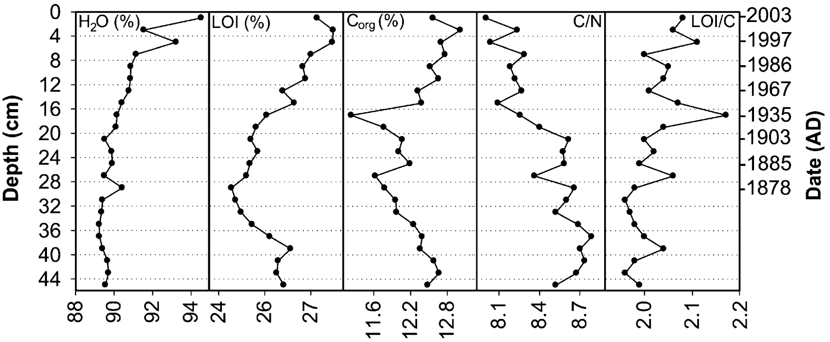

Fig. 2 Lithological characteristics of core PS4 in depth (cm) and age (right column, in ^{210}Pb years) scales

Table 1 Lithological data of surface sediments

Sample location (see Fig. 1)	Lithology	Water depth, m	Organic matter, %	Grain size, dominating fraction
PM3	Till	4.6	1.7	>1000 μm (72%)
PM21	Clayey silt	8.1	5.3	<36 μm (75%)
PM41	Fine sand	2.3	0.2	250–63 μm (99%)
PM23	Medium grain sand	shore	0.2	500–250 μm (74%)

ground concentrations, increase only 1.4 times) and BaP. By the data of Trapido and Veldre (1996) the BaP concentrations in aquatic plants in L. Peipsi varied in the 1970s–1980s from 0.56 to 53.5 ng g^{-1}, its average concentration in plankton was ca 5 ng g^{-1} and in fish tissues from 0.05 to 0.14 ng g^{-1}. It seems that there occurs a big difference in different links of the food chain. The second group (II) contains the PAHs that are absent or present in low concentrations in the lower layers and appear in the upper layers in small concentrations only. In this group are naphthalene (NAP), dibenzo(*a*,*h*)anthracene (DaA) and benzo (*a*)anthracene (BaA). The last (III) group contains PAHs that are present in small concentrations in the lower layers but whose concentrations increase significantly from depths of 20 cm upward (accumulated since AD 1920). Highest increases are for benzo (*b*+*k*)fluoranthene (BbF), indeno(1,2,3-cd)pyrene (INP) and benzo(*g*,*h*,*i*)perylene (BgP).

In the surface samples taken from shallower areas and near the coast, the number of PAHs is smaller. PHE, fluoranthene (FLT) and NAP are all present in samples PM23, PM3 and PM21; however, their concentrations are even lower than in the lower ("background") layers in core PS4 (Fig. 4). The content of other PAHs in those samples is sporadic and concentrations are close to the detection limit.

Discussion

PAHs distribution patterns

The vertical distribution of PAH concentrations in samples from core PS4 falls into two distinct parts. In the lowermost layers (from 45 to 22 cm), accumulated by ^{210}Pb data roughly from the 18th century until the first decades of the 20th century, the concentrations of all analysed PAHs are low and fairly uniform. From 20–18 cm upward the concentrations of most PAHs are increasing towards the surface. First the concentration of naphthalene (ca AD 1890) begins to increase, followed by increases (since AD 1920) in the concentration of other PAHs.

The data obtained show that PAHs belonging to group I have rather low and constant concentration in all samples and they might be regarded as background levels for the studied area. The small variations in the concentrations of PAHs in those sediments are caused by the variations of environmental conditions, such as accumulation and decay of organic matter, processes in the sediment – water interface, microbial activity etc. Some of these individual PAHs are also widespread in samples taken from seawater and biota from uncontaminated areas in the Antarctic (South Georgia) where their presence (Cripps 1989) is explained by the natural transformation from biota.

Table 2 The ^{210}Pb data from the sediment core

Depth, cm	Cum dry mass g/cm^2	^{210}Pb inventory Bq/m^2	Date, AD	Age, years	SE, years	Sedimentation rate		
						g/cm^{2}yr	cm/yr	% error
0	0.0000	3466.7	2006	0				
1	0.0566	3397.3	2005	1	2	0.0846	1.254	23.7
3	0.2023	3139.5	2003	3	2	0.0405	0.530	7.8
5	0.3622	2781.6	1999	7	2	0.0419	0.488	13.0
9	0.7169	1991.0	1988	18	2	0.0259	0.278	10.5
13	1.1054	1156.5	1971	35	3	0.0188	0.189	14.5
17	1.5120	475.7	1942	64	6	0.0102	0.098	22.1
21	1.9397	215.4	1917	89	13	0.0374	0.347	61.2
25	2.3751	159.6	1901	105	16	0.0285	0.262	78.4
29	2.8091	104.4	1894	112	22	0.0184	0.167	75.3

Table 3 Analysed PAHs in core PS4 and their characteristics

PAH	Code	Molecular weight	Group by vertical distribution (see Fig. 4)
Naphthalene	NAP	128	II
Phenanthrene	PHE	178	I
Fluoranthene	FLT	202	III
Pyrene	PYR	202	III
Chrysene	CHR	228	III
Benzo(*a*)anthracene	BaA	228	II
Benzo(*b*+*k*)fluoranthene	BbF	252	III
Benzo(*a*)pyrene	BaP	252	I
Indeno(1,2,3-*cd*)pyrene	INP	276	III
Benzo(*g*,*h*,*i*)perylene	BgP	276	III
Dibenzo(*a*,*h*)anthracene	DaA	278	II

Of course, in the case of L. Peipsi their presence may also be connected with the burning of wood in households, especially fish smoking, which that was an important economic activity around the lake. Of note is that the PAH composition in all surface sediments taken from the shallower areas of the lake is similar to those from the deeper layers of the sediment core PS4 (Fig. 4). The variations in the concentration of these individual PAHs in the upper layers, accumulated since the 1960s, are an indication of anthropogenic impacts. One example is the carcinogen BaP, which was intensively monitored in the L. Peipsi area in the 1970s and 1980s.

The PAHs belonging to groups II and III have clearly here an anthropogenic origin. Their concentrations increase rapidly in the layers accumulated since the 1920s, reaching maximum values in the surface layers. The concentrations of four- to six-ring PAHs (BbF, INP, BgP) were the highest measured.

Numerous studies (Trapido and Veldre 1996; Dahle et al. 2003; Fang et al. 2006; Quiroz et al. 2005) have been conducted to identify the dominant source of PAHs in certain localities. Identifying the exact sources can be a complex process because there are usually many different sources of PAHs. Also some PAHs may undergo destruction and transformation, which may lead to the changes in their composition. In general, two- and three-ring PAHs (such as NAP, PHE) are mostly produced during the burning of solid fossil fuels or incomplete combustion of wood, whereas, four- and five-ring PAHs (such as FLT, chrysene (CHR, BbF) are associated more with oil burning, gasoline and especially diesel powered vehicles (Cripps 1989).

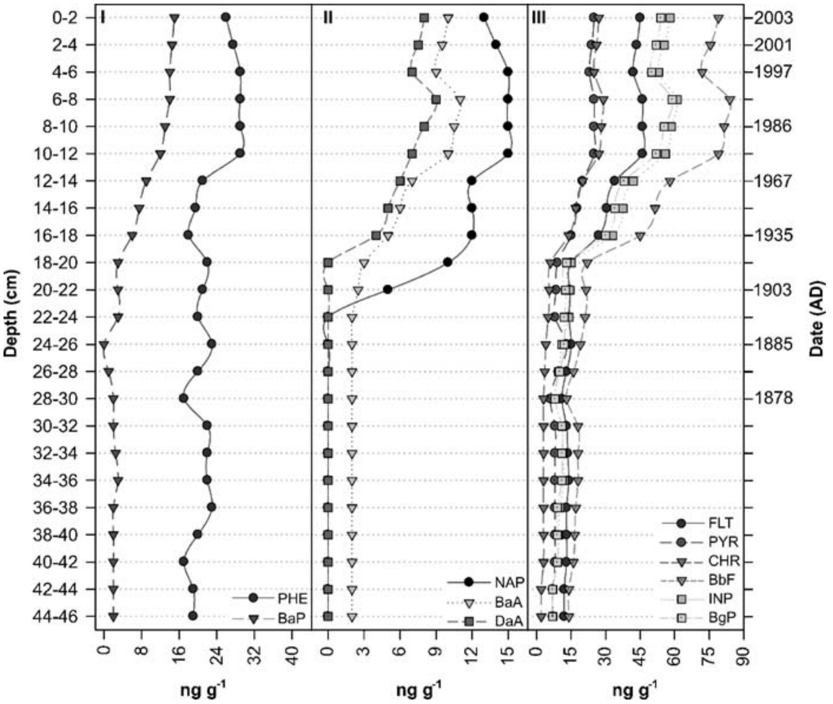

Fig. 3 The concentrations records of PAHs are divided into three groups, depending on distribution regularities. Note that the values of concentrations for different groups differ. The ^{210}Pb ages in AD years are given at right

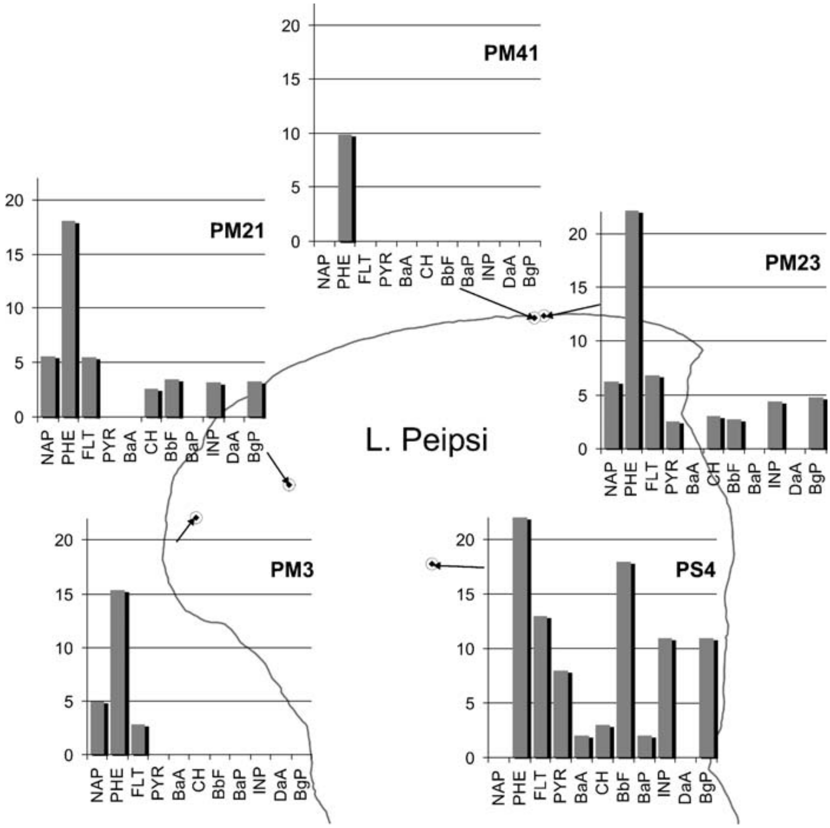

Fig. 4 The PAHs in the surface samples taken from littoral areas of Lake Peipsi and the "background" values (in layers older than AD 1920) in core PS4 (see also Fig. 1)

To compare our data with those obtained for the studied area in the 1980s, the PAH concentrations were recalculated to influx data using the ^{210}Pb age scale (Fig. 5). Previous systematic studies of the content of PAHs were focused mainly on the concentration of BaP in L. Peipsi and its catchment. It was established that the BaP content in the water of L. Peipsi was fairly constant from 1977 to 1987, varying from 1 to 10 ng l^{-1} and contributing about 40% of the total PAHs content (Veldre et al. 1987). The accumulation factor from water into sediments for BaP during the observation period varied from 150 to 430 000 and was dependent on the sediment type. The concentrations in surface sediments varied from 5 to 20 μg kg^{-1}. The intensity of the deposition of BaP on the snow cover in the area of L. Peipsi at the beginning of the 1980s was 0.08–0.09 μg m^{-2} day^{-1} and for total PAHs 0.15–0.23 μg m^{-2} day^{-1} (Veldre et al. 1987, 2001). Extrapolating these values for annual influx, we obtained 30 μg m^{-2} yr^{-1} for BaP and 70 μg m^{-2} yr^{-1} for total PAHs (Table 4).

The increase of the PAHs in sediments accumulated from the 1920s up to the beginning of the 1980s is due, at least partly, to fly ash emissions from the combustion of oil shale in power plants. The historical records for the emissions from power plants and previous studies of the temporal distribution of spherical fly ash particles in the sediments of some small lakes showed that the first signs of the impact of these emissions appeared in the 1920s and increased exponentially since the 1950s (Punning et al. 1997). Evidence of atmospheric transport of PAHs adsorbed onto the smallest fly ash particles has been shown by many researchers (Trapido and Veldre 1996; Teinemaa et al. 2002). Chamber experiments have identified the desorbed PAHs, PHE, FLT, pyrene, BaA, CHR, BbF and BaP (Teinemaa et al. 2002). Their molecular weight is from 178 to 252 and they belong to two- to five-ring PAHs.

The sediment core data show that the influx of most of the analysed PAHs increased continuously in the layers accumulated since the 1920s to the present

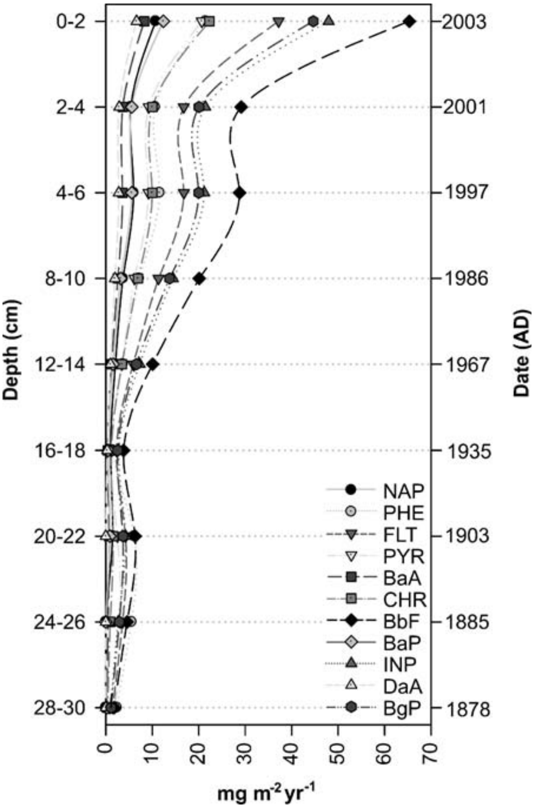

Fig. 5 PAHs influx values into core PS4 since 1878 to the present

(Fig. 5). As the fly ash emissions have clearly decreased after the 1980s (from 300 kilotonnes at the end of the 1970s to 22 kilotonnes in 2003 annually), it is evident that oil shale combustion is not the only source of PAH influx to the lake. This decreasing impact of fly ash emissions on the atmospheric influx into the sediments was also shown in a recent sediment core study from the vicinity of our study site (Nõges et al. 2006). In that core study, the fly ash particles appeared in layers dated by ^{210}Pb to 1920. Maximum concentrations of fly ash particles were estimated to be in the layers dated to 1985, and afterwards a rapid decrease of fly ash particles began. This indicates that in addition to oil shale combustion, PAHs from other important sources exist.

