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Application of Lake Sediment Carbon/Nitrogen Ratio in Post-Glacial Paleoenvironmental Reconstruction

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Declaration:
Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for doctoral or equivalent academic degree.

Merlin Liiv

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Järvesetete orgaanilise aine süsiniku ja lämmastiku suhte kasutusvõimalused pärastjääaegsete keskkonnamuutuste rekonstrueerimisel

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Contents

List of Publications

The list of author's publications, on the basis of which the thesis has been prepared:

I Liiv, M., Alliksaar, T., Amon, L., Freiberg, R., Heinsalu, A., Reitalu, T., Saarse, L., Seppä, H., Stivrins, N., Tõnno, I., Vassiljev, J., Veski, S. (2018). Late glacial and early Holocene climate and environmental changes in the eastern Baltic area inferred from sediment C/N ratio. Journal of Paleolimnology: available online 28. June 2018, https://doi.org/10.1007/s10933-018-0041-0

II Stivrins, N., Liiv, M., Heinsalu, A., Gałka, M., Veski, S. (2017). The final meltdown of dead-ice at the Holocene Thermal Maximum (8500−7400 cal. yr BP) in western Latvia, eastern Baltic. The Holocene 27: 1146–1157.

III Liiv, M., Alliksaar, T., Freiberg, R., Heinsalu, A., Ott, I., Reitalu, T., Tõnno, I., Vassiljev, J., Veski, S. (2018). Drastic changes in lake ecosystem development as a consequence of flax retting: a multiproxy palaeolimnological study of Lake Kooraste Linajärv, Estonia. Vegetation History and Archaeobotany 27: 437–451.

IV Stivrins, N., Liiv, M., Brown, A., Banerjea, R. Y., Heinsalu, A., Veski, S. Investigating the impact of anthropogenic land use on a hemiboreal lake ecosystem using carbon/nitrogen ratios and coupled-optical emission spectroscopy. *Manuscript.*

Author’s Contribution to the Publications

Contribution to the papers in the thesis are:

- I The author was responsible of the lake sediment total organic carbon, total nitrogen and grain size analysis. The author interpreted the obtained paleo-data, wrote the manuscript, and is the first and corresponding author.
- II The author was responsible of the lake sediment total organic carbon and total nitrogen analysis. The author participated in the interpretation of the paleo-data and in the preparation of the manuscript.
- III The author was responsible of the lake sediment total organic carbon, total nitrogen and total sulphur analysis. The author interpreted the obtained paleo-data, wrote the manuscript, and is the first and corresponding author.
- IV The author participated in the fieldworks and was responsible of the lake sediment total organic carbon, total nitrogen and loss-on-ignition analysis. The author participated in the interpretation of the paleo-data and in the preparation of the manuscript.

Introduction

The environment surrounding us is in a constant state of change, some of which is due to natural processes, while other changes occur because of human activities. Reconstructing any type of environmental or biological variability on a longer timescale can be challenging due to the length of available instrumental records, which occasionally cover only the last 100–150 years. These already scarce timeframes are usually insufficient to reflect various ranges of regional/global patterns and provide full insight on baseline environmental conditions in order to make correct conclusions about whether the observed changes fall outside the range of natural variability or not. The necessary information can only be drawn from the past where many answers to environmental problems hide. Luckily, the desired knowledge regarding long-term variations can be obtained by using paleo-datasets.

Paleolimnology is the field of science that uses lake sediments to reconstruct past environmental history. Lake sediments can be considered the “hard drive” of an ecosystem, as they archive current conditions at the time of deposition over annual to millennial timescales. The paleolimnological approach allows us to separate “noise” from “signal”, view the present, and predict future changes against a historical backdrop (Smol, 2008). This field of study has undergone a major transformation from being largely empirical and descriptive to becoming quantitative and applied, while the field continues to expand (Birks, 1998; Saulnier-Talbot, 2016; Domaizon et al., 2017; Burge et al., 2018). Due to that, biological, physical, and geochemical proxy indicators have rapidly evolved and improved, allowing us to seek answers to an enormous range of problems (discussed in depth by Cohen (2003) and Smol (2008)). While early paleo-studies usually focused on a single primary proxy indicator, the focus, nowadays, has changed into a much more integrated one. Ideally, the multi-proxy study is considered the best solution to illustrate the true complexity of the lake ecosystem, where multiple factors interact in sometimes complicated ways. Multi-proxy study approaches the same problem from different angles and helps to narrow down the characteristics that have affected the lake and its surroundings (Birks and Birks, 2006). It is common that paleolimnologists incorporate traditional methods such as bio- and litho-stratigraphy with several modern techniques, such as stable isotopes and DNA analyses, to reinforce the overall interpretation and reduce the possibility of false interpretations. Even though multi-proxy study is extremely labour-intensive and requires careful planning, the results are usually worth the effort.

Lake sediments comprise several components—clastic material, organic matter (OM), and chemical precipitates. The most common elements in lake sediment OM are carbon (C), nitrogen (N), hydrogen, oxygen, and phosphorous (P) (Cohen, 2003). The OM content of lake sediments integrates complex mixtures of lipids, carbohydrates, proteins, and other biochemicals contained in the tissues of living and formerly living organisms in the lake and in its catchment (Meyers and Ishiwatari, 1993). Several simultaneous environmental factors such as local environment, bedrock geology, surrounding vegetation, lake productivity, internal processes (e.g., lake water mixing, OM reworking and degrading, nutrient internal loading), and human impact (Meyers and Takemura, 1997; Cohen, 2003) determine and regulate the elemental content in the lake sediment OM composition. Therefore, the aforementioned variables can vary a lot between different lakes in different locations.

Lake sediment OM contains approximately 50% C (Meyers and Teranes, 2001). The concentration of total organic carbon (TOC) is generally used to determine the abundance of OM in sediments and study lacustrine paleoproductivity and OM preservation after deposition (Meyers and Ishiwatari, 1993; Meyers, 1997; Meyers and Teranes, 2001; Magny et al., 2006; Gälman et al., 2008). Identifying the origin of the OM in sedimentary records is essential for paleolimnological investigations to make useful generalizations about the proportional changes in OM and whether it is produced in the lake or derived from the lake catchment area (Meyers et al., 1984; Meyers and Ishiwatari 1993; Meyers and Teranes 2001). Using the TOC/total nitrogen (TN) ratio (hereafter C/N ratio) meets those needs. C/N ratio analyses are commonly involved in lake sediment studies to distinguish in-lake-produced algal OM from catchment-derived terrestrial OM (Meyers and Lallier-Vergès, 1999; Wohlfarth et al., 2004; Enters et al., 2010; Choudhary et al., 2013; Kołaczek et al., 2015; Pędziszewska et al., 2015; Mahesh et al., 2017), and although there are cases in which the C/N ratio is used as an independent proxy (Kaushal and Binford, 1999), it is usually considered to be a rather complementary method with relatively rigid interpretations. Therefore, it is important to emphasize the potential capability of the C/N ratio in multi-proxy paleo-studies to help reconstruct the unique and multifaceted history of lakes and their surrounding areas.

