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

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

Abstract

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.

Supervisors: Jaan-Mati Punning, Dr (Geography), Prof. of the Tallinn University, Institute of Ecology at Tallinn University
Jaanus Terasmaa, PhD (Ecology), head of the Environmental Research Department of the Institute of Ecology at Tallinn University

Opponents: Wojciech T.J. Stankowski, Dr habil. (Geology), Prof. of the Institute of Geology, Adam Mickiewicz University, Poznań, Poland
Leili Saarse, PhD (Geology and Mineralogy), Institute of Geology at Tallinn University of Technology

The academic disputation on the thesis will be held at Tallinn University. Lecture Hall 223, Narva Road 25, Tallinn, on August 27, 2010 at 14:00.

The publication of this doctoral thesis has been funded by Tallinn University.

ISSN 1736-3616 (doctoral thesis)
ISBN 978-9949-463-12-1 (doctoral thesis)

ISSN 1736-9517 (doctoral thesis, online, PDF)
ISBN 978-9949-463-13-8 (doctoral thesis, online, PDF)

ISSN 1736-3659 (abstract, online, PDF)
ISBN 978-9949-463-14-5 (abstract, online, PDF)

Tallinn University
Narva mnt. 25
10120 Tallinn
www.tlu.ee

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LIST OF PUBLICATIONS

I. Punning, J.-M., Terasmaa, J. & Vaasma, T. 2006. The impact of lake-level fluctuations on the sediment composition. *Water, Air, and Soil Pollution: Focus*, **6**(5–6), 515–521.

II. Punning, J.-M., Boyle, J. F., Terasmaa, J., Vaasma, T. & Mikomägi, A. 2007. Changes in lake sediment structure and composition caused by human impact: repeated studies of Lake Martiska, Estonia. *The Holocene*, **17**(1), 145–151.

III. Punning, J.-M., Terasmaa, J., Vaasma, T. & Kapanen, G. 2008. Historical changes in the concentrations of polycyclic aromatic hydrocarbons (PAHs) in Lake Peipsi sediments. *Environmental Monitoring and Assessment*, **144**(1–3), 131–141.

IV. Vaasma, T. 2008. Grain-size analysis of lacustrine sediments: a comparison of pre-treatment methods. *Estonian Journal of Ecology*, **57**(4), 231–243.

V. Punning, J.-M., Raukas, A., Terasmaa, J. & Vaasma, T. 2009. Surface sediments of transboundary Lake Peipsi: composition, dynamics and role in matter cycling. *Environmental Geology*, **57**(4), 943–951.

VI. Vaasma, T. & Terasmaa, J. (2010). Peipsi järve pindmiste põhjasetete uuringud aastatel 2006–2009 (Surface sediment studies in Lake Peipsi in 2006–2009). In: Kangur, M., Kraav, V., Palang, H. & Punning, J.-M. (eds.). *Year-book of the Estonian Geographical Society, 37*. Eesti Geograafia Selts, Tallinn, 117–130 (in Estonian, summary in English).

Other publications in the relevant area:

VII. Vaasma, T. (2005). Järve sette litoloogiline koostis paleoinformatsiooni kandjana (Lithological composition of lake sediments as a reflector of palaeoinformation). In: Kangur, M., Anniste, K. (eds.). *Tõde ja õigus: Eesti Geograafia Seltsi 50. juubelile pühendatud noorgeograafide sügissümpoosioni artiklite kogumik*. EGSN; EGEA-Tartu, Tartu, 53–61 (in Estonian).

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 pre-treatment 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).

