The Lateglacial-Early Holocene dynamics of the sedimentation environment based on the multi-proxy abiotic study of Lieporiai palaeolake, Northern Lithuania

Laura Gedminienė, Laurynas Šiliauskas, Žana Skuratovič, Ričardas Taraškevičius, Rimantė Zinkutė, Mindaugas Kazbaris, Žilvinas Ežerinskis, Justina Šapolaitė, Neringa Gastevičienė, Vaida Šeirienė, Miglė Stančikaitė


Abstract. New data were obtained from the sedimentary sequence study of Lieporiai palaeolake, Northern Lithuania, employing a multi-proxy abiotic approach, for the description of the Lateglacial-Early Holocene palaeoenvironmental dynamics in the basin. The study reveals significant differences in sediments deposited in the Lateglacial, at the end of Lateglacial/Early Holocene and in the Late Holocene time periods. Six main environmental stages are described. After glacial retreat, the formed landscape was re-organized by very fast currents that might have appeared later than previously thought. Rapid water flow stabilized and lacustrine sedimentation began together with the appearance of scarce pioneer vegetation shortly before 14 600 cal yr BP, (GI-1e). The development of the lake with mostly undisturbed sedimentation continued up to the final stages of the Lateglacial Interstadial. The warm period caused maximum precipitation of Ca and Sr carbonates, which strongly affected sediment saturation with other components. Increase in humidity in the later Lateglacial Stadial (GS-1) period is indicated by the abrupt appearance of the coarser-sized mineral matter accompanied by weathering elements, i.e. Ti, Al, Si, Mg, and the early immigration of Picea. About 11 500 cal yr BP, the mineral matter input started decreasing, and stabilization of the climate regime began about 10 200 cal yr BP. (A)biotic proxies highlight slow sedimentation mechanisms that recover shallow- and trophic-lake stages. The Lieporiai palaeolake record clearly shows the sedimentation hiatus between the Early and the Middle Holocene. Further stages are characterized by paludification processes. Finally, peat accumulation was interrupted by humans.

Keywords: lacustrine sediments, geochemistry, SEM, abiotic data, Lateglacial, Early Holocene, NE Lithuania

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INTRODUCTION

Sediments of numerous lakes and/or palaeolakes, revealing changes in the postglacial environmental and climatic history and interpreted as high-resolution data banks, have been investigated over the last decades of the XX century in the Northern Hemisphere. However, chronologically based multi-proxy data sets are still scarce and unevenly distributed in particular areas of central and eastern Europe, including the Eastern Baltic (e.g. Stivrins et al. 2014; Stančikaitė et al. 2015; Apolinarska et al. 2012; Goslar et al. 1999; Kylander et al. 2013). Although numerous investigations in the area were pursued throughout the last decades of the XXth century, the independent chronological subdivision based on $^14$C data is still lacking in most cases here. In the context of the present knowledge, the biostratigraphical subdivision of sequences and further correlation of the identified environmental fluctuations make the obtained results rather debatable. In addition, some of the data sets for the territory, i.e. geochemical or $^{18}$O and $^{13}$C records, are very scarce (Stančikaitė et al. 2015, 2019). The number of methods used for collecting high-resolution multi-proxy archives of the local and regional postglacial environment history has greatly increased in recent years. The geochemical records of lake sediments (Goslar et al. 1999; Engstrom, Wright 1984; Koinig et al. 2003; Boyle et al. 2015; Kylander et al. 2013) are accompanied by grain-size measurements (e.g. Filipek, Owen 1979), survey of the magnetic susceptibility (Blumentritt, Lascu 2015), tephrachronology (Blockley et al. 2005; Turney 1998) etc. Furthermore, application of modern scientific facilities, e.g. an electronic scanning microscope (SEM), may provide new information about the chemical or structural composition of sediments (Apolinarska et al. 2012), revealing season-scale processes (Ojala, Tiljander 2003).

The area of Lieporiai palaeolake falls into the western part of the boggy area surrounding Rėkyva Lake, located south-eastwards from the investigated site (Lithuanian peatland cadastre 1995). At the beginning of the XXth century, six natural raised bogs existed in this region. Most of them were destroyed during land reclamation. A few years ago, the complex palaeoenvironmental investigations were conducted in Lieporiai and the collected data are currently in preparation. The results of the study, which focused on the high-resolution survey of biotic records including diatom, pollen, plant and macrofossil data and the subsequent analysis of the identified environmental fluctuations in the context of identified climatic shifts with the measurements of particular isotopes ($^{14}$C, $^{18}$O and $^{13}$C), are under development (Kisieliënė, personal communication). However, this study paid scant attention to abiotic parameters. In order to fill this gap, a new sediment sequence, mainly designated for the abiotic investigation, was collected from a small-scale sedimentary basin. The palaeobiological part (pollen and chironomid data) of this sequence is under development and will be discussed in detail separately.

In this paper, we present physical and chemical multi-proxy records (i.e. loss-on-ignition (LOI), magnetic susceptibility (MSus), grain-size, geochemical data and scanning electron microscopy (SEM) micrographs with the chemical composition) with a brief overview of the biostratigraphy identifying changes in the sedimentary regime and defining the responses of the sedimentation environment to external factors, such as climatic changes etc. It should be emphasized that the SEM technique was applied for the analysis of postglacial sediment subsamples in Lithuania for the first time.

The purpose of this paper was (1) to provide an overview of the Lateglacial and Early Holocene ecosystem dynamics revealing individual features of the basin based on abiotic factors; (2) to discuss the processes and reasons causing changes in sedimentation patterns.

