

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 H₂O₂ 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 Tüandre (L. Tüandre) (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. Tüandre 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 H₂O₂). 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 CaCO₃ 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 H₂O₂ 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 H₂O₂ significantly quicker, because Fe is known as a catalyst for H₂O₂ decay (Mikutta et al., 2005). This method is hereafter designated as method HCl+H₂O₂.

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% H₂O₂ 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+H₂O₂+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 (NaPO₃)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. ≥ 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
LO1550	Organic matter removal by thermal combustion at 550 °C for 3.5 h
H ₂ O ₂	Organic matter removal by concentrated (30%) H ₂ O ₂
LO1950	Carbonated matter removal by thermal combustion at 950 °C for 2.5 h
HCl+H ₂ O ₂	Carbonated matter removal by 10% HCl; thereafter organic matter removal by concentrated (30%) H ₂ O ₂
HCl+H ₂ O ₂ +KOH	Carbonated matter removal by 10% HCl; thereafter organic matter removal by concentrated (30%) H ₂ O 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. Tüandre 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 H₂O₂, method HCl+H₂O₂, and method HCl+H₂O₂+KOH) clearly differed (Figs 1 and 2). Methods LOI550 and LOI950 showed dominance of coarse and very coarse silt fractions in the L. Tüandre 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 H₂O₂ while the highest coarse silt content, 29.2%, was revealed by method HCl+H₂O₂ (Table 3, Fig. 1). In chemical treatments the results of method HCl+H₂O₂+KOH indicated the lowest fine (14.8%) and medium silt (18.6%) content (Table 3).

Table 2. Sediment lithology of lakes Tüandre and Peipsi

	Lake Tüandre	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

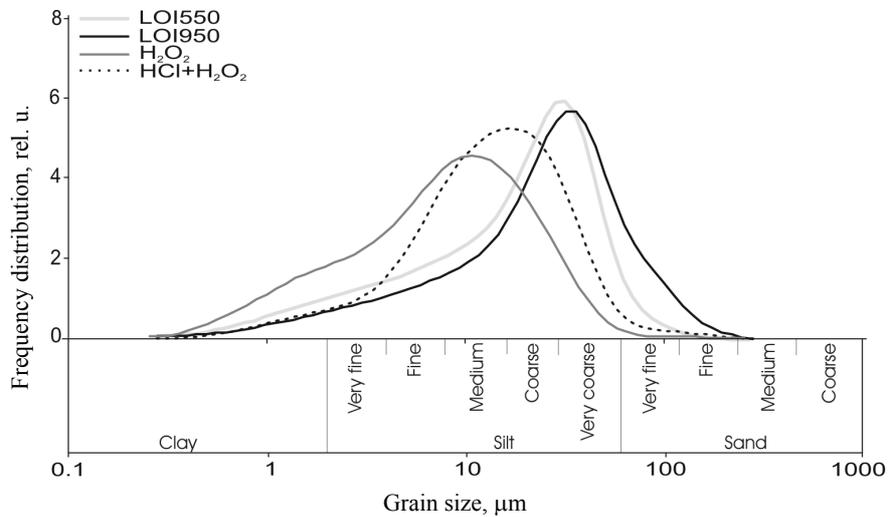


Fig. 1. Grain-size spectra of samples from L. Tüandre after applying different pre-treatment methods. The descriptive terms follow the Udden–Wentworth grain-size scale.

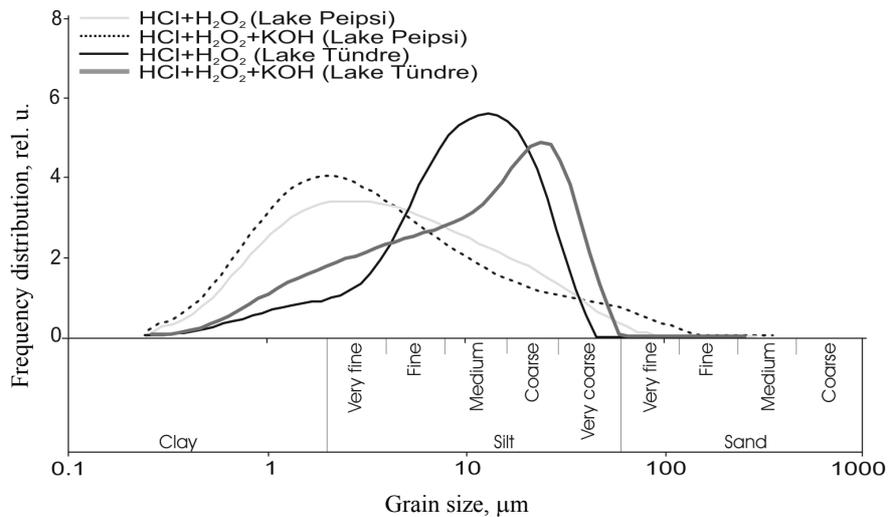


Fig. 2. Grain-size spectra of samples from L. Tüandre and L. Peipsi after applying HCl+H₂O₂ and HCl+H₂O₂+KOH pre-treatment methods. The descriptive terms follow the Udden–Wentworth grain-size scale.