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

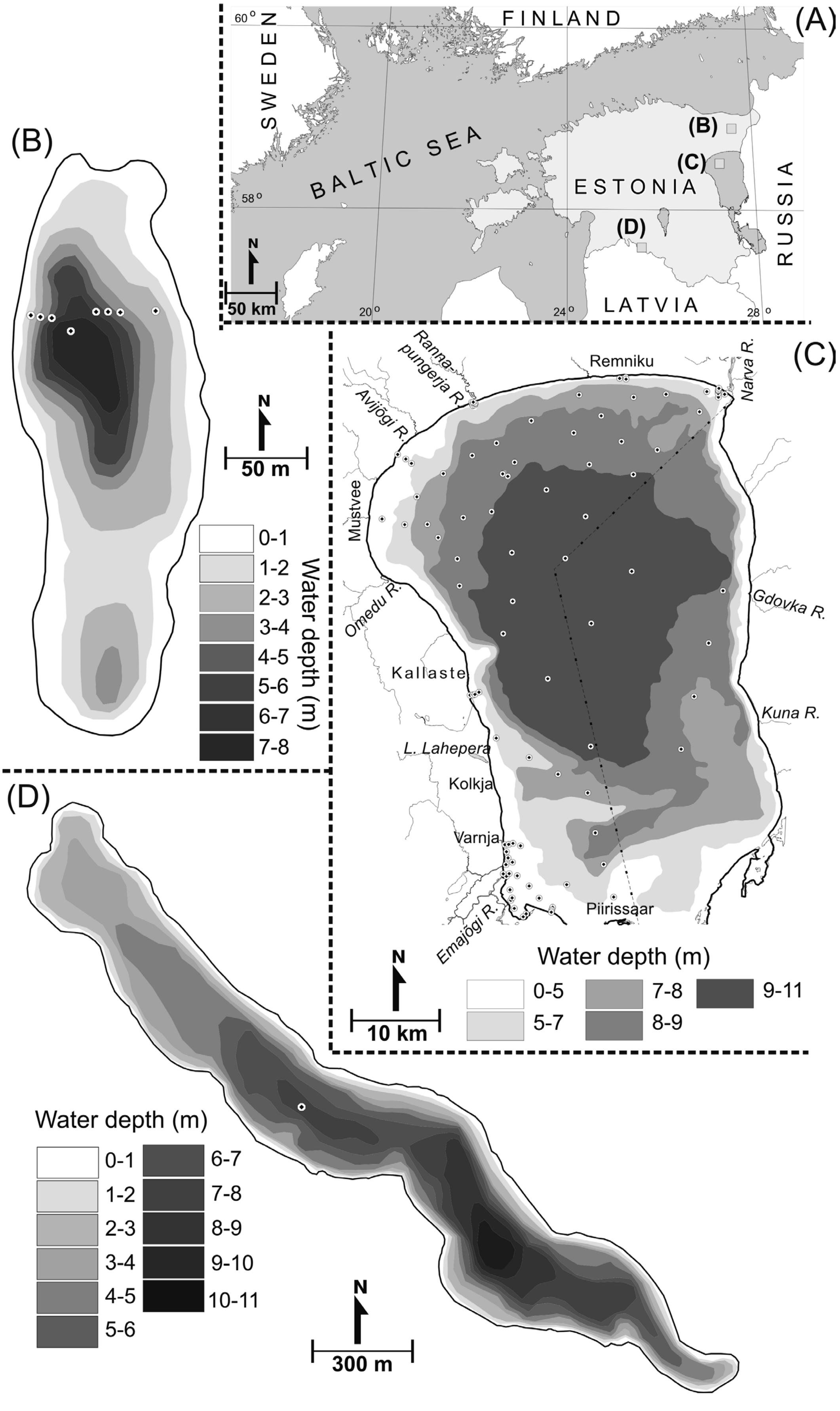

Figure 1. Location of the studied lakes (A) and bathymetric maps of Lake Martiska (B), Lake Peipsi (C) and Lake Tündre (D). Dots denote sampling sites.

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).