STUDY SITE AND GEOLOGICAL HISTORY OF THE AREA

The study area, Lieporiai palaeolake, is located in the northern part of Lithuania (Fig. 1a, b) on the south-western edge of the Šiauliai city (55° 54’ 04” N, 23° 14’ 12” E). Currently, the palaeolake forms an 8 ha boggy meadow at an altitude of 122 m a.s.l. in the lowest part (Fig. 1c). The investigated basin stretches in a small depression surrounded by the hills of the end moraine reaching up to 140 m a.s.l. (Fig. 1c). The investigated basin stretches in a small depression surrounded by the hills of the end moraine reaching up to 140 m a.s.l. (Fig. 1c). According to the previous geological-geomorphological investigations (Guobytė, Satkūnas 2011; Stančikaitė et al. 2015), a few parallel tunnel valleys of subglacial type are crossing marginal formations of the Last Glaciation of the Middle Lithuanian Phase in the area (Guobytė, Satkūnas 2011) (Fig. 1c). The investigated site is situated in one of the highest parts of the palaeovalley, filled predominantly with glaciofluvial deposits. The Middle Lithuanian and North Lithuanian moraines were deposited 17 000 and 15 500 cal yr BP respectively (Raukas et al. 1995; Heikkilä et al. 2009). The surroundings of Lieporiai were deglaciated about 13.5 ± 0.6 $^{10}$Be ka (Rinterknecht et al. 2008) and the lacustrine sedimentation in the surrounding lakes started about 16 000–15 500 cal yr BP (Stančikaitė et al. 2015). During deglaciation, ice-melt water freely flowed behind the glacier forming proglacial lakes. Outwash sediments accumulated in the form of sandurs, deltas and terraces therein (Gedžiūnas et al. 2006). The above-mentioned forms were surrounded by a descent filled with sand rich in organic matter.
Fig. 1 Location of Lieporiai palaeolake (a, b) and geological-geomorphological situation of the area (c): 1 – low-lying marshy plain, filled with peat; 2 – lowering filled with sand, rich in organic; 3 – lowering in morainic relief filled with clayey sand; 4 – plain of glaciolacustrine basin, consisted of silty (a) and various sand (b); 5 – small esker composed of various sand; 6 – kame composed of various sand; 7 – morainic relief: eroded (a), covered by sand (b); 8 – slope of erosional origin (a) and step (b); 9 – erosional-accumulative slope; 10 – abrasional slope (a) and abrasional step (b); 11 – small hill (a) and imperceptible eminence (b); 12 – Iron Age settlement; 13 – sampling point
and low-lying marshy plains filled with peat located in the southeast (Fig. 1c). It should be pointed out that the area surrounding the study site underwent a drastic transformation because of the intensive human interference and only some local patches are still suitable for the environmental reconstruction.

The coring site is situated in the boreo-nemoral vegetation zone and is characterized by mixed and evergreen coniferous forests and grasslands converted into agricultural land. The annual average air temperature was 6 °C, the average precipitation was 592 mm (415 mm in the warm season and 177 mm in the cold season) during 1925–2006 (Šimanauskienė et al. 2013). In this part of Lithuania, the average annual number of days with snow cover is 80–90 days (Galvoniaité et al. 2013).

MATERIALS AND METHODS

Sampling and analysis process

Two overlapping sediment sequences were obtained from Lieporiai palaeolake using a percussion drill (Vibra corer, Cobra model) with 1 m long plastic inner tubes. The total depth of the boreholes was 200 cm. The reported depth represents a compressed sediment depth with the upper-most sample at 44 cm below the surface. Drilling was proceeded until the brown till layer was reached. In the laboratory, overlapping segments were cut into 2 cm intervals for further investigations. All 2-cm-resolution subsamples were subjected to MSus analysis; whole core sediments covering every 2–4 cm interval were subjected to geochemical, LOI, pollen and spore analyses; SEM and grain-size determination were done for the overlapping segments were cut into 2 cm intervals for further investigations. All 2-cm-resolution subsamples were subjected to MSus analysis; whole core sediments covering every 2–4 cm interval were subjected to geochemical, LOI, pollen and spore analyses; SEM and grain-size determination were done for the 78–104 and 74–160 cm intervals respectively. Most studies, if not mentioned otherwise, were performed at the Open Access Centre (OAC) of the Nature Research Centre in Vilnius, Institute of Geology and Geography.

AMS radiocarbon dating and sedimentation rate

The AMS dating was performed on 5 bulk samples at the Center for Physical Sciences and Technology in Vilnius. The 14C content in organic material (TOC) after the physico-chemical pre-treatment was measured. The 14C content in a separate sample (162–160 cm) was analysed in inorganic carbon (TIC) without chemical pre-treatment (Table 2). The ratios of 14C/12C in the graphitised sediment samples were measured using the 250-kV single stage accelerator mass spectrometer (SSAMS, NEC, USA). Graphitisation of the samples was performed using an Automated Graphitisation Equipment AGE-3 (IonPlus AG) (Wacker et al. 2010). The radiocarbon data were calibrated with 1-sigma error. The 14C dates were calibrated using the IntCal13 dataset (Reimer et al. 2013) within OxCal 4.3 software (Ramsey 2009). The median date was calculated from the age depth model. The calibrated age probability range was associated with the 1 sigma (68.27%) and 2 sigma (95.45%) confidence level. The Bayesian statistical method of the OxCal 4.3 (Ramsey 1995) software was applied to construct an age-depth model based on a set of 4 14C ages (R_Date) and one biostratigraphically based age identification with the OxCal age-depth P_Sequence model (Ramsey 2008). The data scale and the sedimentation rate value were calculated according to the obtained median values of the probability distribution of the modelled age. The sedimentation rate expressed as cm yr⁻¹ was calculated for each centimetre of the core.