Abbreviations

AD	calendar age after Christ, *Anno Domini*
AMS	accelerator mass spectrometry
AR	accumulation rate
BC	calendar age before Christ
β-car	beta carotene
C	carbon
Ca	calcium
cal yr BP	calibrated years before present (AD 1950)
CM	carbonate matter
C/N	total organic carbon/total nitrogen ratio
LOI	loss-on-ignition
MM	mineral matter
MS	magnetic susceptibility
N	nitrogen
NGRIP $\delta^{18}O$	North Greenland ice core oxygen isotope record
OM	organic matter
P	phosphorous
TN	total nitrogen
TOC	total organic carbon
TP	total phosphorous
TS	total sulphur
T_{sum}	mean summer air temperature
T_{win}	mean winter air temperature

1 Review of the literature

1.1 OM and its elemental (C, N, C/N) composition in lake sediments

The OM content of sediments is the residue of past biota that has lived in and around the lake (Meyers, 1997). The primary source of OM to lake sediments originates from the particulate detritus of algae of the waterbody and plants that exist on land and in the shallow parts of the lake as bottom-rooted and/or emergent vegetation; only a few percent come from animals (Meyers and Ishiwatari, 1993; Meyers and Lallier-Vergès, 1999). In addition to the above, winds also bring extra materials into the total organic mixture of the lake in the form of land-plant pollen, soot from fires, and fine soil from distant sources (Meyers, 1997). OM formation depends on several factors, which have affected its incorporation into lake sediments; these include lake morphology, catchment area topography, climate, and overall abundance of lake and its catchment areas plants (Meyers and Lallier-Vergès, 1999).

Lake sediment OM consists of a mixture of materials derived from both terrestrial (allochthonous) and aquatic (autochthonous) sources in varying proportions. The distinction of these sources relies on their biochemical differences—non-vascular plants, such as algae, lack woody cellulosic tissues and are N-rich, whereas vascular plants, such as grasses, shrubs, and trees, have tissues that contain C-rich cellulose (Meyers et al., 1984; Meyers and Ishiwatari, 1993; Meyers, 1997). The C/N ratio has long been used to identify the origin of lake sedimentary OM to provide valuable information about past life and paleoenvironmental changes in and around the lake ecosystem (Kaushal and Binford, 1999; Meyers, 2003; Wohlfarth et al., 2006; Choudhary et al., 2009b, 2013; Enters et al., 2010; Pędziszewska et al., 2015; Mahesh et al., 2017). A low C/N ratio, between 4 and 10, has been interpreted as a signal of enhanced aquatic phytoplankton productivity, whereas high C/N ratio values, 20 and greater, can be considered a result of the influx of terrestrial material (Meyers, 1994; Meyers and Lallier-Vergès, 1999). In-between values suggest a mixture of contributions from vascular and non-vascular plants (Meyers and Ishiwatari, 1993; Meyers, 1994; Meyers and Lallier-Vergès, 1999), in some cases, the domination of aquatic macrophytes (Fig. 1) (Herczeg et al., 2001; Lamb et al., 2004; Herzschuh et al., 2005; Panizzo et al., 2008; Pu et al., 2013).

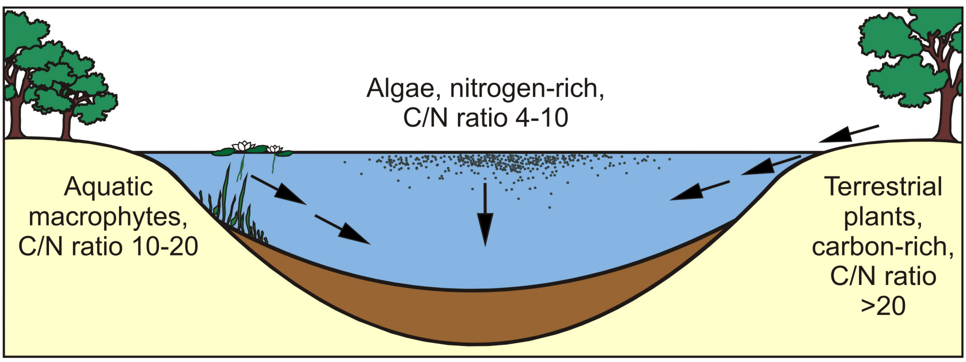

Figure 1. Origin of lake sediment OM and corresponding ranges of C/N ratio values.

Several authors (Meyers, 1990, 1994; Müller and Mathesius, 1999; Punning and Tõugu, 2000; Mackie et al., 2005; Brenner et al., 2006; Parplies et al., 2008) have challenged the source distinction abilities of the C/N ratio with measurements from contemporary algae, macrophytes, and vascular plants that are likely in the composition of studied lake sediment OM (Table 1).

Table 1. C/N ratios of different types of primary OM sources to lake sediments.

Material	C/N ratio	Reference
Algae		
Cladophora	8–9	Brenner et al. (2006)
Filamentous algae	11–16	Brenner et al. (2006)
Mixed plankton	8	Meyers (1990)
Aquatic macrophytes		
Hydrilla	12–15	Brenner et al. (2006)
Nuphar luteum	16	Punning and Tõugu (2000)
Nymphea alba	18	Mackie et al. (2005)
Potamogeton pectinatus	17	Herzschuh et al. (2005)
Terrestrial plants		
Calluna vulgaris	51	Mackie et al. (2005)
Corylus avellana	29	Müller and Mathesius (1999)
Pinus sp.	33	Parplies et al. (2008)
Quercus robur	37	Müller and Mathesius (1999)
Salix	38	Meyers (1994)
Sphagnum spp.	57	Mackie et al. (2005)
Tilia cordata (leaves)	50	Punning and Tõugu (2000)
White spruce (needles)	43	Meyers (1994)

These studies have confirmed that while there can be some degree of overlap, algal OM usually has a distinctly different biochemical composition from material produced by plants growing either on land or on the lake bottom. This gives great confidence in using the C/N ratio in paleo-studies to distinguish different sources of OM in the lake sediments.

Still, despite well-defined source distinctions, the C/N ratio can sometimes give misleading indications of bulk OM origin and, therefore, some caution must always be considered during the interpretation process.

First, lake sediment C/N ratios can be influenced by N availability (Brahney et al., 2006), whose limitation can result in the production of algal cell material, with C/N ratios higher than those commonly regarded as typical of planktonic OM (Talbot and Lærdal, 2000; Heikkilä et al., 2010). Based on a study by Talbot and Lærdal (2000) of Lake Victoria, East Africa, high C/N ratios (up to 25) have been ascribed to N limitation after visual inspection confirmed a dominant algal component. Therefore, it is also crucial to be familiar with the status of the lake to make correct interpretations.