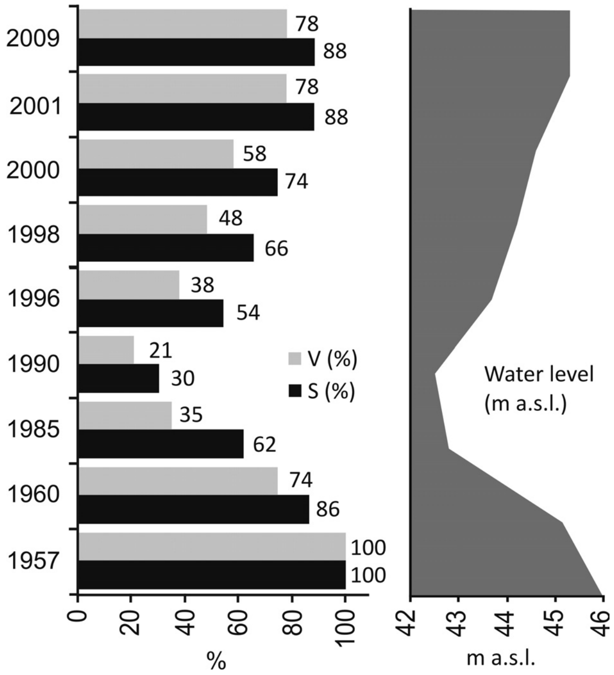

Figure 2. Changes in the surface area (S) and volume (V) according to water-level fluctuations in L. Martiska.

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.