MSus, LOI and grain-size determination

The measurements of MSus of 81 bulk samples (constant volume of wet subsample was 19.6 cm³ each), were obtained using the MFK1-B kappa bridge (AGICO) equipment with a manual holder and SAFYR software. Instrument calibration and empty holder correction were performed. Each specimen was weighed prior to the analysis. MSus was recalculated considering the weight of a room-dried sample and expressed in SI units (10⁹ m³/kg) using standard methods (Thompson 1973; Sandgren, Snowball 2002; Blumentritt, Lascu 2015).

Considering MSus results, 41 samples were selected for LOI measurements and dried at the temperature of 105 °C; then heated at 550 °C and 900 °C to burn out organic matter and carbonates, respectively. Analyses were performed using the basic LOI methodology (Dean 1974; Santisteban et al. 2004). The composition of the fine sediment fraction (<0.2 mm) in the middle part of the core (74–160 cm) was determined using a Fritsch Laser Particle Sizer “Analysette 22”. In total, 26 bulk samples were analysed. The grain size of the sediments in the interval below 160 cm depth was not determined, because it visibly consists of coarse-grained sand and gravel. Due to the high concentration of relatively undecomposed organic matter, this type of sediment analysis was not performed in the upper part of the sequence, i.e. sediments lying in 40–74 cm interval. The differentiation of grain size was performed following Ud- den and Wentworth scale (Blott, Pye 2001).

Geochemical analysis and pyrite concentration determination

Based on MSus, LOI data and distinguished lithological complexes, 48 subsamples were selected for the geochemical survey. Bulk samples were milled to the grain size <30 μm using an MM400 mixer mill in zirconium oxide grinding jars. Pellets (ø 20 mm) were prepared by mixing 2.00 g of milled material and 0.25 g of Licowax binder (Fluxana). Tablets
were pressed using the PP25 press (25 t). Both sides of the pellet were analysed using the EDXRF Spectro Xepos (Kleve, Germany) equipment applying the Turboquant method (Schramm, Heckel 1998) for the pressed pellet calibration procedure elaborated by the manufacturers (software “XLabPro 4.5”) to determine the contents of chemical elements. The average values of both pellet sides were calculated for further data analysis and statistical treatment. This enabled to reduce the influence of joint random errors (Taraškevičius et al. 2013; Stančikaitė et al. 2019).

The number of pyrite framoids was calculated along the pollen, and calculated against the AP + NAP + NPP.

Scanning electron microscopy
Five graphite-coated subsamples from the depths of 79, 97, 101, 107 and 145 cm were analysed. Studies were performed using the SEM Quanta 250 equipment. For easy phase recognition, back-scattered electron imaging (BSE) was used to acquire pictures. The chemical composition of sediment components was determined using the Energy Dispersive Spectrometry (EDS) detector X-Max, the INCA x-stream digital pulse processor and the INCA Energy EDS software. Measurements proceeded at the current of 1.1–1.2 nA and accelerating voltage of 20 kV.

Pollen and spore analysis, concentration determination
A total of 33 samples of the constant volume (0.5 cm³) were selected according to sediment homogeneity for the analysis. The standard chemical preparation (Berglund, Ralska-Jasiewiczowa 1986; Bennett, Willis 2001) of the material was performed at the Tallinn University of Technology, Institute of Geology. In order to determine concentration, tablets of Lycopodium clavatum spores (Stockmarr, 1971) were added. The results are presented as percentages of the sum of arboreal (AP) and non-arboreal (NAP) taxa (AP + NAP = ∑P). Aquatics, spores and non-pollen palynomorphs (NPP) were calculated as percentages of ∑P + sum of corresponding grains = 100% i.e. ∑P + NPP = 100%. The pollen data together with the chironomid-based palaeoclimatic reconstruction will be discussed separately. The selected taxa (Quercetum mixtum (QM), NAP, aquatics sum, Betula, Pinus, Picea) of particular plant groups are presented here.

Statistical evaluation of the data
A stratigraphically constrained cluster analysis, which is a multivariate method for quantitative definition of stratigraphic zones, was performed for each data set applying TILIA and TILIA-graph programs (Grimm 1987). The values were standardized separately and Ward’s method with Euclidean distances was chosen based on which diagrams were zoned by optimal partitioning (LOI, chemical element assemblage (ChEA), grain-size and MSus zones). Data were subdivided into five main assemblage zones (Figs. 2 and 3).

RESULTS
Lithostratigraphy
Based on visual inspection and the analyses performed, the sediment sequence was subdivided into evident lithostratigraphical units (Table 1, Figs. 2 and 3). The bottom part of the core (from 200 to 160 cm) (units 1a and 1b) consisted of clastic sediments, mainly rough unsorted grey sand with the gravel up to 2 cm in diameter. In the middle of the interval, lenses of coarse sand with gravel (ø 4 cm) were discovered. Sediments consist of the terrigenous material with an admixture of carbonates (15–30%). In the depth range 160–118 cm (unit 2a and unit 2b), an interval of sediments consisting of homogenous greenish grey silt (up to 60%) with sand (up to 20% of very fine- and medium-fine-grained sand), enriched with sporadic mollusc shells (126–118 cm, unit 2b) was noted. From the depth of 118 to 108 cm (unit 2c), sediments were found to consist of heavy, dark-