Second, the C/N ratio can also vary due to the presence of inorganic N in the lake sediments. Problems arise, because most analyses measure the C and N contents that remain in sediment samples after the removal of carbonate C, but the residual N combines both, organic N and inorganic N (Meyers and Teranes, 2001). In most lake sediments, OM content is high (TOC ≥ 1), and C/N values are reliable (Meyers, 1997;

Meyers and Teranes, 2001). However, Meyers (1997) showed that in sediments that have extremely low OM content (TOC < 0.3%), the proportion of inorganic N can sometimes be a large fraction of the residual N, and so, C/N ratios could be artificially suppressed, which results in misleading source signatures (Sampei and Matsumoto, 2001). However, this type of uncertainty can be removed by correcting the C/N ratios for inorganic N content following the methods of Talbot (2001), in which the presence of inorganic N is easily detected from a cross-plot of TOC% *vs* TN%. If the trend line (regression line) intersects with the TN axis at a positive value and not through the origin, then some of the N is present in addition to what is associated with the organic C. The value of the excess N can be used to correct the measured C/N ratio such that it reflects only the organically bound N of the sediments (Talbot, 2001; Lücke and Brauer, 2004; Fahlgren, 2017).

As one might expect, OM is constantly being altered and reprocessed between the time of its origin and its burial on a lake bottom. Furthermore, once it reaches the bottom, OM continues to be subject to destruction and selective degradation; therefore, during early diagenesis, elemental compositions may be modified (Meyers and Ishiwatari, 1993; Brenner et al., 1999; Xu et al., 2006; Gälman et al., 2008). Due to the degradation, selectivity towards more N-rich components (Meyers, 1997; Gälman et al., 2008) or, in some cases, C-rich (Meyers and Takemura, 1997; Lamb et al., 2004), causes the C/N ratio to be subject to modification, being either artificially increased or decreased by the decomposition. However, most studies show that once sediments are buried, the C/N ratio remains relatively unaffected, therefore, reflecting the change in the OM input rather than representing a diagenetic artefact, which makes it a reliable OM source tracer in paleolimnological studies (Meyers and Ishiwatari, 1993; Meyers, 1994, 1997; Kaushal and Binford, 1999; Meyers and Teranes, 2001; Routh et al., 2004, 2007; Enters et al., 2006; Xu et al., 2006; Das et al., 2008; Parplies et al., 2008).

1.2 Application of C/N ratio in paleolimnological research

1.2.1 OM origin

The majority of paleolimnological studies have used the C/N ratio for its original purposes—to detect the origin of lake sedimentary OM and biota that produced it (Neumann et al., 2002; Lücke et al., 2003; Meyers, 2003; Sifeddine et al., 2004; Tiljander et al., 2006; Panizzo et al., 2008; Parplies et al., 2008; Henderson and Holmes, 2009; Morellón et al., 2009; Pérez et al., 2011; Pędziszewska et al., 2015; Mahesh et al., 2017). The C/N ratio, due to its well-defined source distinctions (Meyers and Ishiwatari, 1993; Meyers, 1994; Fig. 1), is commonly interpreted rather rigidly. Accordingly, low C/N ratios (< 10) indicate only algal productivity in the lake, while greater wash-in of terrestrial OM and/or aquatic macrophyte dominance is defined by higher C/N ratios (> 10). Regardless of the timeframe, whether results from recent sediment sequences or sequences from last glacial period are considered, the C/N ratio has shown to be an efficient indicator in every scenario, even for sediments in which only a small fraction of OM has been preserved. For example, Mahesh et al. (2017) found that for the last 36,000 yr, the C/N ratio in the sediments of Lake Sandy, east Antarctica, has been predominantly low, indicating that the productivity in the lake has been primarily autochthonous. Similar results were found by Pędziszewska et al. (2015) from Lake Suminko, northern Poland, and in a study by Meyers (2003) from Laurentian Great Lakes, North America, where lake sediment sequences, which covered the Holocene time period, had overall low C/N ratios, therefore pointing to an algal source of OM.

A study by Panizzo et al. (2008) of recent sediments from Lake Bujuku, Uganda, reconstructed last 140-yr record of C/N ratio variations, which indicated that lake productivity was largely dominated by aquatic macrophytes, and a reduction in the ratio, especially in the last 30 yr, was probably due to increasing contribution from phytoplankton.

The C/N ratio is often included in paleo-analysis routinely or sometimes seemingly as a "by-product"; therefore, its importance in the process of solving the study aims can be minimal. However, there are several cases in which identifying changes in the OM origin through the use of the C/N ratio is the main focus of the study (Hassan et al., 1997; Meyers and Takemura, 1997; Das et al., 2008; Choudhary et al., 2009b). Choudhary et al. (2009b) compared the bulk OM characteristics (including different OM sources) in contemporary sediments of three Kumaun Himalayan lakes, whereas Meyers and Takemura (1997) examined Quaternary changes in the delivery and accumulation of OM in sediments of Lake Biwa, Japan. Therefore, this type of C/N ratio interpretation confirms that basic background knowledge of the OM origin is still crucial in paleolimnological studies.

In multi-proxy studies (Wohlfarth et al., 2004; Dalton et al., 2005; Spooner et al., 2005; Briner et al., 2006; Magny et al., 2006), the above-mentioned straightforward approach of categorizing OM to algal and/or terrestrial origin seems to have undervalued the characterizing capability of the C/N ratio. For example, Magny et al. (2006) examined the late-glacial–Holocene transition in the sediments of Lake Lautrey, eastern France, and while their reconstructions were based on several analyses such as pollen, chironomid, OM, oxygen-isotope, mineralogy, magnetic susceptibility (MS), and inferred lake-level data at a high temporal resolution, the lake sediment C/N ratio was used for its basic indicative abilities. However, since OM contributions are likely influenced by factors, such as climate, local environment, vegetation development, and hydrological conditions, whose variations are all interconnected, more comprehensive associations can usually be drawn and will be discussed more broadly in next chapters of the thesis (see chapter 1.2.2 and 1.2.3).

1.2.2 Paleoclimate

Identifying the lake ecosystem responses to climate variability through the use of the C/N ratio can be, at times, complicated because they are driven by several simultaneous environmental factors that strongly influence the contribution of OM to the lake sediments (Meyers and Takemura, 1997) and, thus, the C/N ratio response to climate. Nevertheless, putting these difficulties aside, there are several studies in which the C/N ratio has reflected warmer/colder climate periods (Wagner et al., 2004; Axford et al., 2009), humidity conditions, i.e., rainfall patterns (Meyers, 2002; Pérez et al., 2011), and water-level changes (Roberts et al., 2001; Klemm et al., 2016). As a matter of fact, it is quite natural that due to versatile nature of lakes, some contradictions between different studies can be found. Therefore, various types of perspectives are discussed in the following sections.

Over the years, several studies have reconstructed the response of the C/N ratio to climate warming and/or cooling. Wagner et al. (2004) examined late Pleistocene and Holocene climatic history of Antarctica through the sediment core of Lake Terrasovoje and documented that a low C/N ratio indicated cooler climate, and a high C/N ratio indicated warmer climate. The study concluded that sparse vegetation in the lake surroundings during cold conditions caused a low input of terrestrial OM, and OM is mostly aquatically produced, while during warmer conditions, vegetation in the surrounding areas became denser and allowed more terrestrial plant material to enter the lake system. Almost identical results were observed by Striberger et al. (2012) in the early and mid-Holocene sediments of Lake Lögurinn, eastern Iceland. Furthermore, several other studies (Kashiwaya et al., 1997; Ji et al., 2005) support the above-mentioned statement and, thereby, confirm the close relationship between C/N ratio variations and climatic changes.