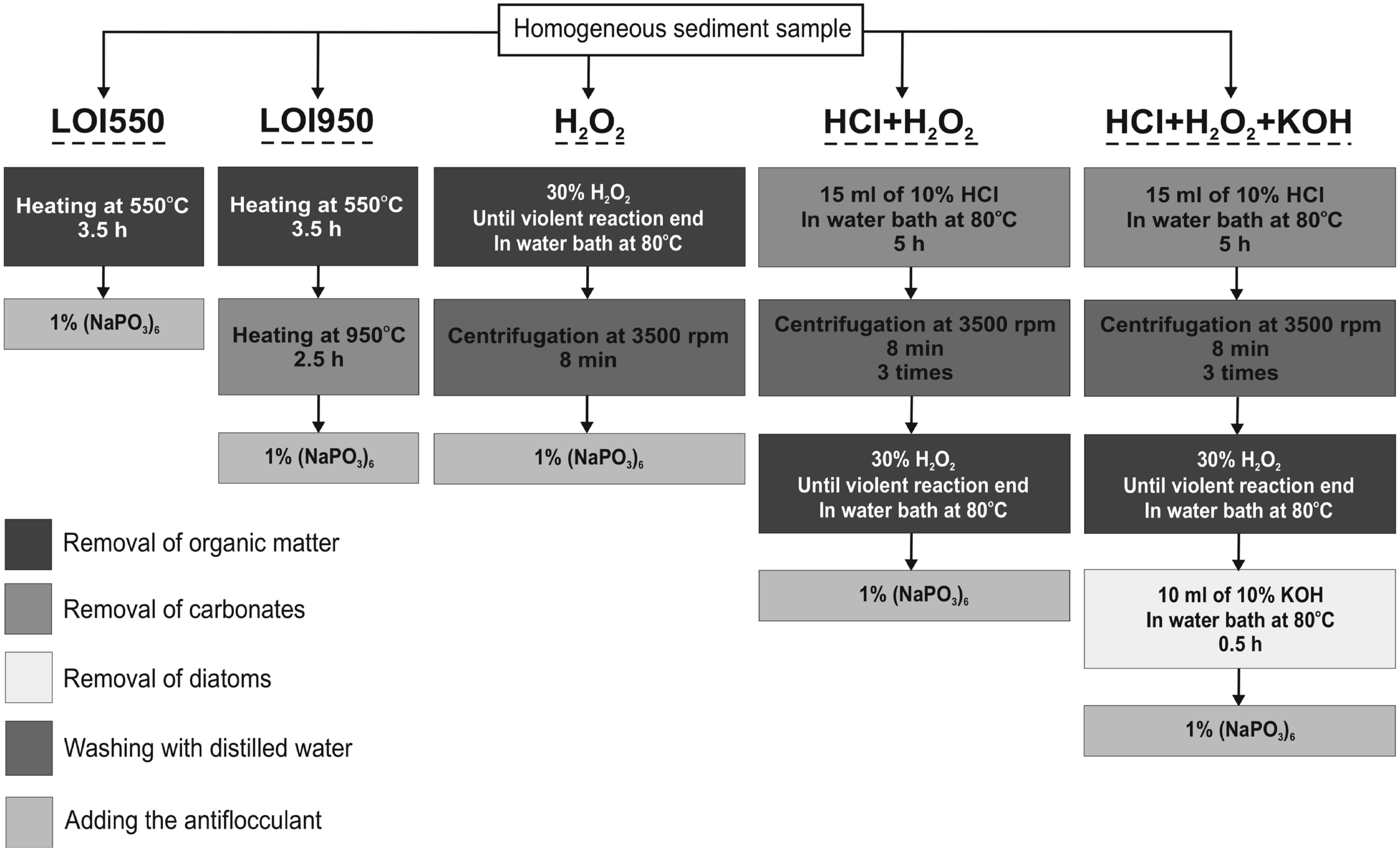

Figure 3. Pre-treatment workflows for grain-size analysis.

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.

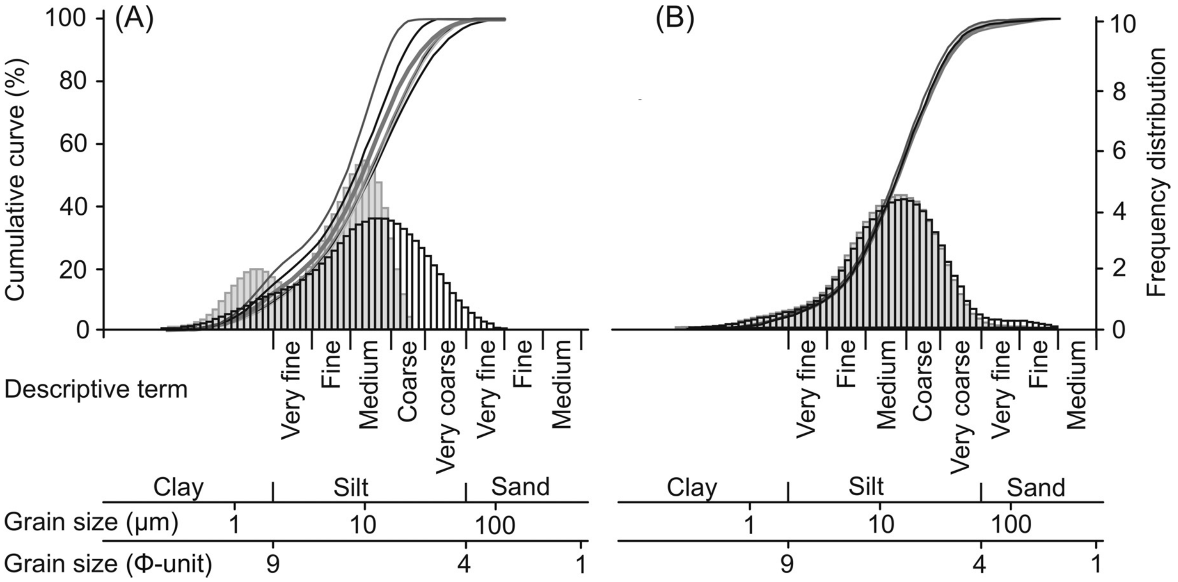

Figure 4. The most contrasting results of repeated measurements with some cumulative curves and two grain-size distributions in L. Tündre: (A) pre-treatment method H_2O_2; (B) pre-treatment method HCl+H_2O_2 (**IV**).

The specific surface area of sediment in L. Tündre was the largest (13729.0 cm^2/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.