<table>
<thead>
<tr>
<th>Lithological unit</th>
<th>Depth, cm</th>
<th>Sediment description</th>
</tr>
</thead>
<tbody>
<tr>
<td>5b</td>
<td>55–44</td>
<td>Peat, black, on the topmost of the layer slightly enriched with darker well-decomposed peat, or rich soil. Organic composites visually change</td>
</tr>
<tr>
<td>5a</td>
<td>68–55</td>
<td>Peat, clayish and silty, enriched with shells on the bottom part</td>
</tr>
<tr>
<td>4b</td>
<td>80–68</td>
<td>Silt, coarse, dark brownish, enriched with gyttja and with a lot of shells</td>
</tr>
<tr>
<td>4a</td>
<td>90–80</td>
<td>Silt with very fine- and fine-grained sand, dark brownish</td>
</tr>
<tr>
<td>3</td>
<td>108–90</td>
<td>Silt with up to 10% of clay, enriched with light and fluffy carbonaceous detrital mud (so-called lake marl)</td>
</tr>
<tr>
<td>2c</td>
<td>118–108</td>
<td>Silt with very fine-grained sand, dark brownish, consist shells</td>
</tr>
<tr>
<td>2b</td>
<td>126–118</td>
<td>Silt with very fine-grained sand, dark brownish, consist sporadic shells</td>
</tr>
<tr>
<td>2a</td>
<td>160–126</td>
<td>Silt with very fine-grained sand, greyish green</td>
</tr>
<tr>
<td>1b</td>
<td>165–160</td>
<td>Sand, various grained, enriched with carbonates</td>
</tr>
<tr>
<td>1a</td>
<td>200–165</td>
<td>Sand and gravel, coarse-grained, with the till on the bottom</td>
</tr>
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</table>
brownish sandy silt, enriched with well-preserved mollusc shells. This interval is characterized by the average MSus value of $36 \times 10^{-9} \text{m}^3/\text{kg}$, with the maximum value reaching up to $150 \times 10^{-9} \text{m}^3/\text{kg}$. The interval from 108 to 90 cm (unit 3) was found to consist of very fine, light and friable silt, with high percentage of carbonates (up to 40%). Simultaneously, the percentage of clayey particles increases reaching up to 10%. The sediment unit 4a (depth 90–80 cm) is characterised by the increasing proportion of very fine and fine-grained sand reaching up to 35%. At the same time, the representation of organic matter in this interval reached 10% while the occurrence of carbonates declined to 7%. The MSus value increased along the interval and, also, a higher pyrite concentration was noted. The described part of the sequence is overlain by silt-enriched gyttja with mollusc shells (80–68 cm, unit 4b). Meanwhile, the percentage of mineral matter (up to 55%), particles of silt (up to 90%) and clay (up to 11%), predominantly, stays rather high in the lower part of the interval. Also, the relatively high amount of carbonate (maximum reaches 34%) material was recorded. Meanwhile, the top part of the section (units 5a and 5b) was found to consist of black, decomposed peat with more than 80% of organic matter. MSus lowered within the zone demonstrating the most negative values while some recovery of the curve was noted in the top-most part of the interval.

**Chronology, accumulation rate**

The chronology of the investigated sequence is based on the median values of four AMS dates (Table 2). The lowermost data (162–160 cm, FTMC-29-1-2, 50 479 ± 802 14C yr BP) were rejected from the model as the estimated age was unexpectedly old. In this case, the carbonate material was extracted and analysed as the presence of the organic constituent in the sediments was minor. The obtained result could be explained by the participation of the so-called “old-carbon” or “hard-water” effect as the representation of Devonian carbonate-enriched deposits close to the present surface was noted in the area (Narbutas, 2004). The age-depth model indicates that the development of sedimentary environment was relatively
Fig. 3 Summary diagram of lithological (LOI and MSus) and selected geochemical data
unstable and rapid water flow stabilized, most probably, shortly before 14 000 cal yr BP, i.e. during the GI-1e event or Bölling warming (Lowe et al. 2008). The decreasing presence of coarse sand particles in the strata proves stabilisation of the sedimentary environment and lower input of the terrigenous material throughout the following intervals of the Lateglacial Interstadial (unit 2a, Fig. 2). At that time, the sedimentation rate increased up to 0.07 cm/year. The beginning of the so-called Lateglacial Interstadial is identified from the decreasing representation of NAP, the rising participation of Pinus and other thermophilous biotic proxies could be interpreted as related to the onset of the Lateglacial Stadial (GS-1) or Younger Dryas cooling in the area, dated back to about 12 600 cal yr BP (Stančikaitė et al. 2015). Meanwhile, the AMS date (FTMC-29-4, 11 270 ± 40 cal yr BP, 89–88 cm) produced “a younger than expected” age contradicting all the above-described biostratigraphical and lithostratigraphical proxies and was rejected. Artificial contamination of the material was highly possible as thickness of the investigated layers was very low. The described layer is overlaid by the dark brownish coarse silt-enriched gyttja with a lot of shells (unit 4b, Fig. 2) suggesting the decreasing transportation of terrigenous particles into the basin. The increasing representation of the organic matter is in a positive correlation with the pollen record showing the ongoing formation of the birch-dominated vegetation with the minor participation of NAP taxa (Fig. 2). The obtained AMS data prove the Early Holocene age of the strata (FTMC-29-5, 8 095 ± 50 cal yr BP, 72–71 cm). Both biostratigraphical and lithostratigraphical data imply the possible sedimentation hiatus occurring in the uppermost part of the sediment sequence. Distinct changes in the bio- and litho-stratigraphical parameters suggest that the hiatus could be located on the boundary between units 4b and 5a (Figs. 2 and 3). The presence of anthropochores suggests a gap of a few thousand years in sediments as Secale cereale spread in the region only during the last thousand years of the Late Holocene (Stančikaitė et al. 2006).

Geochemistry and electron microscopy

Based on the results of element relative standard deviation of paired measurements, a total of 17 elements (Na, Mg, K, Al, Si, Ti, P, S, Zn, Cu, Cl, Ca, Mn, Fe, As, Rb, Sr) were chosen for closer analysis. The medians of chemical values in paired measurements of sediment subsamples were expressed in ppm (parts per million). Nevertheless, ratios of particular elements (Si/Ti, K/Na, Mg/Ti, Mg/Ca, Rb/Ti, Rb/Si, Mn/Fe) were calculated and analysed to supplement the discussion. The average data of each geochemical parameter in lithological units was calculated (Table 3).