Special attention was paid to the content of biogenic SiO₂. 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. Tüandre and L. Peipsi results of sediment samples are compared. Pre-treatment methods HCl+H₂O₂ and

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

Descriptive terms	Lake Tüdre					Lake Peipsi	
	LOI550	LOI950	H ₂ O ₂	HCl+H ₂ O ₂	HCl+H ₂ O ₂ +KOH	HCl+H ₂ O ₂	HCl+H ₂ O 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+H₂O₂+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+H₂O₂+KOH). Like L. Tüdre, L. Peipsi had lower fine and medium silt concentrations (Table 3, Fig. 2) and also a smaller median value compared with method HCl+H₂O₂ (Table 4).

Table 4. Statistical characteristics of different pre-treatment methods

	Lake Tüdre					Lake Peipsi	
	LOI550	LOI950	H ₂ O ₂	HCl+H ₂ O ₂	HCl+H ₂ O ₂ +KOH	HCl+H ₂ O ₂	HCl+H ₂ O 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, μm^2	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, cm^2/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. Tünder 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. Tünder 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 ($7254.8 \text{ cm}^2/\text{g}$) 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. Tünder was the largest ($13\,729.0\text{ cm}^2/\text{g}$) 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. Tünder (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. Tünder. As the size of valves is from 5 to 200 μm (Round et al., 1990), their presence might essentially

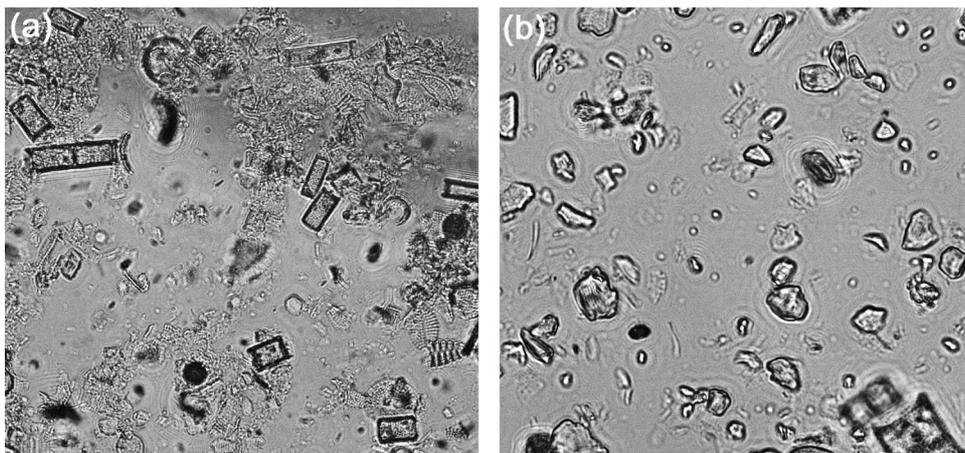


Fig. 3. Microscopic analysis of L. Tünder sediment: (a) samples treated by method HCl+ H_2O_2 , sample with diatoms; (b) samples treated by method HCl+ H_2O_2 +KOH, single grains without diatoms.

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 $\text{HCl}+\text{H}_2\text{O}_2+\text{KOH}$. 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 analogous 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. Tüandre shifted to the coarser silt (26.5 μm) fraction after the application of the pre-treatment method $\text{HCl}+\text{H}_2\text{O}_2+\text{KOH}$ (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 $\text{HCl}+\text{H}_2\text{O}_2$ 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 $\text{HCl}+\text{H}_2\text{O}_2+\text{KOH}$ had changes in the same fraction classes and showed the same trend as in L. Tüandre (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 $\text{HCl}+\text{H}_2\text{O}_2$ (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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REFERENCES