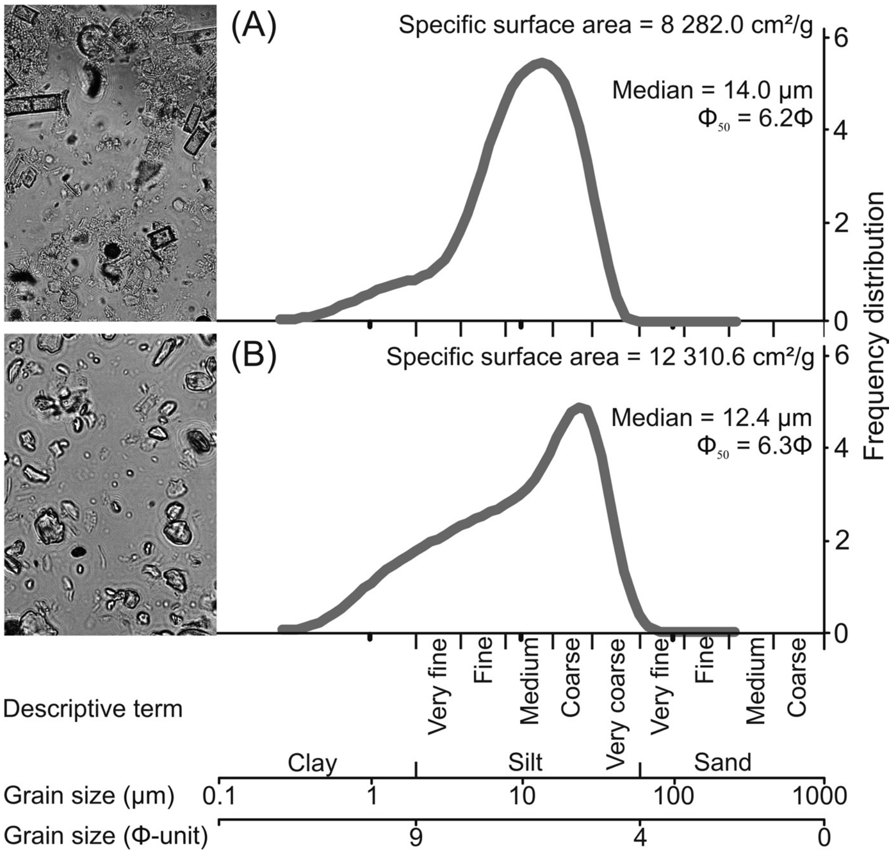

Figure 5. Grain-size distributions and microscopic observations after treatment with $HCl+H_2O_2$ (A) and $HCl+H_2O_2+KOH$ (B) (**IV**).

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.