The influxes of most of the identified PAHs reached their first maximum values in the 1990s, and then, after a stable period began to increase again reaching their maximum values in surface layers. The largest influx values are for BbF, INP and BgP. These five- and six-ring PAHs are associated with diesel fuelled vehicle emissions, which have been increasing rapidly during recent decades.

Fate and transport of PAHs

Because some PAHs are carcinogenic, there is considerable interest in their fate and transport in the environment, uptake into the biological food chain and degradation. L. Peipsi is large and shallow; therefore resuspension and resedimentation play an important role because surface layers have high porosity (water content up to 95%). Although the samples were taken from the deepest area of the lake, resedimentation still occurred as demonstrated by the high variations of fly ash particles from a core studied by Nõges et al. (2006) nearby. Since one of the objectives of this study was to use PAH distribution to study sedimentation processes, we correlated the PAH distribution to the distribution and origin of organic matter and the grain size of sediments. Layers from depths 46 to 22 cm represent a background" conditions when the impact of human activity was absent or weak (no diesel engines, wood burning in ovens with low chimneys).

The concentrations of PAHs in the lower layers are relatively stable and only the layers at depths of 42–40 and 30–28 cm show notably lower concentrations of PHE than other layers. The sediments are characterised by relatively stable accumulation rates, organic matter concentrations and porosity. The C/N ratio falls from 8.7 in deeper layers to 8.0 in surface layers indicating an increase in the share of planktonic matter towards the surface.

Table 4 Annual atmospheric influx (μg m^{-2} yr^{-1}) of some PAHs during the 1986/87 winter (snow samples 95 days, in brackets data calculated for the whole year) and in the 1980s calculated from sediment data (see also Fig. 5)

PAH	Measured in 1986/87	1980 influx calculated from sediment data (core PS4)
Benzo(*a*)pyrene (BaP)	3.37 (13)	7
Benzo(*b*+*k*)fluoranthene (BbF)	10.87 (41.7)	20
Dibenzo(*a*,*h*)anthracene (DaA)	1.16 (4.45)	3

As seen from the correlation matrix (Fig. 6) the correlations (Spearman's) in the concentrations between individual PAHs are very good ($r = 0.88-0.99$; $P<0.0001$) with the exception of PHE, which has a little weaker correlation with other PAHs ($r = 0.56-0.73$; $P<0.003$). All PAHs (except PHE) have a good correlation with LOI (0.59–0.79; $P<0.003$) and they seem to prefer co-precipitate with planktonic matter (have lower C/N ratio; Punning and Leeben 2003). It was also showed by Kirso and Irha (1998) that up to 99% of BaP is consumed from water by algae (especially *Fucus vesiculosus*). According to monitoring data, in 1987 three- and four-ring PAHs (FLT, PHE) prevailed in lake water and five- and six-ring PAHs (BbF, INP, BgP) were predominant in sediments. This means that while PAHs with smaller molecular masses (FLT, PHE, PYR) might be transported in the gaseous phase and are in soluble form in water then those with more than five-fused rings are almost completely associated with solid particles. PAHs of light molecular mass that are transported by air or in solution undergo chemical transformation in sunlight too. The distribution of individual PAHs in sediments shows that most persistent are BbF, INP, BgP, and FLT. Their persistence might be caused, among other factors by their tight link with settling particles and therefore quick emersion from oxidation conditions.

On the basis of earlier and present data we may say, that while in the 1970s the emissions from the oil shale operated power plants were the dominating source of PAHs to L. Peipsi and its catchments, then since the 1980s other sources that increase the influx of PAHs on the background of rapidly decreasing fly ash emissions dominate. A characteristic feature of almost all individual PAHs in Estonia is the short-time decrease in emissions in the second half of the 1980s. By the data of the Estonian Environmental Information Centre (Environmental 2005) the following PAHs were emitted then (in decreasing order): BbF, BaP and INP. By 1993 the emission of PAHs had decreased by ca 42% compared to 1990. After the reduction the emissions have increased again more than twice since 1997. It is in good correlation with the L. Peipsi data speaking about the long-range atmospheric input of PAHs. Taking into account the large area of L. Peipsi and the dominating winds (Fig. 1) the sediment records reflect the changes in the general atmospheric input from large areas.

To pinpoint the main pathways of PAHs into the reference core we studied also bottom surface sedi-

	LOI550 %	Corg/N	Corg %	LOI/C	NAP	PHE	FLT	PYR	BaA	CHR	BbF	BaP	INP	DaA	BgP
H2O %	0.67 0.001	-0.78 < 0.0001	0.47 0.023	0.58 0.004	0.83 < 0.0001	0.40 0.063	0.72 0.0001	0.73 0.0001	0.83 < 0.0001	0.81 < 0.0001	0.71 0.000	0.75 < 0.0001	0.70 0.0003	0.85 < 0.0001	0.75 < 0.0001
LOI550 %		-0.58 0.004	0.83 < 0.0001	0.57 0.005	0.73 0.0001	0.45 0.031	0.64 0.001	0.64 0.001	0.73 0.0001	0.61 0.002	0.63 0.002	0.72 0.0001	0.60 0.003	0.79 < 0.0001	0.59 0.004
Corg/N			-0.24 0.271	-0.74 < 0.0001	-0.82 < 0.0001	-0.45 0.031	-0.78 < 0.0001	-0.81 < 0.0001	-0.81 < 0.0001	-0.80 < 0.0001	-0.77 < 0.0001	-0.75 < 0.0001	-0.77 < 0.0001	-0.82 < 0.0001	-0.80 < 0.0001
Corg %				0.09 0.672	0.48 0.022	0.45 0.032	0.39 0.064	0.38 0.076	0.48 0.022	0.33 0.129	0.37 0.079	0.48 0.023	0.34 0.113	0.57 0.005	0.33 0.128
LOI/C					0.66 0.001	0.26 0.227	0.61 0.002	0.70 0.0003	0.63 0.002	0.69 0.0003	0.60 0.003	0.59 0.004	0.60 0.003	0.61 0.003	0.62 0.002
NAP						0.62 0.002	0.91 < 0.0001	0.89 < 0.0001	0.99 < 0.0001	0.93 < 0.0001	0.92 < 0.0001	0.90 < 0.0001	0.91 < 0.0001	0.93 < 0.0001	0.91 < 0.0001
PHE							0.73 0.0001	0.70 0.0003	0.61 0.002	0.65 0.001	0.73 0.0001	0.56 0.006	0.72 0.000	0.60 0.003	0.70 0.0003
FLT								0.96 < 0.0001	0.92 < 0.0001	0.96 < 0.0001	0.99 < 0.0001	0.86 < 0.0001	0.97 < 0.0001	0.88 < 0.0001	0.98 < 0.0001
PYR									0.91 < 0.0001	0.95 < 0.0001	0.93 < 0.0001	0.77 < 0.0001	0.91 < 0.0001	0.89 < 0.0001	0.94 < 0.0001
BaA										0.94 < 0.0001	0.93 < 0.0001	0.90 < 0.0001	0.93 < 0.0001	0.95 < 0.0001	0.93 < 0.0001
CHR											0.96 < 0.0001	0.84 < 0.0001	0.95 < 0.0001	0.89 < 0.0001	0.97 < 0.0001
BbF												0.89 < 0.0001	0.99 < 0.0001	0.88 < 0.0001	0.99 < 0.0001
BaP													0.91 < 0.0001	0.88 < 0.0001	0.88 < 0.0001
INP														0.88 < 0.0001	0.99 < 0.0001
DaA															0.88 < 0.0001

Fig. 6 Spearman correlation diagram of PAHs and some lithological characteristics

ments from 4 sites in near-shore areas of the lake. As seen from Fig. 4, the compositions of PAHs in the studied sediments as well as their concentrations are very similar to those of background values estimated in the lower sediment layers. This shows absence or limited extent of the transport of PAHs in the water environment in soluble or sorbed in suspended matter form.

Kirso et al. (2006) studied the levels of 16 priority PAHs according to US Environmental Protection Agency list in the airborne particulate matter in Tallinn (capital of Estonia, centre of industry and cargo port, ca 150 km from L. Peipsi) and found that PAHs with molecular mass over 252 dominate, and the highest concentration were measured for BgP, INP, BaP, BbF. They concluded that the non-road transport and treatment of stored fuel of a cargo port are significant sources of emission.

It must be mentioned that there is discrepancy between the emission and presence of BaP in sediments. If in emissions the amount of BaP is biggest among the studied PAHs (Environmental 2005), then its content in sediments is relatively low and stabile. It is well known that PAHs have different sensitivity to environmental conditions and that photooxidation is the major decomposition process beside the biodegradation by microorganisms (Suess 1976). These processes are more significant for the low molecular weight two- and three-ring PAHs, whereas the four- and six-ring PAHs are more resistant which is highly important in aerial transport.

Conclusions

Basing on the earlier studies, we hypothesised that there must be certain accordance between the distribution of PAHs in the sediment sequence in Lake Peipsi and atmospheric emissions from oil-shale combustion. Due to the plurality of pollution sources the PAHs records are more complicated than this. The obtained data allow us to distinguish PAHs of different origins and show that benzo(a) pyrene and phenanthrene have mainly natural sources, their concentrations increase in sediments accumulated since the beginning of the 20th century rather modestly. Most essential is anthropogenic impact on the presence of five- and six-ring PAHs like benzo(b-k)fluoranthene, indeno (1,2,3-cd)pyrene and benzo(*g*,*h*,*i*)perylene. Their dominance indicated mainly pyrolytic inputs. Absence of PAHs in nearshore sediments speaks about aerial input of PAHs and their quick accumulation in co-precipitation with organic compounds, mainly of planktonic origin. The temporal distribution of PAHs in sediments is in certain correlation with the emission of PAHs resulting from wood and fossil fuel combustion in Estonia. The relatively low share of benzo(*a*)pyrene in the contemporary sediments as compared with monitoring data from the 1980s may be explained first by their higher share in the oil-shale industry emissions and easier degradation during the pathway to sediments and in sediments. The atmospheric transformation and high persistency of the five- and six-ring PAHs in sediments suggest that their elevated appearance in the sediments may be used as a time marker (in Estonia ca the 1920s).

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IV

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Grain-size analysis of lacustrine sediments: a comparison of pre-treatment methods

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Abstract. This study presents the results of an experimental investigation of five different pre-treatment methods for measuring the grain-size distribution of allochthonous siliclastic matter in cohesive organic-rich sediments and some comparisons with mineral-rich sediments. The loss on ignition (LOI) methods were the fastest for eliminating organic matter but here a problem of aggregate formation may arise. Oxidation with H_2O_2 was time and resource consuming. Getting reproducible results was hard and the reaction was not completed for grain-size analysis. Therefore the samples were also treated and carbonates were removed with HCl. It was also very important to remove biogenic silica by alkali treatment. The median values in grain-size spectra had trends towards finer grain size after treatment with KOH and observations with light microscope showed changes during treatments. The grain-size distribution measured by a laser particle sizer differed considerably between the five pre-treatment methods studied.

Key words: allochthonous siliclastic matter, biogenic silica, cohesive sediments, lake sediments, particle size, organic matter, pre-treatment methods.

INTRODUCTION

In an aquatic environment different compounds are incorporated within or absorbed on mineral matter depending on the physical, chemical, and biological processes that may change substantially the sediment texture. Extra difficulties arise in analysing fine-grained materials (clay and silt). Fine-grained sediments in an aquatic environment may aggregate into larger, porous aggregates commonly called flocs (Van Rijn, 1993; Roberts et al., 1998; Kim et al., 2005). These sediments are cohesive by definition (Hayter & Pakala, 1989; Paterson, 1997) and their composition and structure are temporally very changeable. The organic matter as well as different micro- and macrocomponents in the aquatic environment will be closely associated with suspended mineral particles, e.g. adsorbed on single particles, forming complexes with metal (usually iron) oxides on the surface of particles, become aggregates and are deposited or transported in this form within the lake. The large specific surface area, surface energy, and electrostatic charge of small and colloidal particles mainly drive coagulation (Gu et al., 1996).

Thus sediment texture gives very diverse information about the sedimentation environment. Depending on the aims of research, different methods are used to describe sediment texture. For example, electron microscopic research enables to fix the three-dimensional structure of particles or aggregates (Konert & Vandenberghe, 1997; Kim et al., 2005). Light microscopic research enables primary estimation of sediment composition and selection of appropriate pre-treatment methods, as well as monitoring the progress of processes. Recent researches show that due to the fragile nature of aggregates, sometimes their properties have to be determined in situ (Mikkelsen & Pejrup, 2001; Thonon et al., 2005).

The grain-size spectrum is influenced by authigenic minerals such as carbonates or diatom valves of diameter range 5–200 µm (Round et al., 1990) and by their fragments. The proportion of diatoms may vary largely, being even up to 50% of the bulk sediment, and it is source material for diatomite (Kadey, 1983).

The methods used for the pre-treatment of samples and grain-size analysis depend on the aim of studies. If we are interested in the distribution of allochthonous siliclastic matter in sedimentation processes, it is necessary to have for analysis purified material, that is the disaggregate flocs and sorbed materials (organics, carbonates, etc.) have to be removed from the grains. The problem is quite easily solved in the case of medium- or coarse-grained particles by using the sieving method for grain-size analysis (Last, 2001a). Complicated problems arise in the case of fine-grained material where secondary side-effects in the sedimentation environment as well as during the pre-treatment process (flocculation, damaged grains, etc.) could seriously affect the reliability of the obtained grain-size spectrum.

The majority of sediment grain-size studies are associated with marine, loess, fluvial, and aeolian sediments (Lu & An, 1997; Buurman et al., 2001; McCave et al., 2006; Almeida et al., 2007), which are usually poor in organic matter. Also these researches commonly study coarse-grained sediments (sand, gravel, etc.), formed in the water environment with a high ion concentration, and the sediments are generally rather well sorted.

The aim of this work is to compare the impact of different pre-treatment methods on the results of granulometric analysis of fine-grained lacustrine sediments, rich in organic matter (ca 40–50%).