There are cases in which paleoenvironmental studies with various timeframes (from last 23,000 years to present) have just briefly suggested that climate cooling is probably reflected by low C/N ratios (Horiuchi et al., 2000; Balascio and Bradley, 2012; Massa et al., 2012), and warmer phases in the climate can be confirmed by higher C/N ratios (Mahesh et al., 2015; Sienkiewicz et al., 2017). However, some studies demonstrate opposite claims. Axford et al. (2009) argues that, over the past 2000 yr, the increase in allochthonous sediment input with high C/N ratio in the sediments of Lake Stora Viðarvatn, northeast Iceland, generally tracks cooling. A study of Parplies et al. (2008) from the sediments of Lake Sihailongwan, north-eastern China, covering the time span between 16,500–9500 cal yr BP suggests that a low C/N ratio, which indicates high phytoplankton productivity, reflects the warm climate optimum stage. This type of controversy clearly suggests that interaction between different environmental factors determines the C/N ratio. Therefore, each individual lake should be considered a unique case with its own behaviour and level of sensitivity. Moreover, the multi-proxy approach can be considered the main key in paleoenvironmental studies to reconstruct the true storyline of the lakes in the maze of their various reaction patterns.

Detecting past humidity conditions, e.g., rainfall, by using C/N ratio has been practiced in many studies (Meyers, 2002; Saarni et al., 2015; Selvaraj et al., 2016). Precipitation is an important transport medium, which has the ability to control nutrient availability in lakes. For example, Meyers (2002) examined Holocene sediment core records from Lake Seneca, New York, and found that high peaks in the C/N values indicated episodes of extreme precipitation. This was based on the argument that increased runoff from the surrounding areas would intensify the delivery of terrestrial OM into the lake under wetter conditions and would be the cause of higher C/N ratios, while unchanged lake sediment C/N ratios indicated normal hydrological conditions. A study by Saarni et al. (2015), which deals with the 3000-yr sediment record from Lake Kallio-Kourujärvi, central Finland, observed the same pattern of changes and supported the Meyers (2002) arguments.

However, there are studies which contradict previous assumptions (Meyers and Lallier-Vergès, 1999; Haberzettl et al., 2005; Pérez et al., 2011). A study by Meyers and Lallier-Vergès (1999) of tropical and temperate sedimentary records, ranging in age from 500,000–10,000 cal yr BP, found that wetter climate results in enhanced algal productivity in lakes (low C/N ratio). This was due to greater wash-in of soil nutrients from surrounding areas, which triggered algae growth and, in turn, overwhelmed the terrestrial C/N ratio signature.

The contradictions of all the above-mentioned studies clearly point out that to make correct assumptions, it is important to emphasize that lakes likely experience different patterns in reaction to environmental changes. Furthermore, because of natural variability of lakes, it is important not to over-interpret the lowest-amplitude variability in C/N ratio results, assuming that it is a signal for precipitation (Xu et al., 2006, 2007).

Previously discussed humidity conditions (e.g., wet-dry cycles) are one of the main drivers in affecting water-level changes in any type of water-body.

Meyers and Teranes (2001) showed that in Lake Victoria, East Africa, the C/N ratio decreased with increasing distance from the shore. This confirms that the land-derived proportion of sediment OM is gradually replaced with in-lake production in deeper waters, and sediment C/N ratios can be applied as an indicator of paleoshoreline proximity.

Interpretations between different studies on water-level changes sometimes contradict each other. Studies by Haberzettl et al. (2005, 2007) of lake-level changes in Laguna Potrok Aike, southern Patagonia, during the late-glacial and Holocene periods, revealed that within periods of low lake level, increased numbers of vascular plants were transported to the coring location, causing a rise in the C/N ratio. Meanwhile, during high-level periods, enhanced input of OM from planktonic and macrophytic origin took place, causing a lowering of the C/N ratio. This is also supported by Klemm et al. (2016) in which high C/N ratios during the last 7000 yr of the sediment core from Lake CH-12, north-central Siberia, were assumed to be related to low water levels, which caused high amounts of terrestrial material to reach the coring position at the centre of the lake, causing an elevated C/N ratio. However, many other studies have found contradicting results. For example, Lent et al. (1995) showed that in the late Holocene sediment record of Lake Devils, North Dakota, increased C/N ratio corresponded to a period of high lake level. Also, Roberts et al. (2001) stated that during the Holocene, the lake sediment C/N ratio of Lake Eski Acigöl, central Turkey, shifted from a high ratio to a low ratio (terrestrial to algal sources), due to lake shallowing.

There is no need to rule out any of these possibilities, because both scenarios can be correct, depending on the circumstances. For example, during water-level rise, some areas, surrounding the lake, naturally flood. Therefore, a lot of terrestrial material would enter the lake, causing a high C/N ratio. However, because of the floods, nutrient enrichment may also take place concurrently, which, in turn, can enhance in-lake production and cause a low C/N ratio. Therefore, as mentioned before, multi-proxy approach would be the key for determining which scenario characterizes the particular lake.

1.2.3 Human impact

While all the above-mentioned studies are clearly valuable and informative, detection of human-induced environmental changes has definitely been the most intriguing one, because it provides direct information of how our actions have changed the nature surrounding us. Regardless of the timeframe, the outcome of any type of disturbance to a pristine environment will usually impact the well-being of lakes. These signals are usually quite accurately stored in the lake sediment OM, where they can be restored using paleolimnological indicators such as the C/N ratio. Due to the drastic changes in land-use practices in the lake catchment areas e.g., rapid urbanization with agricultural run-off, sewage and industrial waste disposal, and the forest clearance, the C/N ratio has often been used to detect their irreversible effect on the trophic state of lakes.

Increasing cultural eutrophication often goes hand-in-hand with enhanced primary productivity (Brenner et al., 1999; Lüder et al., 2006; Choudhary et al., 2009a; Routh et al., 2009). Brenner et al. (1999) examined changes in the trophic state of Florida lakes and found that the C/N ratio displayed a generally consistent (sometimes abrupt) trend of decline towards the top of the sediment profiles. Lowering the C/N ratio reflected a shift in the source of accumulated OM, in which increasing contribution from algae relative to more abundant higher plants was prevalent due to human impact after ca. AD 1900.

However, several studies have noted that the first evidence for eutrophication is initially recorded by an increase in C/N ratio, suggesting an enhanced input of terrestrial OM (Jinglu et al., 2007; Liu et al., 2017). A study by Jinglu et al. (2007) observed human-induced changes in Lake Taihu, China, and in its catchment since the early to middle part of the 20th century. The study revealed that human action had left a clear C/N ratio record in the lake sediments. The first evidence of eutrophication in Lake Taihu was indicated by an increase in the C/N values in the early 1950s. This type of shift was related to the development and intensification of agricultural activity in the lake surroundings. Consequently, this caused soil erosion (rise in C/N ratio), which in turn, accelerated nutrient input into the lake. The addition of nutrients eventually caused elevated phytoplankton productivity, which was reflected in the lowering of the C/N ratio in the upper part of the sediment core.