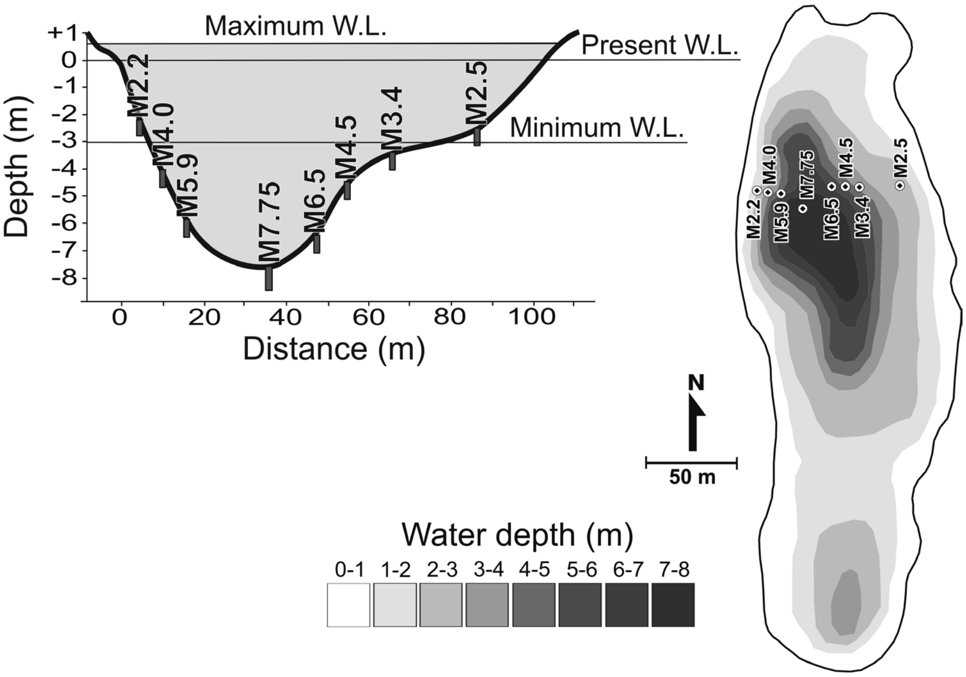

Figure 6. Water levels (W.L.) in L. Martiska and the locations of the sampling sites. The codes of the sampling points also show the water depth at the site.

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.

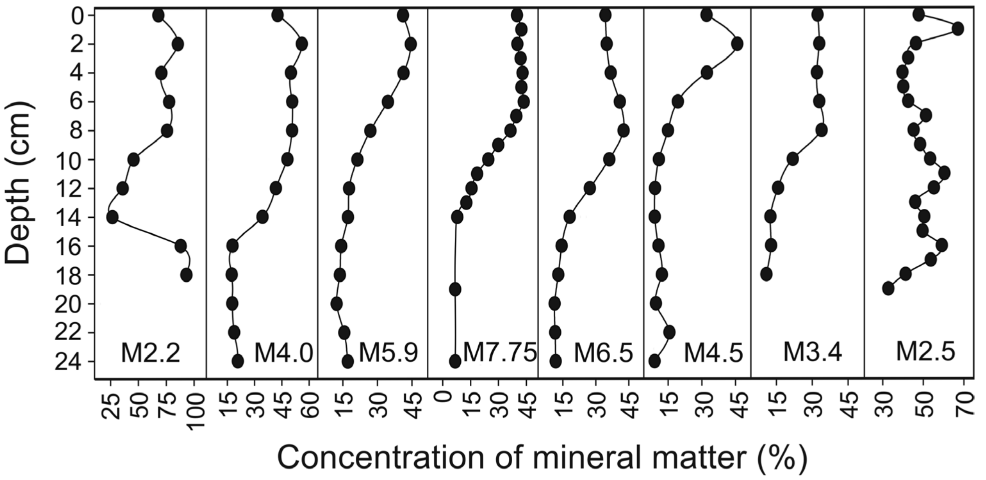

Figure 7. Concentrations of mineral matter in short cores from L. Martiska. For locations see Figure 6. The codes of the sampling points also show the water depth at the site.

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.

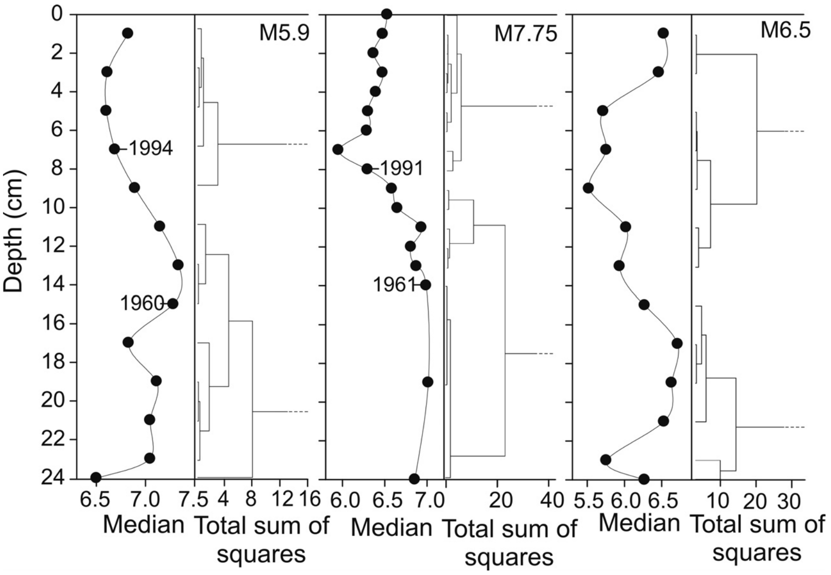

Figure 8. Median values (Φ units) of short cores M5.9, M7.75 and M6.5 and results of cluster analysis (mineral, organic and dry matter, grain size).