METHODS

To determine the influence of sediment pre-treatment methods on the grain-size spectrum of different lacustrine sediments obtained with a laser particle sizer, two lakes of different sedimentation environment were selected: typical South Estonian eutrophic Lake Tündre (L. Tündre) (sampling site: 57°57′19″ N, 25°36′32″ E) and large and shallow mesotrophic Lake Peipsi (L. Peipsi) (sampling site: 58°55′44″ N, 27°13′47″ E). The sampling was performed with a modified Livingstone–Vallentyne piston corer from surface sediments (40 cm thick). The lithology of the core was recorded in the field. Sediments from L. Tündre are dark black very cohesive and homogeneous organic matter rich gyttja. The surface sediment of the L. Peipsi sample consisted of green-grey gyttja with a smaller content of organic matter.

To determine the lithological composition of the sediments (content of water and of organic, carbonate, and mineral matter) the well-homogenized sediments were processed using standard loss-on-ignition (LOI) methods (Boyle, 2001; Heiri et al., 2001). The results of content analysis show the demand for different chemicals in analysis. Similarities of LOI results indicate how homogeneous samples are. For LOI analysis samples were dried at 105 °C up to constant weight. From every sample several subsamples were separately analysed by LOI standard methods. Small differences (ca 1%) in dry weight were an indication of homogeneity of samples.

After data on the lithological composition of the samples for grain-size analysis were obtained, different pre-treatment methods were applied. A total of 230 results of parallel measurements of grain-size distribution were obtained for analysis.

Different methods are used for eliminating organic matter. A widely used approach is thermal combustion. For this samples dried to constant weight were kept in a previously weighed crucible in a muffle furnace and the organic matter was measured as LOI after heating the samples at 550 °C for 3.5 h (Boyle, 2001; Heiri et al., 2001) (hereafter referred to as method LOI550). This method is certainly the easiest but it is necessary to consider that depending on sample lithology and mineral content, problems with grain aggregate formation may occur (Murray, 2002).

To avoid damaging grains during pre-treatment, wet oxidation is often preferred to combustion for organic matter removal. Widely used oxidants are potassium dichromate (Walkley & Black, 1934) and hydrogen peroxide (Schumacher, 2002; Allen & Thornley, 2004). In this research concentrated hydrogen peroxide (30%) was used for organic matter oxidization (hereafter referred to as method H_2O_2). Hydrogen peroxide was continually added to the sample until sample frothing ceased. The samples were heated to 80 °C during hydrogen peroxide addition to increase the speed and completeness of hydrogen peroxide digestion. After the active reaction ended, the samples were washed with distilled water by centrifugation at 3500 rpm for 8 min and the solution was decanted. All chemical procedures were carried out in high-temperature-proof (at least 100 °C) and acid-proof 120 mL centrifuge tubes.

Thermal combustion is also often used to remove carbonates (Murray, 2002). Decomposition of carbonates was accomplished by heating the samples at 950 °C for 2.5 h (Boyle, 2001; Heiri et al., 2001) (hereafter referred to as method LOI950).

Also hydrochloric acid is commonly cited for carbonate removal (Battarbee, 1986; Battarbee et al., 2001; Schumacher, 2002). In this research 15 mL of 10% HCl solution was used added to the wet sample held in a water bath at 80 °C for 5 h. Besides $CaCO_3$ also Fe, Mg, and Al were dissolved. After that the samples were washed with distilled water three times by centrifugation at 3500 rpm for 8 min, and the solution was decanted. Next the organic matter was removed by adding H_2O_2 until the sample colour turned white. When the active reaction ended, the samples were washed with distilled water until a neutral environment was achieved by centrifugation at 3500 rpm for 8 min, and the solution was decanted.

Eliminating Fe ions makes the process of the oxidation of the organic matter with H_2O_2 significantly quicker, because Fe is known as a catalyst for H_2O_2 decay (Mikutta et al., 2005). This method is hereafter designated as method $HCl+H_2O_2$.

Diatom valves, which consist mainly of biogenic silica, also influence grain-size distribution. To remove biogenic silicates (diatom valves and their fragments) alkali was used (Conley, 1998; Lyle & Lyle, 2002). The samples previously pre-treated with 10% HCl and 30% H_2O_2 were now pre-treated with 10 mL of 10% KOH in a water bath at 80 °C for 30 min. After that the samples were washed with distilled water until a neutral environment was achieved by centrifugation at 3500 rpm for 8 min, and the solution was decanted. This method is hereafter designated as method $HCl+H_2O_2+KOH$.

Brief descriptions of the five different pre-treatment methods of this experimental investigation for measuring grain-size distribution are presented in Table 1.

To avoid grain flocculation during pre-treatments, 1% solution of sodium hexametaphosphate $(NaPO_3)_6$ (known as Calgon) was used (Murray, 2002; Andreola et al., 2004).

For estimating the efficiency of different pre-treatment methods a light microscopic study of the samples was conducted. Suspensions were mounted on glass slides using Naphrax® (R.I. $\geq$ 1.74) and examined under a stereomicroscope. The general composition of each sample and sizes of particles were measured using an Olympus BX41 microscope with phase-contrast at 1000× magnification.

Grain-size spectra were obtained with a Fritsch Laser Particle Sizer "Analysette 22". The laser diffraction method for the analysis of sediment grain-size distribution is nowadays well known and widely used (McCave & Syvitski, 1991; Konert & Vandenberghe, 1997; Buurman et al., 2001; Bohling, 2004; Blott & Pye, 2006; McCave et al., 2006; Punning et al., 2008). The used laser particle sizer can measure grain size in the range 0.3–300 µm and to distinguish 62 magnitudes. The laser particle sizer parallel laser-light is scattered to fixed spatial angles, which depend on the particle size and the optical properties of the particles, a lens focuses the scattered light concentric to the focal plane, where a detector measures and the program calculates the particle size distributions.

Table 1. Brief descriptions of the pre-treatment methods studied

Abbreviation	Description of method
LOI550	Organic matter removal by thermal combustion at 550 °C for 3.5 h
H_2O_2	Organic matter removal by concentrated (30%) H_2O_2
LOI950	Carbonated matter removal by thermal combustion at 950 °C for 2.5 h
$HCl+H_2O_2$	Carbonated matter removal by 10% HCl; thereafter organic matter removal by concentrated (30%) H_2O_2
$HCl+H_2O_2+KOH$	Carbonated matter removal by 10% HCl; thereafter organic matter removal by concentrated (30%) H_2O_2; diatoms removal by 10% KOH

For analysing samples with a laser particle sizer 0.2 g of pre-treated mineral matter has to be entered to get the required amount of particles in the detector. Previous experience has shown that to get statistically reliable results a minimum of three reproducible measurements whose standard deviations do not exceed reproducible accuracy have to be made. Reproducible accuracy was achieved by the laser particle sizer's own standard sample Fritsch Standard F500. The maximum standard deviation of the repeated measurements was 8%. The homogeneous sample had an appropriate moisture content (creamy consistency). Repeated measurements showed that in excessively liquid samples the coarse-grained material settled out, as a result of which the distribution of the material became heterogeneous. In case of excessively dry samples it was also hard to get a homogeneous sample consistency.

In this paper the grain sizes follow the Udden–Wentworth grain-size scale (Last, 2001b) and are presented in micrometres. Statistical analyses were made with the laser particle sizer control program and MS Excel.

RESULTS

Sediments from L. Tündre were very porous: their water content was 91.7%. Of the dry matter 48.6% was organic and 51.4% mineral, of which carbonaceous compounds made up 4.1%. In L. Peipsi sediments the mineral matter content (carbonaceous compounds included) was 96.7% and organic matter constituted only 3.3% (Table 2).

The grain-size spectra obtained using the five different pre-treatment methods (Table 1) (four groups – thermal combustion (LOI550, LOI950), method H_2O_2, method $HCl+H_2O_2$, and method $HCl+H_2O_2+KOH$) clearly differed (Figs 1 and 2). Methods LOI550 and LOI950 showed dominance of coarse and very coarse silt fractions in the L. Tündre samples. Method LOI950 showed larger sand concentrations (very fine sand 9.6% and fine sand 1.8%) (Table 3, Fig. 1). The clay content was the highest (11.5%) by method H_2O_2 while the highest coarse silt content, 29.2%, was revealed by method $HCl+H_2O_2$ (Table 3, Fig. 1). In chemical treatments the results of method $HCl+H_2O_2+KOH$ indicated the lowest fine (14.8%) and medium silt (18.6%) content (Table 3).

Table 2. Sediment lithology of lakes Tündre and Peipsi

	Lake Tündre	Lake Peipsi
Water content, %	91.7	50.5
Dry matter, %	8.3	49.5
Organic matter, %	48.6	3.3
$CaCO_3$, %	4.1	3.1
Mineral matter, %	47.3	93.6
Biogenic silica, valves/g	133×10^6	20×10^6

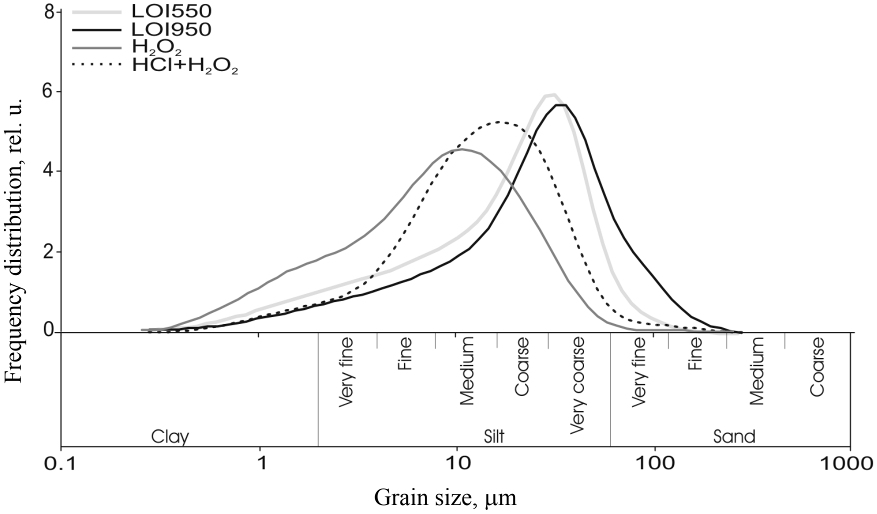

Fig. 1. Grain-size spectra of samples from L. Tündre after applying different pre-treatment methods. The descriptive terms follow the Udden–Wentworth grain-size scale.

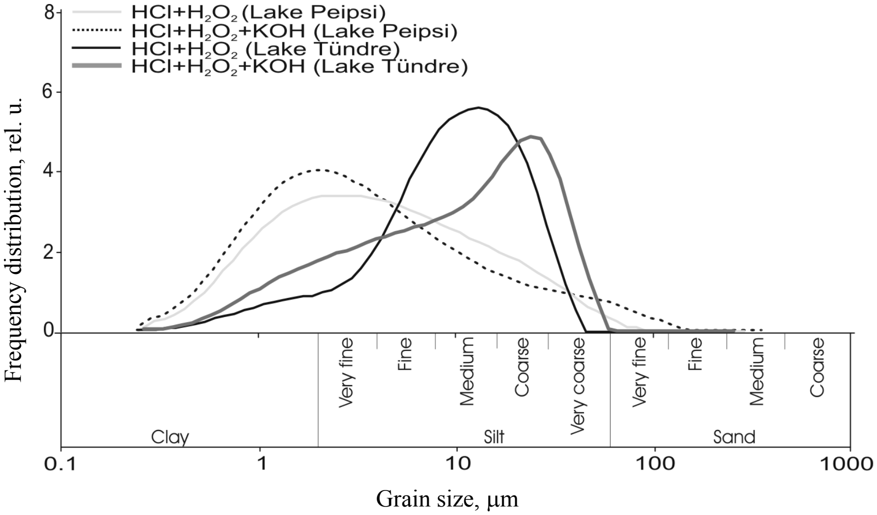

Fig. 2. Grain-size spectra of samples from L. Tündre and L. Peipsi after applying $HCl+H_2O_2$ and $HCl+H_2O_2+KOH$ pre-treatment methods. The descriptive terms follow the Udden–Wentworth grain-size scale.

Special attention was paid to the content of biogenic SiO_2. Diatom valves and their fragments also influence the grain-size spectrum. To analyse the effect of KOH the results are presented in Fig. 2, where L. Tündre and L. Peipsi results of sediment samples are compared. Pre-treatment methods $HCl+H_2O_2$ and

Table 3. Grain-size percentage distribution after applying different pre-treatment methods (Udden–Wentworth grain-size scale)

Descriptive terms	Lake Tündre					Lake Peipsi	
	LOI550	LOI950	H_2O_2	$HCl+H_2O_2$	$HCl+H_2O_2$ $+KOH$	$HCl+H_2O_2$	$HCl + H_2O_2$ $+KOH$
Clay	7.0	5.0	11.5	4.7	10.8	27.5	33.5
Silt							
Very fine	8.4	6.1	14.1	7.1	13.5	24.0	26.5
Fine	10.3	8.0	19.4	16.0	14.8	18.7	16.5
Medium	15.1	12.5	26.5	28.5	18.6	14.6	10.5
Coarse	28.2	25.3	20.7	29.2	26.9	10.2	6.7
Very coarse	27.5	31.8	7.2	12.6	15.4	4.8	5.2
Sand							
Very fine	3.2	9.6	0.4	1.5	0	0.2	1.2
Fine	0.3	1.8	0.1	0.5	0	0	0

$HCl+H_2O_2+KOH$ were used for analysing L. Peipsi sediment samples. The concentrations of clay and very fine silt in L. Peipsi were 33.5% and 26.5%, respectively (method $HCl+H_2O_2+KOH$). Like L. Tündre, L. Peipsi had lower fine and medium silt concentrations (Table 3, Fig. 2) and also a smaller median value compared with method $HCl+H_2O_2$ (Table 4).

Table 4. Statistical characteristics of different pre-treatment methods

	Lake Tündre					Lake Peipsi	
	LOI550	LOI950	H_2O_2	$HCl+H_2O_2$	$HCl+H_2O_2$ $+KOH$	$HCl+H_2O_2$	$HCl+H_2O_2$ $+KOH$
Arithmetic mean diameter, µm	24.3	33.9	12.9	18.5	16.0	8.2	8.1
Mode, µm	32.3	33.7	12.1	17.1	26.5	2.8	2.1
Median, µm	20.9	26.9	9.4	14.0	12.4	4.0	3.1
Variance, µm²	436.6	996.5	172.1	353.1	180.0	114.2	185.2
Mean square deviation, µm	20.9	31.6	13.1	18.8	13.4	10.7	13.6
Coefficient of variation, %	85.9	93.2	101.8	101.5	84.1	130.0	168.0
Span	2.2	2.5	2.8	2.3	2.7	5.1	6.5
Specific surface area, cm²/g	9 132.3	7 254.8	13 729.0	8 282.0	12 310.6	25 206.1	28 841.3

The efficiency of Calgon as an antiflocculant was analysed in L. Tündre sediment samples. The results of grain-size distributions were very similar to the results of the pre-treatments without Calgon. The maximum standard deviation between the results with Calgon and without it was only 6%. The fact that the laser particle sizer has its own ultrasonic system that also disaggregates flocs may be the reason why the effect of Calgon did not come out. This may show the efficiency of the ultrasonic system or a low flocculent concentration in samples: the carbonate (flocculent) content was only 4.1% in L. Tündre and 3.1% in L. Peipsi. Besides, carbonate matter was removed by HCl addition.