While direct human activities have notably increased nutrient input rates to aquatic ecosystems within industrial era, several studies have described the prehistoric dimension of the human impact on lakes (Ekdahl et al., 2004; Russel et al., 2009; Thevenon et al., 2012; Taylor et al., 2013, 2017). Ekdahl et al. (2004) was able to define the prehistorical record of cultural eutrophication from Lake Crawford, Canada, for the past 1000 yr. It was noted that due to the native Iroquoian community settlement and their maize cultivation activities, significant and long-lasting changes in the lake ecosystem were documented. Meanwhile, in the pre-Iroquoian time, the C/N ratio was stable and fluctuated around 16, which has been considered typical for a lake in its natural state. However, the ratio started to decrease as the Iroquoian community settled. Therefore, the abrupt decrease in C/N ratio, typical of algal-derived OM, suggested that trophic state of the lake was irreversibly changed into a more productive one, which was triggered by enhanced nutrient supply linked to early human activity.

The response of the sediment C/N ratio to human activity around the lakes have even been successful in narrowing down specific actions, such as forest clearing (Kaushal and Binford, 1999; Routh et al., 2004, 2007; Enters et al., 2006; Tepper and Hyatt, 2011). Kaushal and Binford (1999) examined the relationship between C/N ratios of lake sediments and historical deforestation surrounding Lake Pleasant, USA. By combining data of known human activity with the results of the C/N ratio, it was demonstrated that a documented abrupt increase in sediment C/N ratio clearly reflected the time of deforestation in the area. Forest clearing apparently enhanced the delivery of both land-plant OM and land-derived sediments to the lake and was the cause of the episodic increase in C/N ratio.

1.3 Implication of the C/N ratio in the paleolimnological studies of the Baltic region

To date, lake sediment paleo-studies in the Baltic region have involved C/N ratio analysis rather moderately and have mainly focused on the basics—detecting whether lake sediment OM is derived from terrestrial or aquatic sources (Rajamäe et al., 1997; Frisk et al., 2004; Šeirienė et al., 2009; Stankevica et al., 2012; Terasmaa et al., 2013; Street-Perrott et al., 2018). For example, paleoenvironmental studies by Terasmaa et al. (2013) from the sediments of Lake Ķūži, central Latvia, and by Stankevica et al. (2012)

from the sediments of Lake Pilvelis, south-eastern Latvia, which both included Holocene sediments, have used C/N ratio only for these particular purposes. Furthermore, paleolimnological studies conducted in the Baltic region have either only involved the analysis of the C/N ratio for surface sediments or involved scarce sampling, making the interpretation quite general. A study by Šeirienė et al. (2009) used C/N ratio analysis in the sediments of two lakes, Lake Varėnis and Lake Baltys, to reconstruct the post-glacial paleoenvironmental changes in eastern Lithuania. Unfortunately, the sampling strategy was not detailed. From ~9.5-m long Lake Varėnis sediment core only five samples were analysed for C/N ratio, and from ~9-m long Lake Baltys sediment core only eight samples were analysed. Therefore, while the main trend of the C/N ratio can still be observed and the origin of the OM detected, it is likely that possible abrupt environmental and limnological changes may have been overlooked.

However, there are some exceptions where the C/N ratio has been used for broader purposes. Detecting the anthropogenic impact on the state of the lake ecosystem using the C/N ratio has proved its indicative ability (Punning and Tõugu, 2000; Punning et al., 2000). Punning and Tõugu (2000) used historical records of human-induced changes on the catchments of Lake Matsimäe, central Estonia, and Lake Viitna, northern Estonia, to interpret the obtained C/N ratio data. A remarkable C/N ratio reduction was correlated with accelerated use of the lake for recreational purposes, which, due to the increase in nutrients, quickly caused enhancement in the proportion of protein-rich plankton in the sediments, suggesting a change in the trophic state of the lake.

While human-induced lake eutrophication processes can be considered a relatively common case scenario, concurrently, natural nutrient enrichment can also take place. Vandel and Koff (2011) showed that in the sediments of Lake Verevi, south Estonia, a decline in the C/N ratio, taking place before historically recorded human-induced eutrophication processes, confirmed that natural eutrophication can be caused by changes in the climate, as the rise in annual temperatures can also increase primary production and induce internal phosphorus loading. Therefore, during the interpretation of the C/N ratio results, it is crucial to look at the bigger picture and consider all the possible factors that have the potential to affect the C/N ratio.

The C/N ratio has been included in many of the studies that have reconstructed water level changes (Punning and Tõugu, 2000; Punning et al., 2003, 2004a, 2004b; Röbler et al., 2011; Terasmaa, 2011). These studies, from Estonian and Latvian lakes, suggest that variations and the overall increase in the C/N ratio took place over the course of the transgression of the lake water level. The lake catchment becomes over-flooded, and the OM with higher C/N ratio is eroded and transported into the lake from its surroundings. Yet, in the study of Punning et al. (2004a), from the recent sediments of Lake Linajärv, northern Estonia, the decrease in the C/N ratio, which was caused by enriched planktonic matter, was also considered to be connected with water-level rise and littoral vegetation habitat movement to the shallower area.

Possibilities of using the C/N ratio as a paleoclimate proxy have been mentioned only briefly. Decrease in the C/N ratio, which indicates higher primary productivity, was associated with climate warming during the Holocene from the paleolimnological records of two lakes in northern Estonia (Punning et al., 2003).

Few studies have combined C/N ratio results in a non-traditional way and, therefore, perfectly demonstrate the versatility of the indicator. A study by Kruusement and Punning (2000) used the C/N ratio as a time marker for dating the Lake Ruusmäe, southern Estonia, sediment core. Based on the remembrance of local inhabitants in the study area, the peat mat in the littoral part of the lake was cut by musk rats, which afterwards, was seen floating on the lake and partly sinking to the bottom during the late 1970s. A rapid increase in the C/N ratio was detected from the lake sediment core, which suggested the abrupt addition of terrestrial OM (peat) into the lake. These two occurrences, the deposition of the peat and the high C/N ratio, were believed to be connected. Therefore, the abrupt rise in the C/N ratio was used to confirm the chronology of the study site.

A study by Punning and Leeben (2003) compared the sediment C/N ratio record of Lake Viitna Linajärv, northern Estonia, with long-term limnological monitoring data from the lake. This comparison demonstrated that all major changes taking place in the lake ecosystem, which were detected through monitoring in previous years, were also recorded by the changes in the sediment C/N ratio. The change in the trophic state of the lake towards eutrophic was indicated by the rapid decline in the C/N ratio, while the drop of the lake water volume and the resulting impact on the nutrient concentration and an influx of allochthonous OM were all expressed in the fluctuations of C/N ratio values, thereby demonstrating that different data can be connected to confirm each-other's accuracy.

2 Objectives

The versatile nature of the lake sediment C/N ratio makes its use as a single parameter in paleolimnological studies quite difficult. This fact indicates the need for other sediment paleo-proxies that can help to clarify any ambiguities in interpretation. Therefore, multi-proxy approach is the key to providing a holistic history of paleoenvironmental changes in the studied lake.