- Allen, J. R. L. & Thornley, D. M. 2004. Laser granulometry of Holocene estuarine silts: effects of hydrogen peroxide treatment. *Holocene*, **14**(2), 290–295.
- Almeida, M. P., Andrade, J. S., Jr. & Herrmann, H. J. 2007. Aeolian transport of sand. *Eur. Phys. J. E*, **22**, 195–200.
- Andreola, F., Castellini, E., Manfredini, T. & Romagnoli, M. 2004. The role of sodium hexameta-phosphate in the dissolution process of kaolinite and kaolin. *J. Eur. Ceram. Soc.*, **24**(7), 2113–2124.
- Battarbee, R. W. 1986. Diatom analysis. In *Handbook of Holocene Palaeoecology and Palaeo-hydrology* (Berglund, B. E., ed.), pp. 527–570. John Wiley & Sons, Toronto.
- Battarbee, R. W., Jones, V. J., Flower, R. J., Cameron, N. G. & Bennion, H. 2001. Diatoms. In *Tracking Environmental Change Using Lake Sediments. Volume 3: Terrestrial, Algal and Siliceous Indicators* (Smol, J. P., Birks, H. J. B. & Last, W. M., eds), pp. 155–202. Kluwer Academic Publishers, Dordrecht.
- Blott, S. J. & Pye, K. 2006. Particle size distribution analysis of sand-sized particles by laser diffraction: an experimental investigation of instrument sensitivity and the effects of particle shape. *Sedimentology*, **53**, 671–685.
- Bohling, B. 2004. Variations in grain size analysis with a time-of-transition laser sizer (Galai CIS-50) using a gravitational flow system. *Part. Part. Syst. Charact.*, **21**(6), 455–462.
- Boyle, J. F. 2001. Inorganic geochemical methods in palaeolimnology. In *Tracking Environmental Change Using Lake Sediments. Volume 2: Physical and Geochemical Methods* (Last, M. L. & Smol, J. B., eds), pp. 83–141. Kluwer Academic Publishers, Dordrecht.
- Buurman, P., Pape, Th., Reijneveld, J. A., de Jong, F. & van Gelder, E. 2001. Laser-diffraction and pipette-method grain sizing of Dutch sediments: correlations for fine fractions of marine, fluvial, and loess samples. *Neth. J. Geosci.*, **80**(2), 49–57.
- Carver, R. E. (ed.) 1971. *Procedures in Sedimentary Petrology*. Wiley Interscience, New York.