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).

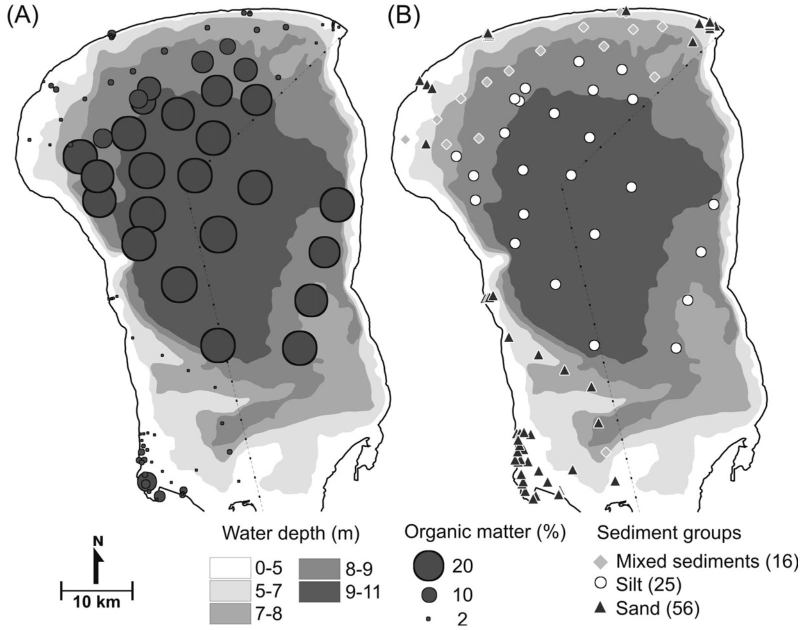

Figure 9. Organic matter content (A) and sediment groups (B) according to cluster analysis (**VI**) (number of samples in parentheses).

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 under-water 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.

ACKNOWLEDGEMENTS

First of all my sincere thanks belong to my supervisor Professor Jaan-Mati Punning, who passed away in November of 2009. No words can describe how grateful I am to his guidance and support. Such a great man is the best mentor.

My warmest thanks go also to my supervisor PhD Jaanus Terasmaa, who has been my supervisor since the beginning of my studies at the university. It was hard work that he has done with me. I am grateful for his support and guidance.

I wish to thank my wife Vicky for supporting and inspiring me when I was lazy. My thanks belong to my parents, Elvi and Jüri. I am grateful to my sisters and their daughters for keeping the smile on my face. My good friends helped me to cope with pressure.

I would like to thank the Chair of Geoecology and Institute of Mathematics and Natural Sciences of Tallinn University and my colleagues from the Institute of Ecology and especially from the Department of Environmental Research – Anto Raukas, Tiiu Koff, Shinya Sugita, Mihkel Kangur, Egert Vandel, Liisa Puusepp, Galina Kapanen and Annika Mikomägi, whose remarks and suggestions during seminars and outside these have been valuable. I thank Andres Kollist, who kindly let me camp on his property on the shore of L. Tündre. Also I thank Hannes Tõnisson for mapping the bottom of L. Tündre and students Katrin Kairo, Marko Vainu and Janno Kuusik.

My special thanks belong to Leili Saarse and Are Kont for criticism in reviewing. I am grateful to Martin Konert from the sedimentology laboratory of Vrije University in the Netherlands for consultations about pretreatment methods of grain-size analysis. I want to express my gratitude to Külli Kangur.

I thank Tiia Kaare and Liina Kivimäe for revising the English language of the thesis.

I am grateful for the financial support from the Estonian Ministry of Education and Research (target financed project SF0280016s07), the Estonian Science Foundation (grants ETF7392 and ETF6857), the Doctoral School of Ecology and Environmental Science, the Doctoral School of Earth Sciences and Ecology and the Centre of Excellence "Studies of Natural and Man-Made Environments" in Tallinn University.

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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