The main objective of the present thesis was to determine the utility of C/N ratio analysis in multi-proxy paleo-studies, in which different proxies have reacted to the same environmental changes, and determine the potential capability of the C/N ratio to reconstruct the development of lakes and their surrounding areas. The usefulness of the C/N ratio in resolving different aspects of the history of a lake is assessed in four studies. The other paleo-proxies used in these studies include sediment OM; mineral matter (MM) and carbonate matter (CM) content; grain size; MS data; biological indicators, such as fossil pollen grains, green algae, diatoms, plant macrofossils, and paleopigments; some geochemistry; and pollen-based temperature reconstructions.

The following specific aims were addressed:

1. to evaluate factors and processes affecting the response of the C/N ratio to extreme climate variability during the late-glacial and early Holocene period in the Baltic region (Paper I);
2. to determine the utility of the indication ability of the C/N ratio to reconstruct kettle-hole lake development (Paper II);
3. to assess the reaction of the lake ecosystem to extreme and millennia-long gradual human impact by using the C/N ratio (Papers III and IV).

3 Material and methods

3.1 Description of study sites

All study sites in the current thesis are formed or affected by the Weichselian glaciation and deglaciation (Zelčs and Markots, 2004; Zelčs et al., 2011; Kalm, 2012).

Three of the studied sites are located in Latvia; Lake Lielais Svētiņu in eastern Latvia, Lake Ķikuru in western Latvia, and Lake Trikātas in northern Latvia. One study site, Lake Kooraste Linajärv, is located in southern Estonia (Fig. 2; Table 2).

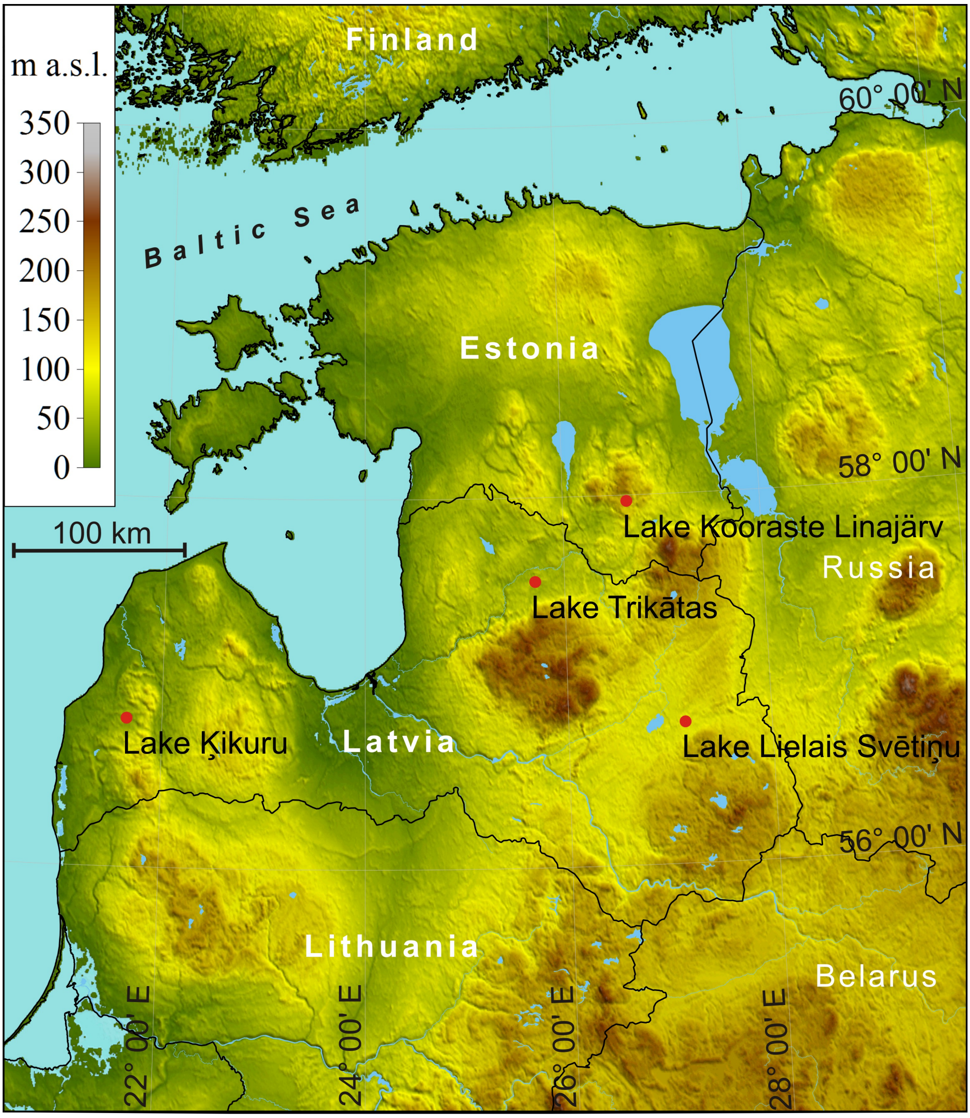

Figure 2. Location of the studied sites.

Table 2. Selected characteristics of the studied lakes.

Study site	**Lake Lielais Svētiņu**	**Lake Ķikuru**	**Lake Kooraste Linajärv**	**Lake Trikātas**
Core coordinates	56°45′33″N; 27°08′57″E	56°48′05″N; 21°39′39″E	57°57′47″N; 26°39′48″E	57°32′28″N; 25°42′52″E
Area (ha)	18.8	21.6	3.3	13
Altitude (m a.s.l.)	96.2	38.7	117	50
Water depth at coring site (m)	4.0	4.3	11.1	4.0
Lake trophy	Mesotrophic-dystrophic	Dystrophic-eutrophic	Hypertrophic	Eutrophic-hypertrophic
Hydrological regime	Minor inflow and outflow	Two inflows and one outflow	No inflow or outflow	One inflow and outflow

Lake Lielais Svētiņu is oblong-shaped (18.8 ha) and shallow (maximum depth 4.9 m) with minor inlets and outlets. The catchment area covers approximately 19.7 km^2. Based on the reconstruction of Latvian landscapes during the late-glacial period, Lake Lielais Svētiņu was a part of the large Lubāna proglacial lake (Fig. 1b in Amon et al., 2014). Lubāna's highest estimated shoreline was 108 m above the present sea level (a.s.l.) (Zelčs and Markots, 2004), and the study site was located in its eastern part.

Lake Ķikuru is round-shaped (21.6 ha) and shallow (water depth 4.3 m), with a thermokarstic origin and a flow-through hydrological regime (two inflows and one outflow). The surrounding landscape was shaped by deglaciation at approximately 18,000–15,000 cal yr BP (Zelčs and Markots, 2004).

Lake Kooraste Linajärv is a small (3.3 ha), deep (maximum depth 12 m), thermokarstic lake with no inflow or outflow. The catchment area is very small, only 3.7 ha, surrounding the lake. Lake Kooraste Linajärv was used for flax retting in the past and is nowadays classified as a hypertrophic lake.