The depth profiles show that the geochemical

Table 2. AMS radiocarbon and calibrated median dates for the Lieporiai sediment sequence samples

<table>
<thead>
<tr>
<th>Depth, cm</th>
<th>Laboratory number</th>
<th>Age, AMS 14C yr BP ± 1σ</th>
<th>Age, calibrated, cal yr BP, median</th>
<th>Dated material from bulk sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMS 14C data</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>72–71</td>
<td>FTMC-29-5</td>
<td>7 263 ± 37</td>
<td>8 095 ± 50</td>
<td>TOC</td>
</tr>
<tr>
<td>89–88</td>
<td>FTMC-29-4</td>
<td>9 884 ± 37</td>
<td>11 270 ± 40</td>
<td>TOC</td>
</tr>
<tr>
<td>112–110</td>
<td>FTMC-29-3</td>
<td>11 877 ± 37</td>
<td>13 600 ± 40</td>
<td>TOC</td>
</tr>
<tr>
<td>139–138</td>
<td>FTMC-29-2</td>
<td>11 965 ± 37</td>
<td>13 975 ± 55</td>
<td>TOC</td>
</tr>
<tr>
<td>162–160</td>
<td>FTMC-29-1-2</td>
<td>50 479 ± 802</td>
<td>–</td>
<td>TIC</td>
</tr>
<tr>
<td>Biostratigraphical data</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>Opening of the vegetation</td>
<td>12 600</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>
composition mostly depends on the lithological content including grain-size, the presence of organic and carbonate constituents etc. (Figs. 3, 4 and in detail see Supporting Online Material Fig. S4). Lithological unit 1a contains the highest concentrations of Si and Na, their values reaching up to 336450 and 4795 ppm accordingly. The highest values of Si/Ti ratio (varying between 300 and 450) were recorded within this unit as well. A visible increase in K, Mg, Si, Ti, Al, Rb, P, S and Fe concentrations is seen in unit 1b, consisting of finer clastic sediments. Meanwhile, this change negatively affected the concentration of Ca, Na, Sr, As, Mn and Cl. Unit 2a starts with relatively high Ti, Mg, Al, K and Zn concentrations, reaching peak values versus concentrations throughout the sedimentation period. Units 2a and 2b show relatively steadily increasing concentrations of Na, S, Cl. According to the results of scanning electron microscopy (SEM), clastic sediments – silt and fine-grained sand – mainly consist of quartz, feldspars and other K-, Si-, Al-, Ti-, Rb-, Fe-bearing minerals (Fig. 4, i). Photomicrographs show the presence of scattered and angular particles suggesting the hypothesis of short transportation. Small oscillation is recorded at the onset of unit 2b (124–126 cm, about 13 800 cal yr BP), where a significant increase in K, Mg, Ti, Al, Rb, Cu, K/Na, Mg/Ti, Rb/Si, Rb/Ti, Mn/Fe curves is noted. The recorded changes are in a positive correlation with the increasing representation of clay-sized particles in sediments. Within unit 2c (an interval from about 13 700 to 13 460 cal yr BP), the depletion of the majority of the analysed elements is visible with the exception of Ca, Sr, Cl, S and K/Na, Rb/Si ratio. As for the peculiarities of the geochemical record of lithological unit 3, carbonates (Ca, Sr) became most abundant, which probably weakens signals of other elements. However, a strong signal of clay minerals is expressed by high Rb/Si and Rb/Ti ratios that increased from 18 to 28 and from 21 to 22 accordingly. At the same time, the share of Mn significantly increases from 329 to 551 ppm and is expressed by a higher Mn/Fe ratio. In the bottom part of this interval (aged from about 13 400 to 13 100 cal yr BP), sediments enriched with coarse-grained terrigenous particles (Fig. 4 e, f, g), bearing a higher concentration of organic carbon (Fig. 4 e, h) and framboidal pyrite (Fig. 4 d, e, h) were discovered. The sedimentation interval between about 13 100 and 12 600 cal yr BP is characterized by increased bioproduction, which is evidenced by the presence of visible detrital material in the strata (Fig. 4, d). The geochemical record shows remarkable changes in lithological unit 4a (about 12 600–10 200 cal yr BP). In the middle of the unit, the representation of Na, Mg, Al, Si, Ti, K, Rb, Cu, Zn, P, Cl clearly increases while that of Ca, Sr, Mn, decreases. Nevertheless, the culmination of Si-bearing minerals is expressed by the increased Si/Ti ratio, which together with decreasing Rb/Si, Rb/Ti ratios and lower representation of clay-sized particles indicates a highly unstable sedimentation regime.

**Table 3. Average values of selected geochemical parameters in lithological units**

<table>
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<tr>
<th>Stage</th>
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<th>4a n = 5, 108–90 cm</th>
<th>3 n = 6, 118–108 cm</th>
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Fig. 4 Scanning electron micrographs of subsamples from lake sediment at 79–145 cm depth interval: autochthonic particles: biogenic calcite-aragonite a, b, d(2), h(2); barite c(1). Products composed due to diagenesis: dolomite c(2), g(2); pyrite framboïds d(3), e(1,2), h(1). Allochthonic particles: plagioclase d(1); quartz e(2), g(3), I(1); biotite f(1); Ca-Mg-Al silicate f(2); K-feldspar g(1,3), I(2). Most of fine-grained material (a-h) enriched with Ca. For detail see Supporting Online Material
Peak values of Fe, S and As concentrations correlating well with the high pyrite concentration and the remarkable peak of the MSus curve were established in the upper part of the interval (about 10 650 cal yr BP). The geochemical composition of unit 4b is very similar to that of unit 3. It is important to mention that in the upper part of this interval, high concentrations of CI and S elements were established. However, the upper carbonate-enriched part of this interval is supplemented with larger shell particles and other autochthonic micrite. (Fig. 4 a, b, c). Lithological units 5a and 5b are enriched with P, S, Mn; higher values of Mg/Ti, Rb/Si show relatively high concentrations of Mg, Rb.