Microscopic observations showed a large percentage of fine-grained matter and silt particles in the cohesive sediments coated with inorganic (oxides, carbonates, etc.) and organic (mainly plant and animal detritus and bacteria) substances adsorbed on the surface.

DISCUSSION

The results show that the pre-treatment methods influence substantially grain-size spectra measured by the laser particle sizer. Depending on the sediment particle structure and the mineral physical and chemical composition as well as the sedimentation environment (electric conduction, temperature, cycling of substances, etc.) very varied structures may occur. Thermal or chemical treatment is accompanied by different transformations reflected in the grain-size spectra and in the results of statistical data (Table 4). It is especially difficult to choose the right pre-treatment method for the analysis of the grain-size distribution of allochthonous matter in cohesive sediments.

Comparison of two thermal treatment methods, LOI550 and LOI950, showed that the grain-size mode values shifted towards the coarse-grained fraction when method LOI950 was used (Fig. 1). In statistics the specific surface area is the best parameter to characterize a spectrum shift. In the case of method LOI950 the specific surface area value (7254.8 cm^2/g) was the smallest among all pre-treatment methods studied (Table 4). The spectrum mode value shift towards the coarse-grained fraction was due to two processes. One reason was that at 950 °C carbonates decompose. At the same time fine-grained matter may aggregate (Murray, 2002). The intensity of aggregation depends on the pore-water content, texture, and composition of sediment. The chemicals used could not crumble grains because these are harmless for siliclastic grains and widely used. Moreover, aggregation was avoided by using Calgon and an ultrasonic system. It can be clearly seen that after thermal combustion the grain-size median value shifted to the coarser-grained (very coarse silt) fraction than in the chemically treated samples (Table 4). This may show the effect of aggregate formation.

Table 4 presents the results of statistical treatment of grain-size distribution by pre-treatment methods. One statistical indicator need not always characterize the object well enough. The most significant of the values presented in Table 4 are discussed below while some of the statistics are just auxiliary indicators.

The H_2O_2 pre-treatment method is the most widely used wet oxidation method for organic matter (Carver, 1971; Konert & Vandenberghe, 1997; Lu & An, 1997; Murray, 2002; Allen & Thornley, 2004; Mikutta et al., 2005). Our multiple experiments showed that pre-treatment of organic-rich sediment until total organic matter became oxidized was very time consuming and the H_2O_2 amount exceeded essentially the stoichiometrically needed amount. Due to the large amount of Fe and its form it was very hard to get reproduced results (standard deviation larger than 10%). After the H_2O_2 treatment part of the samples were treated by method LOI550. In the course of this treatment 12% of the analysed matter was eliminated. This suggests that with method H_2O_2 the oxidation reaction of organic matter was not complete.

Microscopic analyses showed that the samples were red; this means they were Fe oxide coated. To remove Fe oxide, the samples were extracted with HCl as suggested also by Dominik & Kaupenjohann (2000). In that case the H_2O_2 amount necessary and treatment time decreased substantially. After the application of method HCl+H_2O_2 the samples were white and individual grains were clearly distinguishable (Fig. 3).

The specific surface area of sediment in L. Tündre was the largest (13 729.0 cm^2/g) in the case of treatment with method H_2O_2, which means that the percentage of fine-grained matter (clay, very fine silt) was the greatest. This may be due to the carbonate content because also after treatment with method LOI550 the grain size was finer than after treatment of samples with method LOI950 where carbonates were removed. Treatment with HCl decreased significantly the specific surface area value of the samples of L. Tündre (Table 4).

The concentration of diatom valves was 20×10^6 in the sediments from L. Peipsi and 133×10^6 valves per g dry sediment mass in L. Tündre. As the size of valves is from 5 to 200 µm (Round et al., 1990), their presence might essentially

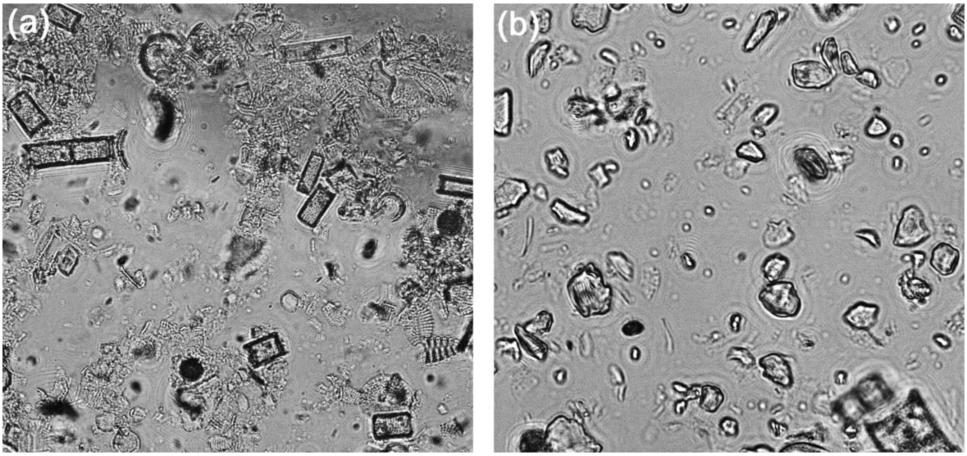

Fig. 3. Microscopic analysis of L. Tündre sediment: (a) samples treated by method HCl+H_2O_2, sample with diatoms; (b) samples treated by method HCl+H_2O_2+KOH, single grains without diatoms.

distort the grain-size spectra. Therefore in the studies of the grain-size distribution of siliclastic matter it is very important to remove also diatoms. After the removal of diatom valves and their segments the grain-size spectrum will change significantly. The most effective elimination method of diatoms, which are composed mainly of biogenic SiO_2, is treatment with alkali (Conley, 1998; Lyle & Lyle, 2002). The microscopic analyses showed the method's efficiency (Fig. 3a, b). Change in the sediment samples after the removal of diatoms can be well monitored by using method $HCl+H_2O_2+KOH$. For example, after the application of this method the median value of the grain-size distribution of the sediment samples from L. Peipsi shifted clearly towards a finer grain-size median (Fig. 2). This is analogues to the results of Reynolds et al. (2004) and is also confirmed by the increase in the specific surface area of sediment from 25 206.1 to 28 841.3 cm^2/g (Table 4).

The mode values of the sediment samples from L. Tündre shifted to the coarser silt (26.5 µm) fraction after the application of the pre-treatment method $HCl+H_2O_2+KOH$ (Fig. 2). The grain-size distribution of the samples treated with this method shows an increase in the percentage of clay and very fine silt (10.8% and 13.5%) compared to method $HCl+H_2O_2$ where the clay content in the samples was 4.7% and of very fine silt 7.1% (Table 3). However, the content of medium silt was smaller (18.6%). Samples from L. Peipsi treated with method $HCl+H_2O_2+KOH$ had changes in the same fraction classes and showed the same trend as in L. Tündre (Fig. 2). The decreasing of fine, medium, and coarse silt percentages after using KOH speaks about a certain amount of diatoms in those samples (Table 3). Clay and very fine silt percentages are increasing and medium and coarse silt contents are about 4% smaller than in the case of treatment with method $HCl+H_2O_2$ (Table 3).

CONCLUSIONS

To get reproducible results of grain-size distribution in studies of allochthonous siliclastic matter from eutrophic organic-rich cohesive lake sediments the autochthonous matter must be eliminated. Influences of different pre-treatment methods on sediment composition and texture were analysed. With the help of a large number of repeated analyses the most appropriate method for fine-grained (clay, silt) organic-rich cohesive sediments was selected. The following pre-treatment methods were tested: thermal combustion at 550 °C and wet oxidation with 30% H_2O_2 were used for removing only organic matter, thermal combustion at 950 °C and wet oxidation with 10% HCl were used for removing carbonate matter, and 10% KOH was used for removing biogenic silica. The efficiency of the pre-treatment method for grain-size distribution analyses depended on sediment cohesiveness (porosity, organic matter concentration, grain size, etc.). It was established that the fastest method for organic oxidation from cohesive sediments was the method with the use of 10% HCl and thereafter 30% H_2O_2. This method also gave the best fineness standard and the results were reproducible.

Sediment samples with greater diatom concentrations had to be pre-treated also with the alkali KOH. After KOH treatment the grain-size distribution changed considerably. Specific surface area showed a higher concentration of fine-grained matter than before treatment.

As an additional method for checking the completeness of the removal of non-siliclastic particles light microscopic analysis was used. This analysis enables to see the sample content, monitor the pre-treatment process, and make primary estimations of the grain-size distribution. In addition, it proves the correctness of distribution and gives the best descriptive characterization. Also the presence of additions can be followed. Light microscopic analysis also helps make the decision about the pre-treatment methods.

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Järvesetete terasuuruse analüüsid: eeltöötlusmeetodite võrdlus

Tiit Vaasma

Nagu saadud tulemused näitavad, mõjutavad eeltöötluse viisid oluliselt laser difraktsiooni meetodil määratud terasuuruse spektreid, mis võimaldab teha ka järeldusi proovide esialgse tekstuuri kohta. Olenevalt setteosakeste struktuurist, mineraalsest, füüsikalisest ja keemilisest koostisest ning ka settimiskeskkonnast (elektrijuhtivus, temperatuur, aineringe jne.) võivad eksisteerida väga erinevad struktuurid. Proovide termilise või keemilise töötlemisega kaasnevad erinevad transformatsioonid, mis peegelduvad terasuuruse spektrites ja nende statistilise töötlemise andmestikus. Sobivam viis kohesiivsete setete eeltöötluseks on keemiline töötlusmeetod ($HCl+H_2O_2+KOH$) eraldades seeläbi nii karbonaatne ja orgaaniline materjal kui ka biogeenne Si.

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ORIGINAL ARTICLE

Surface sediments of transboundary Lake Peipsi: composition, dynamics and role in matter cycling

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Abstract To describe and analyse the role of sediments in the matter cycling in large shallow transboundary Lake Peipsi (L. Peipsi) in north-eastern Europe, detailed surface-sediment mapping was conducted. On the basis of grain size the surface sediments fall into three groups: coarse-grained sediments (prevailingly sands in the lake's southern part), fine-grained sediments (mainly silts) and silty sands, both in the central deeper part within the 8-m depth contour. The groups of deposits have a distinct spatial distribution, determined mainly by the current system in the lake. The main source of bottom sediments is the erosion of the lake floor and shores, the role of the river input seems to be limited. Fine-grained organic-rich sediments are very cohesive, playing the main role in the circulation of various inorganic and organic pollutants like nutrients and xenobiotics. Due to the cohesive character of the sediments their physical and chemical properties are extremely diverse and if the near-bottom shear stress increases (extreme meteorological events, changes in the water level, etc.), the lake floor may be subjected to episodic erosion and resuspension, which may cause remobilisation of impurities in muddy sediments and their return to the food chain.

Keywords Lake sediments · Sediment lithology · Resuspension · Shear stress · Lake Peipsi

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Introduction

Quantitative description of the composition and distribution of suspended sediments is a necessary prerequisite to the determination of the transport and fate of these particles and of the chemical substances associated with them within the lake. A proper understanding of the bottom dynamic conditions (deposition, resuspension, transportation) in large lakes is essential in most sedimentological contexts. Sediments within the erosion and transportation areas usually vary significantly—from sand to loose mud. Depositions within the accumulation areas are comparatively loose, with high water and organic content, mainly in fine-grained sediments. Due to their small fall velocities, fine-grained particles (i.e. those in the silt and clay-size ranges) are transported easily by flows (Rowan et al. 1992). An understanding of the dynamic behaviour of these particles is particularly important in shallow lakes and estuaries, since there they may repeatedly settle to the bottom and be resuspended throughout the water column (Luettich et al. 1990). Changes in the hydrological regime and fluctuations of the lake level alter the lake morphometry and transform the characteristics of sedimentation zones of the lake floor thereby directly influencing sedimentation and resuspension (Davis and Ford 1982; Bloesch 1995; Shteinman and Parparov 1997). Sedimentological studies, especially on the texture of lake sediments, have been successful in investigating lake-level variations in small temperate zone lakes (Digerfeldt 1986; Dearing 1997; Punning et al. 2005).

Often sediment resuspension, transport, and deposition are the largest components of contaminant transport at a given site. The fate and transport of contaminants in aquatic systems are influenced by a range of physical, chemical and biological processes. Physical processes significantly affect the fate and transport of hydrophobic organic contaminants such as, polychlorinated biphenyls and dioxins, as well as many inorganic contaminants such as lead and mercury because they are naturally adsorbed onto the particles in the sediment bed or suspended in the water column. Sediment particles, especially the finer fractions, can adsorb contaminants from water and exert a strong influence on the transport and ultimate distribution of contaminants. Many studies (Rodrigo et al. 1988; Callieri 1997; Georgian et al. 2003) show that the qualitative composition and character of suspended particles—their capacity to dissolute, precipitate and coagulate—dictate the kinetics of particle accumulation, i.e. that gravitational settling is complicated by responses such as particle aggregation. A strong correlation between particulate organic and inorganic matter in the accumulation of matter found in a small lake (Lake Viitna, northern Estonia) during stratification indicates flocculent settling of the particles (Terasmaa and Punning 2006).

Detailed studies on the content of polycyclic aromatic hydrocarbons (PAH) in Lake Peipsi (L. Peipsi) and its catchment (Trapido and Veldre 1996; Punning et al., in press)show that the regional atmospheric and riverside load can contribute a significant part of the total pollution of this lake. Being a large lake, L. Peipsi acts as a regional sink for atmospherically transported particles and chemical compounds as well as those originating from the catchment. Therefore, its sediments can provide valuable information on temporal changes in these inputs.