- Conley, D. J. 1998. An interlaboratory comparison for the measurement of biogenic silica in sediments. *Mar. Chem.*, **63**, 39–48.
- Dominik, P. & Kaupenjohann, M. 2000. Simple spectrophotometric determination of Fe in oxalate and HCl soil extracts. *Talanta*, **51**, 701–707.
- Gu, B., Melhorn, T. L., Liang, L. & McCarthy, J. F. 1996. Competitive adsorption, displacement and transport of organic matter on iron oxide. II: Displacement and transport. *Geochim. Cosmochim. Acta*, **60**, 2977–2992.
- Hayter, E. J. & Pakala, C. V. 1989. Transport of inorganic contaminants in estuarial water. *J. Coast. Res.*, **5**, 217–230.
- Heiri, O., Lotter, A. F. & Lemcke, G. 2001. Loss on ignition as method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. *J. Paleolimnol.*, **25**, 101–110.
- Kadey, F. L., Jr. 1983. Diatomite. In *Industrial Rocks and Minerals* (LeFond, S. J., Jr., ed.), pp. 677–708. American Institute of Mining, Metallurgical, and Petroleum Engineers, New York.
- Kim, J.-W., Furukawa, Y., Dong, H. & Newell, S. W. 2005. The effect of microbial Fe(III) reduction on smectite flocculation. *Clay. Clay Miner.*, **53**(6), 572–579.
- Konert, M. & Vandenberghe, J. 1997. Comparison of layer grain size analysis with pipette and sieve analysis: a solution for the underestimation of the clay fraction. *Sedimentology*, **44**, 523–535.
- Last, W. M. 2001a. Mineralogical analysis of lake sediments. In *Tracking Environmental Change Using Lake Sediments. Volume 2: Physical and Geochemical Methods* (Last, M. L. & Smol, J. B., eds), pp. 143–187. Kluwer Academic Publishers, Dordrecht.
- Last, W. M. 2001b. Textural analysis of lake sediments. In *Tracking Environmental Change Using Lake Sediments Volume 2: Physical and Geochemical Methods* (Last, M. L. & Smol, J. B., eds), pp. 41–81. Kluwer Academic Publishers, Dordrecht.
- Lu, H. & An, Z. 1997. Pretreatment methods in loess-palaeosol granulometry. *Chinese Sci. Bull.*, **42**, 237–240.
- Lyle, A. O. & Lyle, M. W. 2002. Determination of biogenic opal in pelagic marine sediments: a simple method revisited. In *Proceedings of the Ocean Drilling Program, Initial Reports. Volume 199* (Lyle, M., Wilson, P. A., Janecek, T. R., et al., eds), pp. 1–21. College Station, TX (Ocean Drilling Program).
- McCave, I. N. & Syvitski, J. P. M. 1991. Principles and methods of geological particle size analysis. In *Principles, Methods, and Application of Particle Size Analysis* (Syvitski, J. P. M., ed.), pp. 3–21. Cambridge University Press, Cambridge.
- McCave, I. N., Hall, I. R. & Bianchi, G. G. 2006. Laser vs. settling velocity differences in silt grain-size measurements: estimation of palaeocurrent vigour. *Sedimentology*, **53**, 919–928.
- Mikkelsen, O. A. & Pejrup, M. 2001. The use of a LISST-100 laser particle sizer for in-situ estimates of floc size, density and settling velocity. *Geo-Mar. Lett.*, **20**, 187–195.
- Mikutta, R., Kleber, M., Kaiser, K. & Jahn, R. 2005. Review: removal of organic matter from soils using hydrogen peroxide, sodium hypochlorite and disodium peroxodisulfate. *Soil Sci. Soc. Am. J.*, **69**, 120–135.
- Murray, M. R. 2002. Is laser particle size determination possible for carbonate-rich lake sediments? *J. Paleolimnol.*, **27**, 173–183.
- Paterson, D. M. 1997. Biological mediation of sediment erodibility: ecology and physical dynamics. In *Cohesive Sediments* (Burt, N., Parker, R. & Watts, J., eds), pp. 215–229. John Wiley and Sons, Chichester.
- Punning, J.-M., Terasmaa, J., Vaasma, T. & Kapanen, G. 2008. Historical changes in the concentrations of polycyclic aromatic hydrocarbons (PAHs) in Lake Peipsi sediments. *Environ. Monit. Assess.*, **144**, 1–3, 131–141.
- Reynolds, R. L., Rosenbaum, J. G., Rapp, J., Kerwin, M. W., Bradbury, J. P., Colman, S. C. & Adam, D. 2004. Record of Late Pleistocene glaciation and deglaciation in the southern

- Cascade Range. I: Petrologic evidence from lacustrine sediment in Upper Klamath Lake, southern Oregon. *J. Paleolimnol.*, **31**, 217–233.
- Roberts, J., Jepsen, R., Gotthard, D. & Lick, W. 1998. Effects of particle size and bulk density on erosion of quartz particles. *J. Hydraul. Eng.*, **124**(12), 1261–1267.
- Round, F. E., Crawford, R. M. & Mann, D. G. 1990. *The Diatoms*. Cambridge University Press, Cambridge.
- Schumacher, B. A. 2002. *Methods for the Determination of Total Organic Carbon (TOC) in Soils and Sediments*. Ecological Risk Assessment Support Center, Office of Research and Development, US Environmental Protection Agency, Las Vegas.
- Thonon, I., Roberti, J. R., Middelkoop, H., Van der Perk, M. & Burrough, P. A. 2005. *In situ* measurements of sediment settling characteristics in floodplains using a LISST-ST. *Earth Surf. Process. Land.*, **30**, 1327–1343.
- Van Rijn, L. 1993. *Principles of Sediment Transport in Rivers, Estuaries, and Coastal Seas*. Aqua Publications, Amsterdam.
- Walkley, A. & Black, I. A. 1934. An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Sci.*, **37**, 29–38.

Järvesetete terasuuruse analüüsid: eeltötlusmeetodite võrdlus

Tiit Vaasma

Nagu saadud tulemused näitavad, mõjutavad eeltötluse viisid oluliselt laser difraktsiooni meetodil määratud terasuuruse spektreid, mis võimaldab teha ka järeldusi proovide esialgse tekstuuri kohta. Olenevalt setteosakeste struktuurist, mineraalsest, füüsikaliseist ja keemiliseist koostisest ning ka settimiskeskonnast (elektrijuhtivus, temperatuur, aineriinge 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 eeltötluseks on keemiline töötlusmeetod ($\text{HCl} + \text{H}_2\text{O}_2 + \text{KOH}$) eraldades seeläbi nii karbonaatne ja orgaaniline materjal kui ka biogeenne Si.