DISCUSSION

Stage I (before 14 600 cal yr BP, lithological units 1a–1b, 200–160 cm)

The lowermost layers of the investigated sediment sequence consist of fluvial deposits suggesting strong water currents and quick non-lacustrine sedimentation in the basin as the deposited material is unsorted, sharp-edged, coarse-grained, predominantly consisting of heterogeneous mineral matter. In addition, the obtained 

14C
data (~50 500 14C yr BP) also point to the re-deposition of sediments including intensive supply of allochthonous material into the basin. Re-deposited particles might have been enriched with Devonian dolomites widespread in northern Lithuania (Narbutas 2004). The continuous representation of the so-called weathering elements including Ti, Al, K, Mg (Fig. 3) also points to the high steady inflow of eroded material. The cold-water stream is likely to have been enriched with dissolved and fine-grained carbonates (Devonian dolomites and limestone mostly likely) as, according to LOI data (Fig. 3), they are well represented in the material. At that time, conditions were inappropriate for vegetation stabilization in the closest watershed. Meanwhile, the decreasing presence of the coarse-grained particles in the uppermost part of the interval suggests some stabilization of the sedimentation environment (Fig. 2, unit 1b). The increased Si/Ti ratio points to the change in the silicate source and Rb/Ti ratio indicates that the water flow rate decreased towards the end of this sedimentation stage. Nevertheless, elements associated with finer fractions, i.e. Ti, Al, K, Mg, Rb etc. (Koinig et al. 2003; White, Blum 1995), accumulated together with the first organic remnants (unit 1b) as LOI diagram shows 0.5–1% of organic matter. Meanwhile, the highest recorded concentrations of P could point to: (i) a reverse from oxic to anoxic zone (ii); biological activity enhancement towards the end of this sedimentation stage. The latter hypothesis is supported by biological proxies, i.e. the sporadic occurrence of such pollen as Caryophyllaceae, Artemisia, Pinus proves the formation of pioneer vegetation communities with high percentage of heliophytes in the area. Similar pollen spectra were discovered in the appropriate interval of Ginkūnai core situated at a distance of about 7 km from Lieporiai palaeolake (Stančikaite et al. 2015) and on the regional scale (Veski et al. 2012; Stivrins et al. 2014).

Stage II (14 600–13 400 cal yr BP, lithological units 2a–2c, 160–108 cm)

The newly obtained data suggest that the onset of lacustrine sedimentation could be associated with the so-called Bölling warming. A sudden transition from coarse-grained deposits to clay, silt and very fine grained-sand enriched with a low amount of organic and carbonate material indicates some stabilization of the sedimentation regime (Figs. 2 and 3). The percentage of the mineral matter in the sediments is still high and siliciclastic elements, i.e. Ti and Al, predominate. Besides, the part of the carbonate matter recorded during LOI procedures significantly decreased. Although the geochemical analysis shows a very insignificant change in Ca and Sr curves, the onset of this stage is reflected by a drastic increase in Mg and Mg/Ca ratio, which was recorded throughout the rest of stage II, suggesting: (i) a change of a given sediment source; (ii) rapid warming reflected by carbonate composition changes, which might also evidence the first appearance of bioproductivity. Similar geochemical composition was previously analysed by Namiotko et al. 2015, who suggested that increase in magnesium enriched calcite had significant positive associations with the benthic low-magnesium calcitic ostracods; (iii) slightly anaerobic conditions in the saturated lake favourable for modern dolomite formation (Vasconcelos, McKenzie 1997); or (iv) some combination of these.

Simultaneously, the content of Rb, K, Al in sediments increased and it is associated with a finer fraction. The further development of the geochemical record shows low variability of Si/Ti and K/Na curves and rather stable presence of K, Ti, Rb and etc. pointing to stable terrigenous matter sources throughout the rest part of stage II. This is also proved by the rather stable MSus record. However, the decreasing Mg/Ti ratio and stable Ti participation may be indicative of the constantly lowering water table or the decreasing watershed throughout stage II. Only a small oscillation of Al, Rb, K concentrations and Rb/Si and Sr/Si ratios, probably induced by quick changes in clay minerals, is noted in the transition zone from lithological unit 2a to 2b at the 126–124 cm depth. This interval, which is dated to approximately 13 800 cal yr BP, could be correlated with the concurrent changes in Ginkūnai core (Stančikaite et al. 2015), in which
higher participation of *Artemisia*, Chenopodiaceae and a drop in *Pinus* curve were noted. The indicated instability could be caused by the rapid water table decline due to the short term Older Dryas cooling event 13 800 cal yr BP. Zn profile also shows some irregularity that suggests a hypothesis of water level decrease. This tendency was previously analysed by Tessier *et al.* (1989). It marks the moment when particular zinc accumulation changed to autochthonous and Zn accumulated in lake sediments by diffusion of dissolved Zn from lake water to sediments resulting in sub-surface peaks. The recorded low As and Mn/Fe ratio (Engstrom, Wright 1984) as well as high pyrite concentration allow speculating about anoxic conditions throughout the interval. Moreover, these factors also suggest that at that time the climate was already favourable for thin soil formation. The mobility of Fe increased because of the appearance of humic acids (Engstrom, Wright 1984). Over time, expansion of certain plant species, i.e. *Juniperus*, Ericaceae, *Artemisia*, Chenopodiaceae, *Salix* gradually decreased. At the end of this stage, *Pinus* became most abundant and even increased upwards indicating moderate forestation of the region with open pine-birch forest, though open grasslands were still abundant. The indicated vegetation might have stabilized the soil layer. Stabilization of the climatic regime and formation of the soil layer lead to favourable conditions for the bioproduction. Gradually increasing lacustrine biota probably consumed most of the nutrients dissolved in water, which made water body transparent, oxygen-enriched and oligotrophic. However, at the end of this period, *Juniperus* flourished again, aquatic plants vanished indicating dryer conditions about 13 700–13 400 cal yr BP (unit 2c).