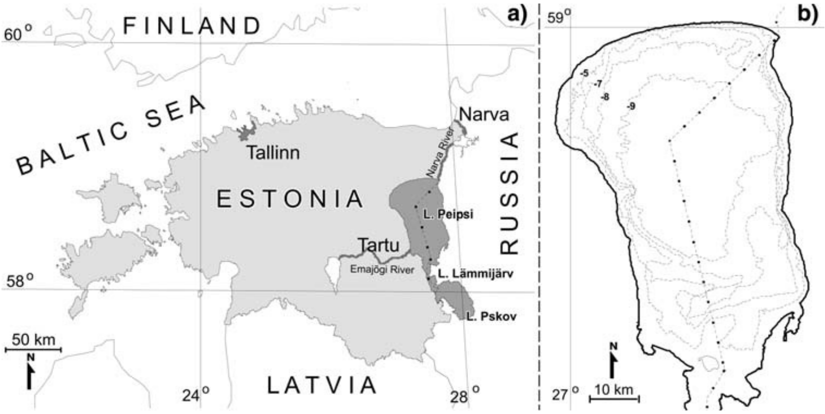
In this paper, we describe the largest part of the lake, Peipsi proper. This part plays the most important role in the fishery and transport, which both depend highly on bottom deposits, topography and shore types. As L. Peipsi is shallow and has a large surface area, waves may be as high as 2.3–2.4 m (Jaani 2001) reaching the bottom and reworking it, mixing waters of the lake and resuspending accumulated sediments. This phenomenon has a significant impact on the resuspension and resedimentation and thus on the distribution of pollutants within the lake and makes it possible to return deposited impurities to the food chain. To examine natural and human-induced changes in matter cycles and the role of various geological and physico-geographical factors in the formation of bottom deposits is the main task of this paper.

Study area

The submeridionally elongated L. Peipsi on the border of Estonia and Russia (surface area 3,555 km^2, maximum length approximately 150 km and width 42 km) consists of three parts: L. Peipsi proper, Lake Lämmijärv and Lake Pskov (Lake Pihkva in Estonian) (Fig. 1a). Its catchment area (47,800 km^2) is currently shared mainly between Estonia and Russia, smaller parts belong to Latvia and Belarus. A flat lowland area 30–45 m a.s.l. with peculiar landforms rarely higher than 80 m surrounds L. Peipsi (30 m a.s.l.) The 50–60-m deep glacially eroded depression, which presently holds L. Peipsi was formed in the Ordovician and Devonian sedimentary bedrock. Till covers the bedrock over the entire lake bottom and is overlain by a 10-m thick bed of glaciolacustrine clay or silt. The distribution of lake marl and gyttja is limited to the deeper central part of the lake while the thickness of the calcareous layer varies from a few centimetres to 1.9 m. Gyttja deposits, up to 5-m thick, are greenish in their lower portion and change to dark black towards the top (Hang et al. 2001). Its bottom deposits are described in a collection of papers in Russian (Raukas 1981) and in monographs in Estonian (Pihu and Raukas 1999) and in English (Miidel and Raukas 1999).

The present-day lake is shallow; its average depth at medium water level is 7.1 m. The central part of the lake is

Fig. 1 Location of L. Peipsi (**a**) and its bathymetry (**b**). Depths are given in metres



9–11-m deep; the coastal zone is shallow and transformation to the rather monotonous floor descends for some kilometres in the eastern and western coasts (Fig. 1b). The area and depths of the lake are highly dependent on the water-level fluctuations.

The average velocity of the wind is 4–5 m $\sec^{-1}$. The strongest winds blow in October, while June is the calmest month. South-westerly and southerly (45–50%) winds predominate in the depression of the lake causing high rises in the water level in the northern part of the depression and intensive erosion of the coast (Tavast and Raukas 2002). Longshore drift is there from west to east, and therefore the outflow of the Narva River, located in the NE corner of the lake, needs to be regularly scoured of sandy sediments, blocking the outflow. About 12,500 m^3 of sand is accumulated here annually.

Wind drift and gradient (compensation, flow, seiche and internal pressure streams) exist in L. Peipsi (Kallejärv 1973). The surface water moves in the direction of the wind in the northern part of L. Peipsi, and anticyclonic and cyclonic circulation is characteristic in the southern part. Near the bottom of the northern part of the lake, compensation streams form; in the shallow southern part, the surface currents reach the bottom. Waves are steep and short, and with the wind force of of 8 m $\sec^{-1}$, their height is 60–70 cm (Sokolov 1983). Waves of such height are most common in L. Peipsi (57%). The highest waves (240 cm) were recorded in 1961 and 1962 with the wind force of 20 m $\sec^{-1}$.

Presently, eutrophication is a major problem in L. Peipsi. Several studies have been undertaken to track the water quality trends of the lake, but important questions still remain unsolved, particularly about the role of internal and external phosphorus loading. Although nutrient loading decreased in the 1990s (Blinova 2001; Kangur et al. 2002), phosphorus concentrations in L. Peipsi remain high (some 50 mg m^{-3}), partly due to the release of phosphorous from a large phosphorous pool in the bottom sediments.

Methods

First systematic and detailed studies of bottom deposits of L. Peipsi were performed in the 1970s and 1980s. In 2005–2007 we repeated the mapping of sediments with the aim of compiling a detailed map of the bottom deposits, studying the dynamics of surface sediments and understanding the role of cohesive sediments as an exchange pool of pollutants accumulated especially in the 1970s–1980s when extensive industrial and farming activities were pursued in the catchment.

Sampling

The sampling density depended on the heterogeneity of the deposits and the bathymetry of the lake. In the 1970s sampling was performed from a ship. In most cases, the length of tours was 6–8 km and the distance between the sampling points 4–6 km. As the floor of L. Peipsi is monotonous and the sediments are more or less similar, such sampling density was sufficient to receive a reliable map of the bottom deposits (see Raukas and Rähni 1981 with later modifications in Raukas 1999). The sampling from the shallow coastal zone was sparse.

During the summer seasons of 2006 and 2007, 58 grab samples of a thickness of 5 cm were taken from surface sediments from a research vessel. The site location was determined by GPS Garmine 12 (horizontal accuracy 3–5 m). During the winter season of 2006/2007, three short sediment cores were taken from site PS04. The core sampling was performed with a modified Livingstone–Vallentyne piston corer from the ice. The lithology of the core was recorded in the field. Sampling was continuous over the core with intervals of 2–3 cm.

Analysis

In the 1970s and 1980s pipette analysis (Arinushkina 1970) was used for analysing fine fractions and aggregates were broken down with sodium pyrophosphate. To remove organic matter, samples were burnt and pre-treated with hydrogen peroxide. In 2006–2007 the samples were treated with hydrochloric acid and hydrogen peroxide and the grain-size spectra for particles were measured using a Fritsch Laser Particle Size "Analysette 22". Coarse grain compounds bigger than 250 μm were extracted before laser spectrometry. To avoid flocculation an ultrasonic disperser and addition of sodium hexametaphosphate (Calgon) were applied. For some samples (especially sand) also determination of grain-size wet sieving for coarser fractions was used; sieving was carried out on five (1,000, 500, 250, 63, 36 μm) metallic-woven mesh sieves in a Vibratory Sieve Shaker "Analysette 3" PRO. The results are given as medium diameter of particles following the Udden–Wentworth grain-size scale (Last 2001).

Dry matter in sediments was determined by drying the samples at 105°C to constant weight. Organic matter was measured as loss-on-ignition (LOI) upon heating at 550°C for 210 min. The carbonate content was calculated as the loss of weight after burning the LOI residue at 950°C for 150 min (Heiri et al. 2001).

The ^{210}Pb dating of the core taken from site PS04 was performed in the Centre for Environmental Monitoring and

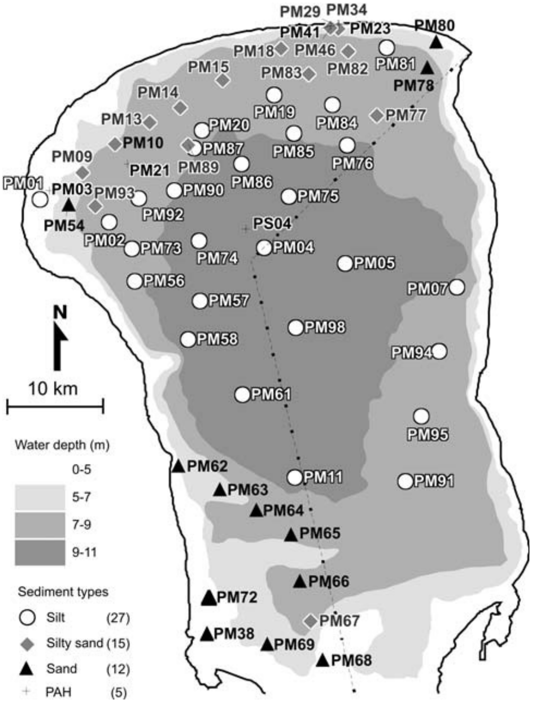


Fig. 2 The sampling sites and sediment types (see Table 1) on the background of water depth intervals. *PM* surface 5-cm thick samples, *PS* short sediment core (45 cm)

Technology, Ukrainian Hydrometeorological Research Institute, by direct gamma assay using an EG&G Ortec HPGe GWL series well-type coaxial low background germanium detector (Appleby et al. 1986).

Results

On the basis of grain size, the surface sediments sampled in 2006–2007 could be roughly separated into three groups (Fig. 2; Table 1): coarse-grained sediments (prevailingly sands in the nearshore area) and in the southern part of the lake, fine-grained sediments (mainly silts) and silty sands, both in the central deeper part of the lake. Within sampling sites, the median diameter variability of particles ranged from approximately 58.3 to 192.8 μm for sand, from 13.1 to 18.2 μm for silt and from 5.0 to 102.2 μm for silty sands. As there are clear differences in the mean median sizes between the groups and every group is characterised by a firm grain-size distribution curve and distinct statistical parameters, in further analysis we will treat all data as three groups with different genesis and qualities (Fig. 3; Table 1).

The granulometrically-characterised groups of sediments have a distinct spatial distribution. The silt sediments are restricted mainly to the lake centre within the 8–11-m contour. Of the three groups the sands are best sorted, their coefficient of variation is lowest, 47.0 against the worst-sorted silty sand (coefficient of variation 111.8). The silty sands consist practically of three granulometric fractions: clays, silts and sands. Of these three, sands constitute the largest portion and are represented as very fine- and fine-grained sands. Therefore, the span and uniformity of this sediment type are the greatest. Due to the presence of clay and fine-grained silts the specific surface area of these sediments is also significantly larger than that of the other types (Table 1). Different types of sediments differ also in their lithological composition. So the silts have the highest organic matter content; the silty sands are primarily composed of mineral grains with visually variable amounts of shell fragments, slag, and plant and rock fragments.

Table 1 Lithological and statistical characteristics (mean and range) of sediment groups (see Figs. 2, 3)

	Silt	Silty sand	Sand
Water depth (m)	9.3 (4.4–11.8)	7.1 (3.5–8.6)	6.6 (3.0–9.3)
Organic matter (%)	18.8 (1.5–27.0)	4 (0.8–12.5)	0.7 (0.2–1.4)
Carbonate (%)	4.1 (2.8–5.5)	3.9 (1.3–12.4)	2.7 (0.2–9.5)
Arithmetic mean diameter (μm)	17.9 (14.8–22.2)	56.6 (21.9–100.4)	153.5 (128.5–193)
Mode (μm)	23.2 (20.4–25.9)	88.9 (2.3–281.9)	147.8 (88.4–194.3)
Median (μm)	15.2 (13.1–18.2)	37.6 (5–102.2)	141.1 (58.3–192.8)
Average deviation (μm)	11.2 (8.8–17.7)	46.1 (13.4–82.2)	50.5 (37.8–62.2)
Coefficient of variation (%)	81.6 (65.2–123.1)	111.8 (64.9–160.4)	47.01 (27–74.3)
Skewness	1.5 (0.5–3.3)	1.3 (0.2–3.3)	0.03 (−0.5–1.1)
Curtosis	5.4 (−0.3–15.9)	1.8 (−1.3–15.1)	−0.05 (−0.9–1.6)
Span	2.2 (1.8–3.3)	6.2 (1.7–15.9)	1.3 (0.7–2)
Uniformity	0.7 (0.6–1.2)	1.8 (0.5–3.9)	0.4 (0.2–0.6)
Specific surface area (cm^2 cm^{-3})	9,696 (8,005–11,300)	10,269 (4,746–20,976)	1,810 (687–3,990)

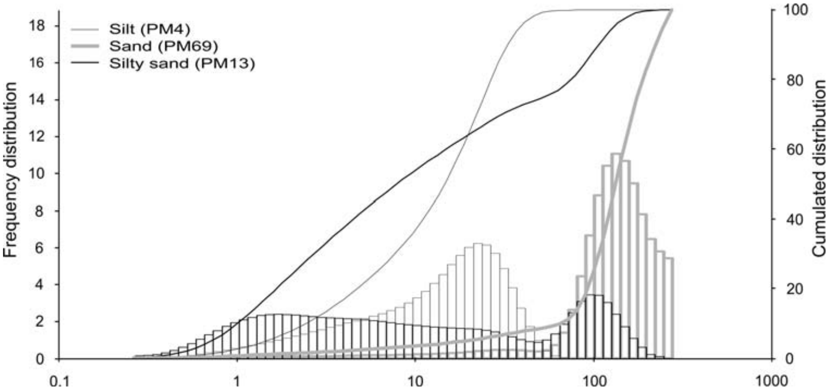


Fig. 3 Typical grain-size spectra for different textural classes of sediments. The *y*-axis on the left side shows frequency distribution in relative units (columns) and on the right side, cumulated distributions in percentage (*lines*). On the *x*-axis the medium diameter scale (μm) of particles follows the Udden–Wentworth grain-size scale

In principle, our data on the spatial distribution of the sediment types within L. Peipsi differed slightly from the data published in the 1980s (Raukas 1981). In comparing the data it should be taken into account that the measurements of the location of the sampling sites in the 1970s were made with an accuracy of some hundreds of metres, in 2005–2007, tens of metres.

The ^{210}Pb-activity curve is given in Fig. 4. The calculated sedimentation rate in site PS04 is 0.03–0.04 g m^{-2} y^{-1} and increases in the surface layers up to 0.08 g m^{-2} y^{-1}.

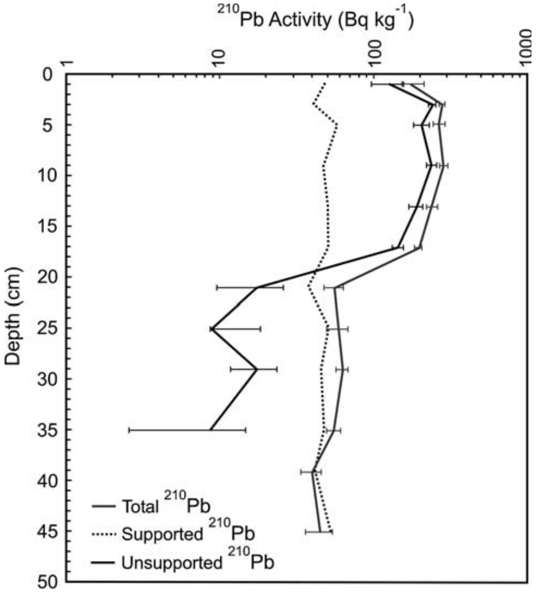


Fig. 4 ^{210}Pb in sediment core PS04 (Fig. 2) showing unsupported (*solid line*) and supported (*dotted line*) ^{210}Pb concentrations versus depth. Deviations of unsupported ^{210}Pb concentrations from a simple exponential relationship might be explained by an interruption of the process of sediment accumulation or sediment mixing

Discussion

Physical and chemical properties of particles

The essential differences in the texture and specific surface area of particles of different types determine their different role in the matter transformation within a lake. In L. Peipsi the content of organic matter in the silty muds is much higher than in other types of sediments reaching 27.0% (Table 1). The rather low C/N values (8.0–8.8) of organic matter point to its autochthonous origin (the proportion of planktonic matter may be up to 90%; Punning and Leeben 2003).