Lake Trikātas is a small (13 ha) and shallow (water depth 4 m) with a flow-through hydrological regime (one inflow and outflow). Currently, the lake is highly polluted and is characterised as eutrophic/hypertrophic. The surrounding landscape comprises a mixture of cultivated land and pasture. A former distillery, dairy, and working primary school are located next to the lake.

3.2 Methods

3.2.1 Coring and sampling

All the study sites were cored during field work expedition in the winter. Sediment samples were obtained from the deeper part of the basin through the ice by using a Russian-type corer, 7.5 or 10 cm in diameter and 1 m long. The uppermost unconsolidated sediment of Lake Trikātas was sampled using a Willner-type sampler, while the upper part of unconsolidated sediments of Lake Kooraste Linajärv were recovered using freeze-core technology—applying a mixture of dry ice and ethanol as the freezing medium into a rectangular metal corer. The sediment cores were transformed to 1-m plastic semi-tubes, wrapped in plastic film, and delivered to the laboratory where they were kept in a cold room and sub-sampled afterwards.

3.2.2 Chronology

The chronology of Lake Lielais Svētiņu sediment core (Paper I) is based on thirteen ^{14}C dates, 12 determined by Accelerator Mass Spectrometry (AMS) from terrestrial plant macrofossils and 1 by conventional method from bulk gyttja (Table 3). For Lake Ķikuru (Paper II), twelve conventional ^{14}C dates were determined from bulk sediment samples and four AMS ^{14}C dates from terrestrial plant remains (Table 3). For Lake Kooraste Linajärv (Paper III), the chronology for the upper 60.3 cm was based on varve counts, for the lower part using three AMS ^{14}C dates from terrestrial macrofossils and wood remains (Table 3). The age-model of Lake Trikātas sediment sequence (Paper IV) was established by six AMS ^{14}C dates from terrestrial origin material and from the findings of microscopic volcanic ash shards—tephra of Askja AD 1875 eruption (Table 3).

Conventional ^{14}C dates of bulk gyttja were determined in the Department of Geology, Tallinn University of Technology (Papers I-II), AMS ^{14}C dates of plant remains and bulk sediments were conducted at Poznan Radiocarbon Laboratory, Poland (Papers I-IV) and the Scottish Universities Environmental Research Centre, United Kingdom (Paper IV).

Radiocarbon dates were converted to calendar years using the IntCal13 calibration dataset (Reimer et al., 2013) (Papers I–IV). The age-depth model was produced using various deposition models: OxCal 4.1 (Bronk Ramsey, 2008, 2009) in Paper I; Clam 2.2 (Blaauw, 2010) in Paper II; OxCal ver. 4.2.4 Bayesian P sequence (Bronk Ramsey, 2008, 2009; Bronk Ramsey and Lee, 2013) in Paper III; and Bacon 2.2 (Blaauw and Christen, 2011) in Paper IV. The radiocarbon ages were calibrated at 95.4% probability range, and the weighted averages before the present were used (cal yr BP, 0 = 1950 AD).

Table 3. Applied dating methods of the studied lakes and number of samples that were dated.

Study site	**Lake Lielais Svētiņu**	**Lake Ķikuru**	**Lake Kooraste Linajärv**	**Lake Trikātas**
Dating method	^{14}C	^{14}C	varves, ^{14}C	Tephra of Askja AD 1875, ^{14}C
Number of samples dated	13	16	3	6
Reference	Veski et al. (2012), Stivrins et al. (2015), Paper I	Paper II	Paper III	Stivrins et al. (2016a), Paper IV

3.2.3 Loss-on-ignition

The lithology of the lake sediments (Papers I–IV) was studied using the loss-on-ignition (LOI) method following Dean (1974) and Heiri et al. (2001). Sediment sub-samples were dried at 105 °C for 24 h or until the weight remained constant. After weighing, samples were combusted at 550 °C for 4 h, and the OM content was measured as LOI (Papers I–IV). The MM and C bound with CM was estimated as the difference between LOI at 950 °C (for 2 h) and LOI at 550 °C. The MM content was calculated by subtracting OM and CM from the total dry sample weight.

3.2.4 TOC, TN, TS, C/N ratio analysis

The FLASH 2000 CHNS-O Analyzer capability includes the determination of the amount (%) of C, hydrogen, N, sulphur, and oxygen contained in organic and inorganic chemical products, and in substances of different nature and origin. In the current study, the CHNS-O Analyzer was used for the measurements of TOC, TN, and total sulphur (TS). The determination of TOC and TN was performed through high-temperature combustion in a single sample analysis, whereas TS determination was performed separately.

Several steps of preparation must be carried out before proceeding with sample measurements. First, knowing the approximate content of OM (LOI 550 °C) is recommended to weigh the correct amount of the sample and calculate the amount of material in terms of what is needed for bypass, standards and reference analyses. Depending on the content of OM (high, 50–80% or low, 2–6%), 8 (high) to 15 (low) mg of freeze-dried finely homogenized powdered sediment was weighed into silver containers (5 × 9 mm). To remove inorganic C, the samples in silver capsules (resistant for acid) were initially pre-treated with a few drops of 4 M HCl and dried on a hotplate at 80 °C for 4 hours. Once dry, the capsules were left to cool and carefully wrapped with tweezers to form granules. Before the analysis, the silver containers were packed into tin containers (5 × 9 mm). The lower melting point of tin relative to silver helps to improve the efficiency of the combustion of the samples in the reaction tube. For TS analyses, 8 mg of vanadium pentoxide (V_2O_5) catalyst was added to the bypass, standard, and reference samples, and to each untreated sample in the tin container to ensure the complete conversion of sulphur to sulphur dioxide (SO_2).

A special reactor and adsorption filter were required for the measurements and were prepared following the FLASH 2000 Elemental Analyzer Operating Manual. Configuration "NCS" was used for the TOC, TN, and TS measurements. The reactor was filled with quartz wool, copper(II)oxide (CuO) wire, and electrolytic copper to complete the sample oxidation after combustion (Fig. 3), while the adsorption filter was filled with quartz wool and magnesium perchlorate ($Mg(ClO_4)_2$) to retain water. Analytical conditions, such as the flow intensity of helium and oxygen (140 mL min^{-1} and 250 mL min^{-1}, respectively) and cycle run time (650 s for TOC and TN analyses, 800 s for TS analyses) was set according to the Organic Elemental Analysis CookBook suggestions. High purity HiQ® helium and oxygen gases were used.

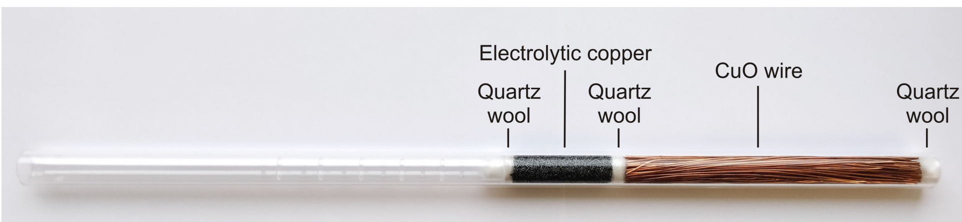

Figure 3. Filled reactor for TOC, TN, and TS measurements.