**Stage III (13 400–12 600 cal yr BP, lithological unit 3, depth 108–90 cm)**

The maximum precipitation of Ca and Sr carbonate was noted between 13 300 and 12 600 cal yr BP. At the same time, light silt enriched with clay-sized particles containing the highest concentration of carbonates as well as Ca and Sr deposited in Ginkūnai Lake (Staněkaitė *et al.* 2015). These changes in the sedimentary environment suggest climatic amelioration that could be correlated with the GS-1a interval. Such high precipitation of carbonates in the lake might be due to the improved climatic conditions and stabilization of sedimentation. This change is closely related to the decrease of weathering elements in the reservoir or its long-term supersaturation (Pawlowski *et al.* 2016) with carbonates, and is largely controlled by grain size (Kylander *et al.* 2013), as the composition of sediments in stage I significantly differs from that in stage II (Figs. 2 and 4). Less intensive transportation of eroded material into the lake is proved by the decreasing MSus curve and the lower participation of aluminosilicate elements (Ti, Al), as indicated in the geochemical record.

SEM analysis determined biochemical calcite precipitation along with geochemical indicators. According to Apolinarska *et al.* (2012), in the uppermost Allerød and lower YD sediments, calcite of such a type was accumulated owing to the activity of autotrophic organisms in the lake. New data show that a remarkable rise of Ca and Sr curves is in a positive correlation with the higher participation of organic material. Obviously, these changes could be interpreted as indicators of the rising biomass production. The latter fact is also proved by the changing pollen record showing the increasing density of the vegetation cover and formation of the pine-dominated forest in the area. Moreover, carbonate leaching in the lake catchment could also be explained by the establishment of the conifer-dominated forest (the culmination of *Pinus* pollen curve, the presence of *Pinus stomata*), which could enhance mobility of carbonates because of the lower soil pH (Apolinarska *et al.* 2012). The newly formed vegetation, typical of many sites in central and northern Europe (Veski *et al.* 2012; Stivrins *et al.* 2014; Pawłowski *et al.* 2016; Apolinarska *et al.* 2012; Heikkila *et al.* 2009), might have stopped shore erosion, the primary source of inorganic minerals and elements, affecting the degree of dilution of other components of sediments.

Nutrient reduction and gradual temperature increase resulted in the well-oxygenated lake stage. The systematically increasing Mn/Fe ratio that could be suggested as an oxygen indicator was also analysed by Engstrom, Wright (1984) and Koinig *et al.* (2003). Such conditions were ideal for the formation of diageneric carbonates (Müller *et al.* 1972). This theory can explain the appearance of well-expressed rhomboidal dolomite crystals that are common in the bottom part of this unit (Fig. 4 g). It is important to mention that high Mg/Ti ratios show sediment enrichment with magnesium versus Ti and have a significant correlation with increased bioproduction. However, a decreasing Mg/Ca curve shows that carbonate precipitation did not have such a significant dilution effect on Mg participation as on that of other elements.

**Stage IV (12 600–10 200 cal yr BP, lithological unit 4a, depth 90–80 cm)**

Relatively calm sedimentation conditions with deposition of carbonaceous detritus lasted until the onset of the Younger Dryas (GS-1), 12 600 cal yr BP, according to the pollen record (Fig. 2). An abrupt input of the coarser-sized mineral matter and a rise in MSus values at that time were noted (Fig. 3). The recorded reverse could be connected with: (i) a local flood or rise of the water level, as similar changes...
occurred in eastern and central Poland (Goslar et al. 1999; Pawłowski et al. 2016); (ii) an increase in the minerogenic input indicating climatic deterioration and aridification, which was previously explained in Stančikaitė et al. (2015). Scarce vegetation associated with the cooling of GS-1 interval was recorded in central Latvia (Veski et al. 2012; Stivrins et al. 2014) and in other parts of Europe (Heikkilä et al. 2009; Dean, Schwab 2000). During this period, plants typical of open habitats (i.e. Artemisia, Caryophyllaceae) developed together with scattered Betula forests in the area. At the same time, pine was suppressed from the catchment, but Picea entered the area indicating increasing wetness. Numerous studies (Heikkilä et al. 2009; Veski et al. 2012; Stančikaitė et al. 2019) recorded early immigration of this tree to the region. The recorded chemical and physical properties together with an increase in the so-called weathering elements, i.e. Ti, Al, Si, K, Mg, Rb, prove activated erosion episodes in the watershed as well as low biological productivity of the lake. The raised Zn curve points to the change in aqueous solution acidity. Lake pH values could have increased to exceed pH 7 in surficial sediments (Tessier et al. 1989). Such water pH was previously indicated by the flourishing of Amphora pediculus diatoms in Ginkūnai Lake (Stančikaitė et al. 2015).

From about 11 500 cal yr BP, the input of mineral matter started decreasing, while the proportion of clay-sized particles, Ca, Sr and Rb/Si increasing, indicating stabilization of the shores and watershed and recovery of the water level. The pollen record evidences the formation of a new vegetation cover, wherein NAP pollen flourished. Decreased Mn/Fe ratios and increased Fe, As and pyrite framboïd concentrations, especially in the upper part of the interval about 10 600 cal yr BP indicate chemical processes that occurred during diagenesis of modern sediments (Wilkin et al. 1996). The above-mentioned processes, which are usually linked to the oxic-anoxic transition zone, could be related to increased groundwater levels and an increase in humic acids (Engstrom, Wright 1984).