The essential role of flocculation and thus of the fact that silt particles act as a pollutant carrier in L. Peipsi is evidenced by the distribution of PAHs in the surface sediments studied by us recently (Punning et al., in press). The generation, deposition and redeposition of PAHs as widely-distributed pollutants and relatively-persistent compounds in water and sediments have been extensively studied during the last decades (Zhang et al. 1993; Trapido and Veldre 1996; Pikkarainen 2004; Vaine et al. 2007). Our data showed that in the mud sediments the content of different PAHs was much higher than in sand and till. The concentrations of PAHs in the surface sediments from sites PM3, PM21, PM23 and PM41 are very similar to those of background values (0.001–0.01 mg kg^{-1}) estimated in the lower sediment layers (accumulated before significant human impact) in the studied core from site PS04 (Fig. 2). The concentration in recent sediments from site PS04 for different PAHs is from 0.01 to 0.08 mg kg^{-1}. All PAHs concentrations have a good correlation with LOI (0.59–0.79; $P < 0.003$) (Punning et al., in press). This shows that PAHs in the water environment are closely related to the fine-grained particle distribution and are sorbed mainly on the autochthonous organic matter.

Phosphorous, which is related directly to the trophic state of a lake, is also sorbed onto the surface of settling particles (Stumm and Morgan 1996). In the core taken from surface sediments at site PM11, both phosphorous compounds (total and inorganic, reaching 1.6 and 1.17 mg g^{-1} DM, respectively) are much higher than in the older, more consolidated sediments (Punning et al. 2008). Concentration of particulate phosphorous is mainly affected by flocculation, growth of phytoplankton and, depending on the energy regime, by resuspension as shown by Jensen et al. (2006).

It is well known that fine-grained suspended particles have tendencies of repackaging into large aggregate particles called flocs (Van Rijn 1993; Roberts et al. 1998; Kim et al. 2005). During this process, most of the particulate organic matter as well different micro- and macrocomponents will be closely associated with suspended mineral particles, e.g. adsorbed on iron oxide on the surface of particles and deposited or transported in this form within the lake. The large specific surface area, surface energy and electrostatic charge of small and colloidal particles mainly drive coagulation. During adsorption of organic matter onto iron oxides, strongly binding organic compounds displace those which are weakly bound (Gu et al. 1996).

To estimate aggregatisation of fine-grained particles we also applied various methods of sample pretreatment for the laser particle-size spectrometry and microscopical observations of the treated fractions. The handling of samples with HCl and H_2O_2 revealed that the median diameter of particles for the silt fraction decreased from 20 to 8 μm, indicating the presence of aggregates. Microscopic observations also showed the silt particles in the mud sediments to be coated with inorganic (oxides, carbonates, clay minerals, etc.) and organic (mainly plant and animal detritus and bacteria) substances adsorbed on the surface. Thus, those sediments are cohesive by definition (Hayter and Pakala 1989; Paterson 1997) and their deposition and redeposition depend on many external and internal conditions. Corresponding sediments are characterised by an extremely high diversity because due to the dependence on physical–chemical and biological processes the cohesive sediments are rather unstable; they can change their composition very easily.

Settling fluxes and sediment accumulation

The data obtained suggested separation of three areas in L. Peipsi on the basis of texture and lithological composition of the surface sediments. The Quaternary deposits in the coastal zone of the nearshore areas and in the southern part of the lake are mostly represented by well-sorted sands. The largest sand area is in the southern shallow part of the lake with low wave action. It is a zone with stable accumulation of sedimentary material derived from the glaciofluvial delta in the southernmost area of L. Peipsi (Raukas 1999).

As the bottom sediments play an essential role in the formation of the ecological state of a lake through the dynamics of particulate matter and nutrients and contaminants associated with it as well as through the exchange of matter in the water–sediment interface (Lick and Lick 1988), it is very important to reconstruct the origin and pathways of different particles in the lake and the processes leading to their sedimentation and resedimentation.

Till in the NW part of the lake consists of unsorted particles, which have two peaks corresponding to clay and sand fractions on the grain-size diagram (Fig. 2). The mineral composition is dominated by quartz (84–94%) and feldspars (6–16%). Other minerals are represented in amounts less than 1%. The deposits contain also a sizeable fraction of coarse (>200 μm) material such as fragments of shells, gravel and conglomerate.

The largest areas of the floor of L. Peipsi are covered with fine-grained organic-rich sediments, called lake mud or gyttja. The main constituents of lake mud are silt and organic matter, which have been carried into the lake due to the erosion of the lake's bed and shores and to a lesser amount by rivers. We should take into consideration also great water-level fluctuations. During a high level of the water a large amount of sediment material will be transported into the lake from the shoreline and from soft surficial beach sediments, including a lot of organic matter.

The sources of bottom sediments are different; unfortunately we have no direct measurements of the share and intensity of the accumulation of sediments of different origin in L. Peipsi. Such studies have been done for the semiclosed Archipelago Sea (Moonsund) in the northwestern part of Estonia which has similar parameters to L. Peipsi territory; 2,243 km^3 and average depth 4.9 m (maximum depth 24 m). Similar to L. Peipsi, there is one river (Kasari) and numerous smaller streams flow into this sea. According to Lutt (1975), the erosion of the sea bottom and its shores gives annually about 75,000 tonnes of solid material and river input is only some 10,000 tonnes. So we believe that the proportions are also more or less similar in L. Peipsi.

As the C/N data indicate the organic matter in the central deeper part of the lake is probably autochthonous. Silt fractions are most common, accounting for 40–70%. The colour of the lake mud varies from light to beige to black, but is mainly greenish-grey and its consistency is between jelly-like and plastic. The average water content is 80–90%; after drying the colour would change. The spatial distribution of mud is in good accordance with the bathymetry of the lake coinciding mainly with the depth contour of 8 m (Fig. 3).

The composition and distribution of the bottom deposits of L. Peipsi show that the general process of sediment formation consists of many stationary processes: erosion of sandy coasts and primary bottom sediments, mainly glaciofluvial deposits and till; river input; sediment transport towards the Narva River outflow; resedimentation due to the bottom shear stress with an important role of autigeneous material. The granulometric composition of deposits determines greatly the physical and chemical properties of particles like cohesiveness, sorption ability, redeposition, etc. (Van Rijn 1993).

In the course of changes in environmental conditions, the dynamics of particle transport and thus their aggregate formation, redeposition, chemical and biological fate and role in the return of pollutants from sediments back to the food chain will change. In L. Peipsi the periodical water-level fluctuations have an essential impact on the sedimentation processes. During the last hundred years, the water-level changes of an amplitude of 3.04 m and about 11-year periods (Jaani 1973) have been registered. At the highest (31.76 m a.s.l.) water level, the surface area of the lake was estimated at 4,330 km^2 and the volume of water at 32.13 km^3. At the lowest water level (28.72 m a.s.l.), these values were 3,490 km^2 and 20.98 km^3, respectively. Thus, the surface area of the lake may vary by the value of 840 km^2 and the water volume by 11.15 km^3. It is clear that such large variations in water depth and water volume will affect the sedimentation process and the ecological state of the lake.

Laboratory experiments and field observations have shown that sediment distribution in large lakes is mainly controlled by wave energy. Rowan et al. (1992) identified the boundary depth of mud deposition as the depth of the abrupt transition from coarse-grained noncohesive sediments of high-energy erosional environments to fine-grained cohesive sediments of low-energy depositional environments. Luettich et al. (1990) carried out a field investigation in Lake Balaton and showed that episodic increases in the suspended sediment concentration are forced by wind-generated surface waves. The process of sedimentation, proceeding under the contemporary physico-geographical conditions, is characterised by a host of specific features, the combined effect of which causes deposition and redeposition areas to change. As the northern part of the depression of L. Peipsi is tectonically lifting, newer areas will be under erosion, giving new portions of material to redeposit and accumulate.

Due to the erosion of the northern sandy coast with high dunes, the enrichment of the foreshore is in progress and all material is moving to the east in the direction of the outflow of the Narva River, causing the clogging of the outflow. As a result of longshore erosion, modern lake sediments are absent in extensive areas there, or till and varved clays are covered with a thin layer of residual sediments ranging from several to some tens of centimetres in thickness.

The bottom deposit map compiled (Fig. 2) is in good accordance with the previous ideas about the current system in L. Peipsi (Jaani and Raukas 1999). Fine-grained sediment transport from the shallower, central area of the lake occurs because of the action of currents and/or waves on the sediment bed. It occurs when the current-induced shear stress is sufficient to overcome the cohesion of bottom sediments. In the central area, where the water depth reaches 11 m and the average long-term bottom shear stress is lower than the critical one, a semistable area of fine-grained particle accumulation has developed. In L. Peipsi the energy of wave action and internal currents are enough to transport sediment particles (mainly flocs) of clay and silt size (Blake et al. 2004). During this process, the dominating portion of impurities (various pollutants, nutrients, organic compounds) as well as planktonic and benthic seston accumulate and concentrate in mud sediments.

The essential external force that determines the deposition or erosion and transportation of sediment particles is induced by wind fetch and wind force. Raudsepp et al. (2006) modelled the resuspension of mud sediments in the north-eastern part of L. Peipsi. They found that with the wind speed of 15 m s^{-1}, the wave height reaches 1.6 m and the near-bed current speed is up to 20 cm s^{-1} in the central area of the lake. Such current speed is rather extreme; in 2002 the maximal near-bed water velocity reached 1.9 cm s^{-1}. According to Kuhrts et al. (2004), the critical velocity for resuspension of cohesive organic-rich sediments is 1.4 cm s^{-1}. Sediment particles transported as suspended load are moving at or very close to the velocity of fluid. It clearly follows from our core studies that when the near-bottom shear stress increases (extreme meteorological events, changes in the water level, etc.), the sediment bed may be subjected to episodic resuspension.

The results of core PS04 studies speak about an essential role of resedimentation in the past; the best example is the ^{210}Pb profile of this core, which reveals the disturbances in the sediment sequence (Fig. 4). In an undisturbed sediment core, the activity of ^{210}Pb will decrease exponentially with increasing depth until it reaches the background level. However, the mixing of sediment by organisms or other processes will disrupt the smooth profile and reduce the accuracy of the estimated dates and sediment accumulation rates as seen from Fig. 4. The effect of sediment mixing is also seen from the distribution of fly-ash particles in sediments in the core taken nearby (Nõges et al. 2006). Sediment resuspension is also evidenced by the great variations of diatom communities in the surface sediments over the relatively short distances (Davydova 1981; Punning et al. 2008).

Analogous results were obtained by Lund-Hanseni and Petersson (1999), who conducted detailed studies in a shallow lagoon at both a shallow water position (4 m) and in the central part of the lagoon at a water depth of 7.5 m. They estimated that the maximum wave-induced resuspended vertical particle flux was 10 times higher at the shallow water position and 3.8 times higher at the deep-water position compared to the net sedimentation rate in the lagoon.

The great spatial as well temporal variety of physical and chemical properties of the mud deposits in L. Peipsi made it difficult to conduct regular monitoring, comparison of data, and their interpretation and is one of the reasons why despite the long history of investigations and the involvement of a large number of researchers many problems of topical interest in the sedimentation processes and development of the ecosystem have not yet been resolved.

Changes in the water volume undoubtedly affect sedimentation processes and the chemical composition of the water near the bottom and consequently chemical processes in the interface of water and bottom sediments; these processes have been insufficiently studied in L. Peipsi. Each site has specific physical, chemical and biological factors affecting the lithology and texture of sediments.

Conclusions

This study showed the great importance of particle texture and properties in the distribution of pollutants, especially nutrients and xenobiotics in a large shallow lake. On the map of the bottom sediments, three distinct areas could be separated in L. Peipsi. Their lithological characteristics reflect clearly the impact of current systems of the lake: in the near-shore area the erosion of sandy shore sediments with clear longshore transportation exists and in the central deeper area deposition of fine-grained particles, transported due to complicated current systems from near-shore areas and mixed with autochthonous organic material, plays the most important role. These sediments are clearly of cohesive character as evidenced by their texture and attached organic matter associated with iron oxides. When the near-bottom shear stress increases (extreme meteorological events, changes in the water level, etc.), the sediment bed may be subjected to episodic resuspension. The origin and dynamics of particulate matter and bottom sediments give valuable information to successfully understand the dependence of the matter cycling and ecological state of the lake on the external and internal environmental factors. The detailed bottom sediment map will open possibilities for understanding the matter exchange on the water–sediment interface and compiling the budget calculations for the nutrients in L. Peipsi.

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PEIPSI JÄRVE PINDMISTE PÕHJASETETE UURINGUD AASTATEL 2006–2009

Tiit Vaasma, Jaanus Terasmaa

Sissejuhatus

Peipsi järve pindmiste põhjasetete uuringute tulemusi on korduvalt publitseeritud (Raukas 1981; Miidel, Raukas 1999; Habermann jt 2008; Punning jt 2009), kuid arvestades Peipsi järve tähtsust nii looduslikust kui ka majanduslikust aspektist, on selle teemalisi uuringuid olnud liialt vähe. Aastate lõikes on setete kaardistamine üha täiustunud ja koostise määramise täpsus tõusnud. Peipsi järve pindmiste setete uuringutel on suur teaduslik ja praktiline väärtus, sest settimisprotsessi mõistmine aitab kaasa nii paleoinformatsiooni korrektsele interpreteerimisele kui ka järvesisese aineringe mõistmisele. Sisaldavad ju setted ka mitmeid looduskeskkonnale kahjulikke ühendeid, mis teatud tingimuste kokkulangemisel võivad uuesti veekeskkonda tagasi pääseda. Selleks ongi vaja sette koostise ja jaotuse kvantitatiivseid kirjeldusi. Käesolevate uuringute eesmärgiks on nüüdismeetoditega kaardistada Peipsi Suurjärve pindmiste põhjasetete litoloogiline koostis, kusjuures põhirõhk on sette lõimise kirjeldamisel. Peipsi järve pindmiste setete uuringud jätkuvad.