Stage V (10 200–7 200 cal yr BP, lithological unit 4b, depth 80–68 cm)

The obtained data suggest stabilization of the sedimentation regime about 10 200 cal yr BP. This interval represents the final phase of an open water body. During the further stages, the transition from the lake to the peat bog regime was noted in Lieporiai. Subsequently, a complete change in the lake’s trophic stage including the onset of the paludification processes was revealed. Due to lower soil pH and increased humic acids, the movement of Ca and Sr from soil to the basin was intensified. Favourable conditions and enrichment of the basin with carbonates may have caused the bioproduction of molluscs. An increased Mn/Fe ratio (at about 75 cm depth) points to highly oxygenated, transparent and shallow water basin stage with low pH. Shallowing processes led to gradual overgrowing and gradual development of the new vegetation structure suggesting progressively warmer climatic conditions. The Early Holocene is confirmed by the spread of Betula forests together with the appearance of alder and spruce. Such transition is evident regionally (Stančikaitė et al. 2006, 2015; Stivrins 2014; Karasiewicz et al. 2019). However, at that time, sedimentation was extremely slow and, therefore, a short section represents a relatively long period of time. By the middle of this stage, high and/or increasing concentrations of Rb, Mg in comparison with silicate elements (Si, Al), Ti and high carbonate concentrations started decreasing probably due to the decreased humification, which was accompanied by some vegetation disturbances. Obviously, the progressively warmer climate suffered some instability, which was not significant. It might have been a signal of 8.2 ka event, detected in high-resolution records in western and central Europe, and previously discussed in Veski et al. 2004.

Stage VI (Middle–Late Holocene, lithological units 5a–5b, above 68 cm)

The borderline between Early and Middle Holocene in Lieporia palaeolake is clear-cut. The two geological epochs are separated by a very abrupt change in the sedimentation regime or even in the sedimentation hiatus, which is clearly visible in geochemical and pollen records. Besides, the transition zone starts with the peak of Cl. Chlorine is a common element that dissolves in surface groundwaters or geological formation fluids and can be a conservative tracer in most aquatic and geological environments (Kochler, Wassenaar 2010).

Further changes could be related to paludification processes. However, due to high organic concentration, abiotic multi-proxy approach had weak signals. Even so, with regard to elemental ratios and LOI, this interval could be split into two stages. The first one generally covers the Middle Holocene, which is characterized by higher concentrations of most of the analysed elements (except Mn, As, Fe) with a slightly decreasing trend. The interval is characterised by the highest S, As, Cu concentrations, an increasing Mg/Ti ratio, and a slightly increasing, but low Mn/Fe ratio. Such a composition can be explained by soil acidification, which usually leads to the depletion of elements (Karasiewicz et al. 2019; Pawłowski et al. 2016).

In comparison, the sediments deposited during the Late Holocene, have a very high Mn/Fe ratio, which
indicates an oxic state suggesting favourable conditions for mineralization of the sediments, suitable for various living microorganisms. The surface organic sediment layer is characterised by the heterogeneity of chemical composition, slightly enriched with the so-called weathering elements.

From the beginning of this stage, changes taking place in vegetation were characteristic of the Holocene thermal maximum period discussed regionally (Stivrins et al. 2014; Pawłowski et al. 2016; Karasiwicz et al. 2019). Common trends for broadleaf forests with an admixture of Pinus, Picea and with some heliophilous communities in the understory were recorded. However, our new pollen data show a drastic decrease in Betula species, a higher concentration of herbs and grasses, including Secale cereale, Asteraceae, Lactuceae. Such changes were predetermined by some local factors and could have been caused by increased human activity. Nevertheless, high Fe, Cu, Mn concentrations could be related to the human impact, i.e. pollution and/or iron smelting (Salatkienė 1994) processes.

CONCLUSIONS

According to the abiotic proxies obtained from the sedimentary sequence analysis, the sedimentary regime of Lieporiai palaeolake underwent six intervals of changes during the Lateglacial-Early Holocene. The lake came into existence before 14 600 cal yr BP. The Lateglacial Interstadial was characterised by the maximum precipitation of Ca and Sr carbonates as well as the flourishing of Pinus-dominated forests. The diversity of sediments deposited during the Lateglacial Stadial was increased by the weathering elements. Decreasing humidity lead to the vegetation cover thinning and provoked erosion processes. Climate stabilisation as a response to increased temperature dates back to about 10 200 cal yr BP. The sedimentation hiatus with a visible gap in geochemical and pollen records functions as a borderline separating the Early Holocene from the Middle Holocene. The natural lake evolution was altered by the anthropogenic influence only during the last stage, probably during the last thousand years.

A significant positive correlation was found to exist: (i) between precipitation of chemical elements, i.e. Si, Ti, Al, Mg, K and grain size; (ii) between Fe, pyrite framboid concentration and MSUs.

Sediment oversaturation with silicates, carbonates, organic or other components affected the degree of dilution of element contents. Numerous factors (changes of trophic stage, bioproduction, pH, redox conditions, weathering, erosion, water table fluctuation, stratification, enrichment with oxygen, temperature etc.) influence sediment oversaturation with certain products and change sediment composition and the sedimentation pattern.

ACKNOWLEDGMENTS

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Rinterknecht, V.R., Bitinas, A., Clark, P.U., Rais-

Supporting Online Material
Figure S4
Fig. S4 Scanning electron micrographs of subsamples from lake sediment at 79-145 cm depth interval with a detailed chemical composition of chosen sediment components: autochthonic particles: biogenic calcite-aragonite a, b, d(2), h(2); barite c(1). Products composed due to diagenesis: dolomite c(2), g(2); pyrite framboids d(3), e(1,2), h(1). Allochthonic particles: plagioclase d(1); quartz e(2), g(3), l(1); biotite f(1); Ca-Mg-Al silicate f(2); K-feldspar g(1,3), l(2). Most of fine-grained material (a-h) enriched with Ca.