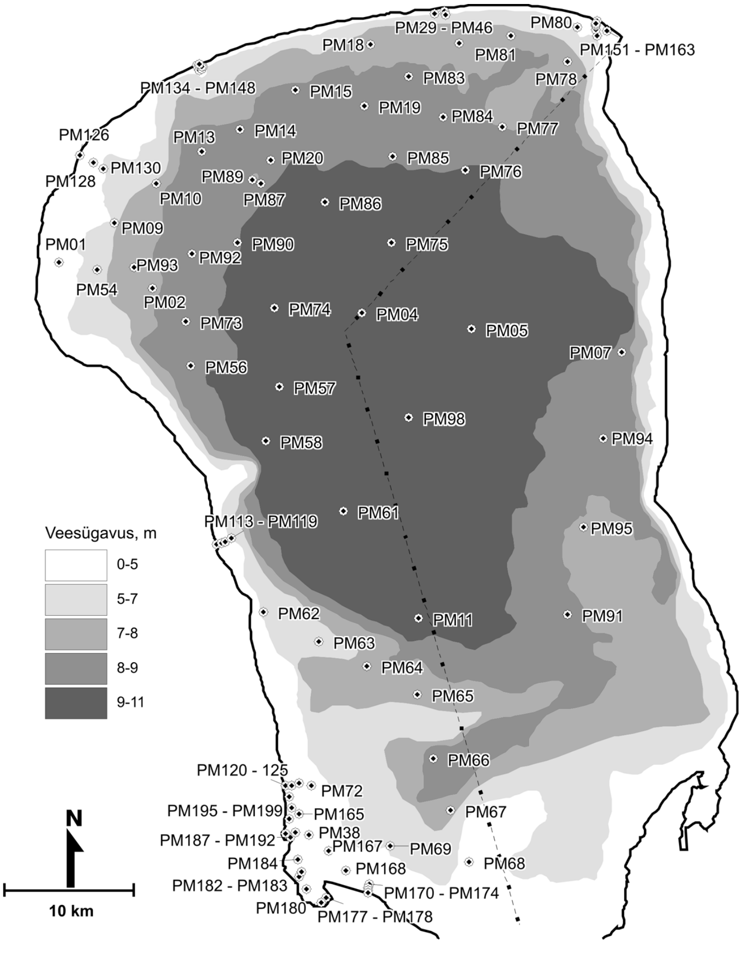
Peipsi järv on Euroopas suuruselt neljas järv pindalaga 3555 km^2, millest Eesti alale jääb 44% ehk 1570 km^2. Järve maksimaalne pikkus on 152 ja laius 47 km. Nii eelnevad parameetrid kui ka keskmine sügavus (7,1 m) ja maksimaalne sügavus (15,3 m) (Jaani, Raukas 1999) kõiguvad suuresti koos veetaseme muutustega. Valgala (47 800 km^2) jaguneb peamiselt Eesti ja Venemaa vahel, väiksemal määral ulatub see ka Lätti ja Valgevenesse. Veetaseme pikaajalised kõikumised Peipsis väljenduvad tsükliliselt kestusega 19 ja 33 aastat, mõõdetud maksimaalseks amplituudiks on saadud veidi üle 3 meetri (Jaani 1973; Jaani jt 2008). Suurjärve pindala, mida antud artiklis käsitletakse, on keskmise veetaseme juures (30 m ü.m.p.) 2611 km^2 (Jaani, Raukas 1999).

Peipsi põhjasette kujunemist on oluliselt mõjutanud mitmed protsessid. Peamiseks on randla ning madalike kulutus, kuid ka jõgede kaudu toimuv purdmaterjali ja vees lahustunud ainete sissekanne. Oluline mõju on ka tuulel (ja lainetusel) kuid ka sademetel, rüsijääl ning elustikul, oluliseks on muutunud inimtegevus (Raukas 2008). Lainekõrgus Peipsis võib ulatuda 2,3–2,4 m (Jaani 2001), ulatudes niiviisi settepinnani, segades vett ja resuspendeerides akumuleerunud setet. Enamesinevaks lainekõrguseks Peipsis loetakse 60–70 cm, mis on valitsevaks üle 50% juhtudest (Sokolov jt 1983). Raudsepp jt (2006) on Suurjärve kirdeosa kohta välja arvutanud, et 15 m s^{-1} tuulekiiruse juures ulatub laine kõrgus 1,6 m kõrguseni ja põhjalähedane veeliikumise kiirus järve keskel on 20 cm s^{-1}, ranna lähedal 55 cm s^{-1}, mis on väga ekstreemsed kiirused. Näiteks Kuhrts jt (2004) on leidnud kohesiivsete setete resuspendeeruma panevaks jõuks 1,4 cm s^{-1}. Reesupensioon, mis võib olla tingitud ka veetaseme muutustest, loob aga võimaluse toit- ja saasteainete ringesse tagasi minekuks settest. Peenterine materjal omab olulist rolli loodusliku absorbendina erinevatele orgaanilistele ja anorgaanilistele ainetele, mis võivad teradele suspendeeruda ka veesambast. See sõltub füüsikalis-keemilistest ja bioloogilistest protsessidest ja võib seeläbi oluliselt muuta veekeskkonnas liikuvate osakeste struktuuri (Roberts jt 1998; Kim jt 2005).

Metoodika

Aastatel 2006–2009 läbiviidudud uuringute käigus võeti 97 pindmist 5 cm paksust setteproovi nii suvel laevalt kui talvel jää pealt (joonis 1). Seoses poliitiliste oludega on enamus proove võetud Eesti poolelt, kuid ühisekspeditsioonide käigus koos Eesti Maaülikooli teaduritega on õnnestunud vähesel määral võtta setteproove ka Venemaale kuuluvast järveosast (joonis 1). Lisaks üle Suurjärve paiknevatele punktidele on detailsemad andmed veel rannalähedastelt profiilidelt.

Võetud setteproovid pakiti eelnevalt kaalutud ja tähistatud plastik-karpidesse. Sügavamast järveosast võeti proovid Tallinna Ülikooli Ökoloogia Instituudis modifitseeritud Livingstone-Vallentyne tüüpi ripp-puuriga, rannavööndis kasutati setteammutit. Proovivõtu punktide asukohad määrati kindlaks Garmin GPSMap 60 ja Garmin Oregon seadmete abil. Veesügavus on mõõdetud 10 cm diameetriga mõõtekettaga ning kajaloega. Proovivõtupunktide kaugused rannast, keskmise veetaseme juures, on mõõdetud kasutades selleks Veeteedeameti 2004. a aluskaarti (1:50000) ja tarkvarapaketti Mapinfo, statistiline analüüs viidi läbi programmi XLSTAT abil.



Joonis 1. Peipsi Suurjärve sügavuskaart (Veeteedeameti 2004. aasta aluskaardi põhjal (1:50000)) koos proovivõtupunktide asukohtadega.

Laboris proovid kuivatati 105°C juures konstantse massini ja määrati proovi kuivmass. Orgaanilise aine sisalduse määramiseks asetati proovid eelnevalt kaalutud põletustiiglitesse, mis asetati 3,5 h muhvelahju 550°C juures kuumutamiseks. Karbonaatse aine sisaldus arvutati pärast 2,5 h 950°C juures kuumutamist kao järgi (Heiri jt 2001).

Varasemates uuringutes (1970–1980) kasutati terasuuruste jaotuse määramiseks pipettmeetodit, antud uurimuse andmed on saadud kasutades laserosakestemõõtjat Fritsch Laser Particle Sizer “Analysette 22”. Antud seade mõõdab fraktsioone vahemikus 0.3–300 µm jaotades need 62 erinevasse suurusklassi. Et mõõta mineraalaine terasuuruste jaotust töödeldi proove eelnevalt vesinikperoksiidiga ja vesinikkloriidhappega. Vältimaks osakeste flokuleerumist mõõtmise ajal kasutati nii ultraheli süsteemi kui ka naatriumpürofosfaati (Vaasma 2008). Jämeteriste proovide korral rakendati sõelumismeetodit kasutades metallsõelasid silma läbimõõduga 2000, 1000, 500, 250, 100, 63µm ja Vibratory Sieve Shaker “Analysette 3” PRO seadet.

Terasuuruste jaotuse tulemused on esitatud Udden-Wentworthi logaritmilise skaala järgi (Last 2001), mitte Raukas ja Rähni (1981) poolt kasutatud skaalas. Põhjasette koostise kirjeldamiseks on savi ja aleuriidi fraktsioonide (0.06–63 µm; 14–4 φ) puhul kasutusel üldnimetajana peened mineraalsed setted ja liiva fraktsiooni (63–2000 µm; 4– -1 φ) puhul teralised setted (Saarse 1982) (tabel 1).

Tabel 1. Terasuurused Udden-Wentworth skaala järgi (Last 2001), iseloomustav termin Saarse (1982) järgi

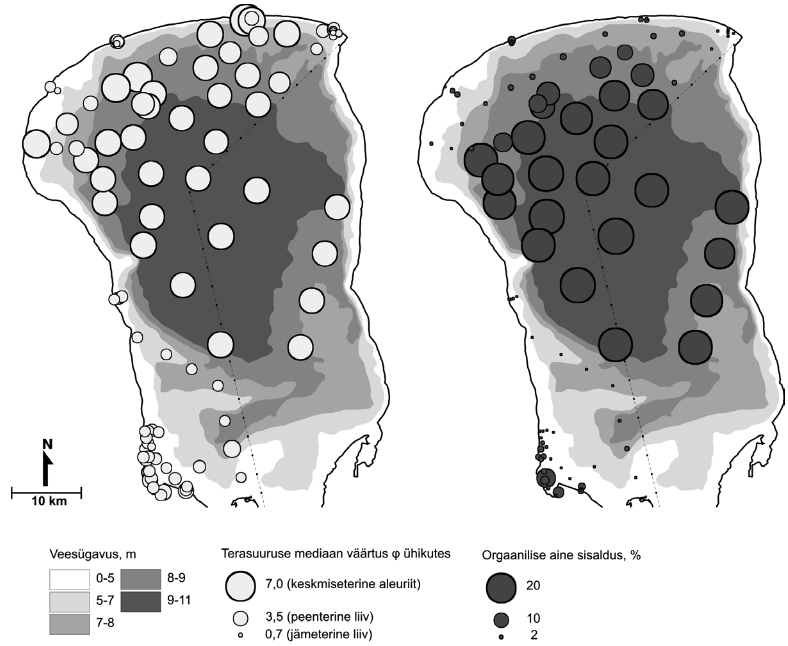
Iseloomustav termin	Osakeste diameeter			Suurusklass	
	(Φ-ühikud)	(mm)	µm		
Teralised setted	0	1	1000-2000	väga jäme	liiv
	1	0,5	500	jäme	
	2	0,25	250	keskmine	
	3	0,125	125	peen	
	4	0,0625	62,5	väga peen	
Peened mineraalsed setted	5	0,03125	31,25	väga jäme	aleuriit
	6	0,01563	15,63	jäme	
	7	0,00781	7,63	keskmine	
	8	0,00391	3,91	peen	
	9	0,00195	1,95	väga peen	
	14	0,00006	0,06		savi

Setete üldistavaks klassifitseerimiseks ja settegruppide väljaeraldamiseks on artiklis kasutusel Shepardi (1954) poolt loodud jaotust, kus grupeerimisel arvestatakse erineva terasuurusega fraktsioonide osakaalu sette koostises.

Tulemused ja arutelu

Põhjasetete koostis

Ulatuslikult on Peipsi Suurjärve keskosa põhi kaetud järvemudaga, mille mineraalse osa terasuuruse mediaan väärtused on vahemikus 5,5–6,3 φ ühikut (joonis 2). Põhiliselt on seal peened mineraalsed setted (>87,4%) ning orgaanilise aine sisaldus ulatub 27,0% (joonis 2). Veesügavused on seal suurimad ulatudes 6,4 meetrist (PM89) kuni 11,8 meetrini (PM58). Järve läänerannalt mõõdetuna algab peene mineraalse sette tsoon umbes 4,3 km kauguselt, põhjaosas 6,7 km omades loodeosas 13 kilomeetrist (PM90) sissesopistust ja idarannalt 3,3 km kauguselt. Sete on järve keskosas värvuselt mustast tumehallini. Järvenõo sügavamasse ossa kuhjunud orgaaniline ja peenterise mineraalaine fraktsiooniga sete on sinna sattunud mitmete tegurite koostoimel. Siiani pole päris selge, kuidas materjal sinna on jõudnud, sest selliseid setteid kuskilt ei murrutata. On oletatud, et teoreetiliselt võib sealne materjal olla pärit moreenist ja viirsavist (Raukas 2008).



Joonis 2. Peipsi Suurjäve pindmiste põhjasetete terasuuruse mediaan väärtused φ ühikutes (helehallid sõõrid) ja orgaanilise aine protsentuaalne sisaldus (tumehallid sõõrid).

Orgaanilise aine päritolu kirjeldamiseks tehtud C/N analüüside väärtuste järgi (8,0–8,8) võib öelda, et peamiselt on tegemist autohtoonse materjaliga. Aleuriidi ja savi osakestele absorbeerub veesambast orgaaniline aine ning seeläbi hõljuva aine erikaal suureneb ja materjal viiakse flokulantidena põhja. Sellest annab kinnitust ka Punning jt (2008) polüaromaatsete süsivesikute (PAH) uuring, kust järeldub, et PAH-ide sisaldus on märksa suurem mudastes setetes (0,01–0,08 mg kg^{-1}) kui rannalähedastes teralistes setetes ja moreenis (0,001–0,01 mg kg^{-1}).

Kui võrrelda omavahel Raukase (2008: lk. 96, joonis 5) poolt esitatud kaarti orgaanilise aine sisaldusest Peipsi põhjasettes ja käesolevas artiklis esitatud tulemusi (joonis 2), siis saab öelda, et järve keskosas on orgaanilise aine sisaldus jäänud samaks. Küll aga tulevad erinevused sisse rannaäärsel alal. Kui Raukas (2008) järgi on orgaanilise aine sisaldus küllaltki suur (20–30%) ka Emajõe suudmes ja järve põhjaotsas, siis uued andmed seda ei kinnita. Rannalähedases tsoonis on orgaanikasisaldus väike, enamikel juhtudel alla 5%; ka Kalli jõe suudme juures on vaid ühes punktis (PM183) orgaanilise aine sisaldus veidi kõrgem (12,9%). Selline erinevus varasemate töödega võib olla tingitud nii orgaaniliste setete ümberpaiknemises kui proovivõtukohtade erinevustest. Näiteks Peipsi Suurjärve põhjaotsas on setete esinemine küllaltki sporaadiline ning leidub väikeseid süvikuid ja ranna lähedal veealuste vallide vahelisi nõgusi, kus olenevalt aastaajast ja valitsevatest tuultes võib orgaaniline aine piiratud aja jooksul settida ning samas mingil teisel ajahetkel puududa.

Suurjärve rannaäärsete alade põhi on peamiselt kaetud teraliste setetega (joonis 2), mille päritoluks on ilmselt ranna abrasioon. Suurjärve lõunapoolsel rannalähedasel alal on Kvaternarisetetest peamiselt esindatud vähese orgaanilise aine sisaldusega (<12,9%, keskmiselt 1,7%) hästisorteeritud teralised setted (joonis 2). Sealne (Kolkjast kuni järve keskteljeni ja sealt Piirissaareni, jätkudes veel Venemaa poolel) madalaveeline (kohati vaid 0,7 m) ala on vähemaktiivse lainetuse mõju piirkonnas. Piirissaare lähistel on materjal glatsiofluviaalse delta päritolu (Raukas 2008) mediaan väärtusega 2,7 φ ühikut (joonis 2).

Järve põhja- ja loodeosa pindmised põhjasetted koosnevad sorteerimata osakestest, mille terasuuruse jaotuses on kaks tippu – savi ja liiva fraktsioonis. Terasuuruste mediaanväärtused on vahemikus 3,5–7,6 φ ühikut. Leidub ka rohkelt suuremaid osakesi (>200 µm) samuti karbidetriiti ja kruusa. Kõige varieeruvamad setted ongi järve põhjaosas ja jõgede suudmealadel. Järve loodesopis ja Lahepera järve lähistel ning veel üksikutes kohtades (Venemaal) esineb moreeni ning Emajõe suudmealal turvast (Raukas 2008).

Läbiviidud analüüsi tulemusel saab väita, et Peipsi Suurjärve veerukalded on väga väikesed (analüüsitud proovivõtupunktides keskmiselt vaid 0,1%) ning seega sette transpordi seisukohast ebaolulised. Korrelatsioonanalüüs näitab tugevaimat seost veesügavuse ja lõimise ning mineraalse ja orgaanilise aine vahel (tabel 2). Kuna järve elutegevus on mõjustatud järve suuruse ja põhja kuju poolt, siis mõjub see ka settiva aine hulgale järves (Jonasson 1996). Järvepõhja iseärasustest sõltub erosiooni-, transpordi- ja akumulatsiooniala paigutus ning settinud materjali omadused (Terasmaa 2005). Suurepindalalise ja madala järve korral avaldab tuul siselainetuse kaudu sette moodustumisele suuremat mõju.

Tabel 2. Sette koostise ning proovivõtukohti kirjeldavate parameetrite omavahelised seosed. Kõik tabelis toodud väärtused on statistiliselt usaldusväärsed (p<0,05)

n=97	**Sügavus, m**	**Kaugus rannast, m**	**Teralised setted, %**	**Peened mineraalsed setted, %**	**Orgaanika sisaldus, %**	**Mediaan, φ ühikutes**
Sügavus, m	1	0.85	-0.70	0.69	0.68	0.61
Kaugus rannast, m	0.85	1	-0.57	0.56	0.59	0.51
Teralised setted, %	-0.70	-0.57	1	-1.00	-0.85	-0.84
Peened mineraalsed setted, %	0.69	0.56	-1.00	1	0.85	0.84
Orgaanika sisaldus, %	0.68	0.59	-0.85	0.85	1	0.71
Mediaan, φ ühikutes	0.61	0.51	-0.84	0.84	0.71	1

Veesügavus ja kaugus rannast on suurjärvede puhul statistiliselt olulised proovivõtukohti kirjeldavad parameetrid. Kui väikejärvede puhul on näidatud (Terasmaa 2005; Terasmaa, Punning 2010), et sette koostise mõjutajana olulisel kohal on eelkõige veerukalded, siis Peipsis tänu oma suurele dünaamilisele suhtarvule (DR=6,16) (Hakanson, Jansson 1983; Lindström jt 1999) on settimine mõjutatud mitte ainult lainetegevuse vaid ka hoovuste ning suubuvate jõgede poolt. Rannalähedases tsoonis domineerivad teralised setted, veesügavuse suurenedes muutuvad fraktsioonid peenemaks. Kuid selles seaduspäras leidub mitmeid erandeid, näiteks punktides PM01 (Mustvee lähedal) ja PM34, PM46 (Remniku lähedal) domineerivad ka rannalähedases alas peened mineraalsed setted (mediaan ~7 φ ühikut) (joonis 2). Siinkohas võib analoogiliselt orgaanilise aine sisalduse ebareeglipärase suurenemisega tegu olla veealuse vallide takistava mõjuga peenterise sette ärakandele.

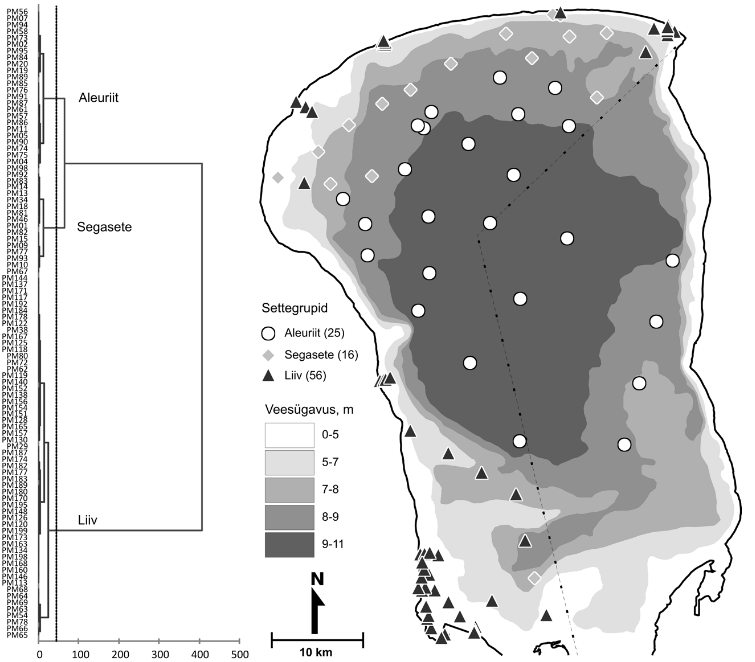
Põhjasetete grupeerimine

Üle kogu Peipsi Suurjärve võetud pindmiste põhjasetete lõimisanalüüsi tulemusena koostatud andmebaasiga viidi läbi klasteranalüüs, mille tulemusel saab setted jagada kolme erinevasse gruppi (joonis 3, tabel 3). Käesolevas artiklis on järve põhja- ja loodeosa pindmised põhjasetted defineeritud kui segasetted, mis hõlmavad endas nii avanenud moreeni kui ka hilisjääaegseid järvesetteid (valdavalt viirsavid). Segasetete nimetuse alla on lõimise alusel, vastavalt Shepardi (1954) poolt toodud jaotusele, koondatud aleuriidikas liiv, liivakas aleuriit ning savikas aleuriit. Kaheks ülejäänud grupiks on sama jaotuse (Shepard 1954) järgi liiv ja aleuriit.

Selline üldistav klassifitseerimine lubab järves eristada kolm erinevate settimistingimustega ala. Klasteranalüüsis on lisaks sette litoloogistele karakteristikutele kaasatud ka proovivõtupunktide kaugusi rannast ja veesügavusi (tabel 3). Kõige selgepiirilisemalt eristub sügava ja stabiilsema settimisega aleuriidikate setetega ala, kuid ka rannalähedane, madalaveeline ja laugepõhjaline liivaga kaetud ala. Suurjärve edelaosas on ulatuslikult paljandunud liivad ka sügavamal alal, ühes punktis maksimaalselt kuni 9,3 m kuid keskmiselt tunduvalt madalamas (tabel 3). Kuna liiva gruppi jäävaid punkte on suhteliselt rohkem ja sinna langevad ka kaldaäärsete profiilide punktid, siis võib veesügavuse keskväärtus olla veidi moonutatult madal.

Valdavalt järve põhjaotsa jääv segasetetega ala, kus veesügavused võivad ulatuda 8,8 m ja kaugused rannast kuni 8,7 km on raskemini piiritletav, sellist põhja leiab laiguti ka teistest järve osadest. Tihti on just selles osas põhi kaetud ka rändkarpidega, kes kinnituvad moreeniga seotud kividele.

Võrreldes käesolevas artiklis leitud mineraalaine lõimisel baseeruvat grupeerimist (joonis 3) Peipsi Suurjärve pindmistes setetes varempublitseeritud andmestikuga (Raukas 2008: lk. 94; Hang, Miidel 2008: lk 84),



Joonis 3. Klasteranalüüsi tulemused ja vastavatesse settegruppidesse jaotatud proovivõtupunktide paiknemine Peipsi Suurjärves (proovivõtukoha indeksid vt jooniselt 1). Settegrupi nimetuse järgi olevates sulgudes on toodud proovide arv.

siis nähtub, et üldjoontes on pilt jäänud samaks – rannalähedases alas ja järve edelanurgas ulatuslikud liivaalad, keskosas domineerivad aleuriidid ning põhjaotsas segasetted (moreen, viirsavi). Mõnevõrra on erinevad fraktsioonide liigitused, mis tuleneb erinevatest mõõtemeetodistest. Samuti on küsimus erinevates klassifitseerimise skaalades, mille puhul piirid erinevate fraktsioonide vahel on erinevad.

Suuremad erinevused on üksikutes kohtades – näiteks järve loodeosas olevad punktid (PM126–PM130) on liivadel, kuigi mõlemad varem tehtud tööd (Raukas 2008; Hang, Miidel 2008) paigutavad selle piirkonna paljanduvaks moreenialaks. Võimalik, et põhjuseks on moreenile peale kantud liivad, kuid välistada ei saa ka varasemate tööde teistsugust üldistusastet, mille puhul rannalähedast polnud vaadeldud eraldi tsoonina.

Tabel 3. Proovivõtupunktide litoloogilised ja batümeetrilised karakteristikud vastavalt esitatud grupeerimisele

		Sügavus, m	Kaugus kaldast, m	Teralised setted, %	Peened mineraalsed setted, %	Mediaan, φ ühikutes	Orgaanika-sisaldus, %
Segasete (n=16)	Minimaalne	4,4	250	3,9	46,5	3,5	1,5
	Maksimaalne	8,8	8700	53,5	96,1	7,6	12,9
	Keskmine	7,5	4160	28,2	71,8	5,6	4,0
	Mediaan	7,8	4650	28,5	71,5	5,7	3,0
	Standardhälve	1,2	2761	17,3	17,3	1,3	3,1
Aleuriit (n=25)	Minimaalne	6,4	3300	0,0	87,4	5,5	12,5
	Maksimaalne	11,8	17700	12,6	100,0	6,3	24,2
	Keskmine	9,4	10028	1,5	98,5	6,0	21,1
	Mediaan	9,4	9900	0,4	99,6	6,0	22,6
	Standardhälve	1,1	4001	2,7	2,7	0,2	3,3
Liiv (n=56)	Minimaalne	0,7	10	68,2	0,0	-0,3	0,0
	Maksimaalne	9,3	11500	100,2	31,8	3,7	12,9
	Keskmine	3,8	1507	96,4	3,6	2,5	1,7
	Mediaan	3,5	590	99,1	0,9	2,7	0,7
	Standardhälve	2,3	2484	7,0	7,0	0,7	2,2

Kokkuvõte

Peipsi Suurjärve kohta saab üldistatuna öelda, et rannalähedaste erosiooni- ja transpordialade setete koostis varieerub suuresti – leidub liiva- ja mudapõhja, paiguti avaneb moreen. Akumulatsioonialadel, kus veesügavus ja kaugus rannast suur, kuhjub peamiselt peenterine materjal segatuna autohtoonse orgaanilise ainega. Kuna antud materjal allub kergemini sette transporti mõjutavatele teguritele (hoovused, lainetus, bioturbatsioon), siis kandub seda suuremates kogustes rannast kaugematele aladele. Detailne põhjasetete kaardistamine ning sette päritolu ja dünaamika mõistmine annab olulist informatsiooni mõistmaks järve arengulugu ja ökoloogilise seisundi tasakaalustatust.

Võrdlusest varasemate töödega selgub, et suurimad erinevused esinevad rannaäärsel alal. Näiteks orgaanilise aine sisaldus Emajõe ja Kalli jõe suudmes on tunduvalt väiksem (maksimaalselt 12,9%) kui varasemad tulemused näitavad. Selline erinevus varasemate töödega võib olla tingitud nii orgaaniliste setete ümberpaiknemises kui proovivõtukohtade erinevustest. Analoogilised erinevused ilmnevad ka lõimise jaotuses, kuna Peipsi Suurjärve põhjaotsas on setete esinemine sporaadiline ning olenevalt aastaajast ja valitsevatest tuultes võivad peened mineraalsed setted või orgaaniline materjal piiratud aja jooksul settida ning hiljem ära kanduda.

Statistiline andmetöötlus näitas, et sette koostise ruumilisele jaotusele omavad olulist mõju veesügavus ning kaugus rannast. Selgus, et Peipsi Suurjärve veerukalded on väga väikesed (analüüsitud proovivõtupunktides keskmiselt vaid 0,1%) ning sette transpordi seisukohast ebaolulised.

Klasteranalüüs võimaldas Peipsi Suurjärve pindmised põhjasetted jagada kolme gruppi: liiv, segasetted, aleuriit. Grupeerimise aluseks on sette üldine litoloogiline koostis, lõimis, proovivõtukohtade kaugused rannast ning veesügavused.

Peipsi Suurjärve pindmiste põhjasetete uuringud näitasid setete suurt varieeruvust ning vajadust uuringute jätkamiseks, omades suurt teaduslikku ja praktilist väärtust. Settimisprotsessi selgitamine ning lõimiselise jaotuse teadmine aitab kaasa järvesisese aineringe mõistmisele.

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SURFACE SEDIMENT STUDIES IN LAKE PEIPSI IN 2006–2009

Tiit Vaasma, Jaanus Terasmaa

Summary

Surface sediment studies of Lake Peipsi *s.s.* show high variability in sediment composition. On the basis of grain size the surface sediments in Lake Peipsi *s.s.* fall into three groups: sand (coarse-grained sediments in the southern part of lake and on the near-shore areas), mixed-sediments (mainly till and varved clay; mainly in the northern part) and silt (in the central part). Their lithological characteristics reflect clearly the impact of currents in the lake: in the near-shore area the erosion of sandy shore sediments with clear longshore transportation exists and in the central deeper area the deposition of fine-grained particles, transported from the near-shore areas due to complicated current systems and mixed with autochthonous organic material. Sedimentation in the lake is controlled by different forms of energy input. Water depth and distance from shore are the primary parameters to describe sediment sampling points in the large lakes. In Lake Peipsi *s.s.*, thanks to its high dynamic ratio (DR = 6.16) the deposition is affected mainly by wave activity.

Comparisons with the previous studies show that the largest differences occur in the coastal areas. For example, the content of organic matter in the mouth of River Kalli and Emajõgi is much lower (maximum 12.9%) than the earlier results show. This may be due to the redeposition of the organic sediment or due to slight difference in location of the sampling site. Similar differences also occur in the distribution of grain-size because lake sediments in the northern part of the Lake Peipsi *s.s.* are distributed sporadically.

Lake sediment studies have great scientific and practical value. Clarification of the sedimentation dynamics and seston fluxes lead to better understanding and more precise interpretation of the information hidden in the sediments.

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