Before starting an analytical cycle, a leak test was conducted out to check system pneumatic tightness. For correct sample analysis, all pneumatic lines must be leak-free. If any type of leakage was identified, an additional leak check with Restek's Electronic Leak Detector was performed to locate it. Any leakage was fixed immediately.

For the measurements, cystine or BBOT ($C_{26}H_{26}N_2O_2S$) were used as a bypass and standard (both from ThermoFisher Scientific), and high organic sediment or the algae *Spirulina* were used as reference material (both from IVA Analysentechnik e. K). Contamination possibilities were eliminated by several blank runs before the measurements of the bypass, standard and reference granules. Prior the analysis of TS, the analyser signal sensitivity was amplified by 10-fold (Gain ×10) due to the low percentage of an element present in the samples.

At first, elemental peak positions were defined by measuring the bypass material. Then, measurements of the standard followed to generate the calibration curve. Finally, reference material with known elemental composition was measured to check the accuracy of the calibration curve. If necessary, the calibration curve was manually corrected by excluding/including any standard values to generate a better curve.

The samples were placed in the carousel of the elemental analyser, from which they were sequentially dropped into a continuous flow of helium carrier gas in a 900 °C furnace. To promote rapid and complete sample and capsule combustion, a pulse of oxygen gas was added. The product element measurement occurred inside the elemental analyser in a chromatographic column. Sample analyses were done in triplicate, and the average was calculated by selecting the two (in some cases all three) samples that had the most overlapping results. To discuss properties and/or changes in OM chemical structure, the C/N values are expressed as atomic ratios, mass ratios multiplied by 1.167 (the ratio of atomic weights of N and C) (Meyers and Teranes, 2001).

After the measurements of the study samples, analysis of reference material followed to ensure measurement accuracy.

3.2.5 Magnetic susceptibility and grain size analysis

The MS, expressed in SI units (Papers I, II) was measured with a Bartington MS2E high-resolution scanning sensor (Nowaczyk, 2001). The MS of the analysed sediment section was measured at 1-cm resolution on the cleaned sediment surface covered with thin plastic film.

The grain size of samples (Paper I) was analysed using a laser diffractometer Horiba Partica LA-950V2. Before analysis, the OM was removed with 30% H_2O_2 treatment at 90 °C. When the active reaction ended, the samples were washed with distilled water, centrifuged, and decanted three times to achieve a neutral environment. To avoid grain flocculation, a 0.1% solution of sodium pyrophosphate ($Na_4P_2O_7$) was added to the samples (Vaasma, 2008) and a built-in laser diffractometer ultrasonic probe was utilized. Samples were analysed in duplicate, and the mean value of the two measurements was used. Results in 93 particle size classes were represented as percentages and summarized in main granulometric classes following the Udden-Wentworth grain-size scale (Last, 2001).

3.2.6 Biostratigraphy and statistical analysis

The procedures and descriptions of the analytical methods of pollen, plant macrofossils, diatoms, green algae, fossil pigments, total phosphorus (TP), total iron, pollen inferred temperature reconstructions, and statistical analyses used in this thesis are fully described and referenced in the following papers (Table 4).

Table 4. Origin of paleo-proxies used in current thesis.

Study site	Lake Lielais Svētiņu	Lake Ķikuru	Lake Kooraste Linajärv	Lake Trikātas
Paleo-proxy	Pollen, plant macrofossils, green algae, fossil pigments, pollen inferred temperature reconstructions, statistical analysis	Pollen, plant macrofossils, diatoms, statistical analysis	Pollen, plant macrofossils, diatoms, green algae, TP, total iron; statistical analysis	Pollen, plant macrofossils, diatoms, geochemistry, statistical analysis
Reference	Veski et al. (2012, 2015), Stivrins et al. (2014, 2015), Amon et al. (2014), Paper I	Paper II	Paper III	Stivrins et al. (2016a, 2018), Paper IV

4 Results and discussion

4.1 C/N ratio response to climate change

Identifying lake ecosystem responses to climate changes can be complicated because usually they are driven by several simultaneous environmental factors. Unfortunately, this makes the interpretation process even more complex, and ambiguity between different studies is a common case scenario. As noted previously, the C/N ratio responses to climate vary—in several studies it is suggested that a low C/N ratio indicates cooler climate conditions and a high ratio indicates warmer conditions (Kashiwaya et al., 1997; Wagner et al., 2004; Ji et al., 2005; Striberger et al., 2012), while in other studies, it is stated that climate cooling can be tracked with a higher C/N ratio (Axford et al., 2009) and warming with a lower ratio (Parplies et al., 2008).

In light of the above-mentioned findings, we tried to reconstruct interactions between the C/N ratio and paleoclimate. For the study, the late-glacial and early Holocene period (14,600–10,700 cal yr BP) was chosen, as this time interval incorporates many abrupt and well-distinguishable climate shifts suitable for such kind of study. Furthermore, studying the late-glacial and early Holocene period will eliminate the human factor and, therefore, all the observed changes in the lake and its catchment area can be confidently identified as natural, climate-driven or environmentally driven.

Lake Lielais Svētiņu from eastern Latvia was chosen for this type of study because it includes complete record of Bølling–Allerød–Holocene sediments and already has a large set of paleo-proxies that has helped to shape our knowledge about climate and vegetation change in the eastern Baltic area (Amon et al., 2014; Veski et al., 2012, 2015; Stivrins et al., 2015, 2016b, 2018; Kisand et al., 2018). These paleo-proxies serve as great background information for present multi-proxy study, in which C/N ratio and grain size analysis are added to provide new insights, strengthen previously made conclusions, emphasize the interaction of different environmental factors, and help to assess how the aquatic environment reacted to extreme climate oscillations.

Statistical analyses were performed to explore the associations of the C/N ratio with multiple climatic, biological, and geochemical sediment variables. In hierarchical partitioning, the only outstanding biological variables were the log fossil pigment beta carotene (β-car) accumulation rate (AR) and log tree pollen AR, accounting for 25% and 16%, respectively, of the explained variance in the C/N ratio. Pollen-inferred summer temperature (T_{sum}, Veski et al., 2015), the only significant climate variable, accounts for 23% of the C/N ratio variance. Of the sediment characteristics, all three variables, mean grain size, MM content, and MS are significant, with MS having the highest explanatory power (15% of the total explained variance) (Fig. 4).

Correlations among the variables confirm a strong positive relationship between C/N ratio and T_{sum}, log tree pollen AR, log β-car AR, and mean grain size, whereas MM and MS are negatively correlated with C/N ratio (Table 5).

As confirmed by the statistical analyses, C/N ratio integrates the signal of several environmental variables and, thus, is closely related with climate change, vegetation development, and hydrological conditions, whose variations are all interconnected. Statistical analyses revealed that under a colder climate (lower T_{sum}), the C/N values are low, indicating that the OM has predominantly a phytoplankton origin and, under warmer conditions (higher T_{sum}), when there is more phytoplankton biomass in the lake (β-car), higher C/N values prevail, showing that vegetation biomass around the lake had also developed and increased the input of terrestrial OM into the lake sediment mixture.

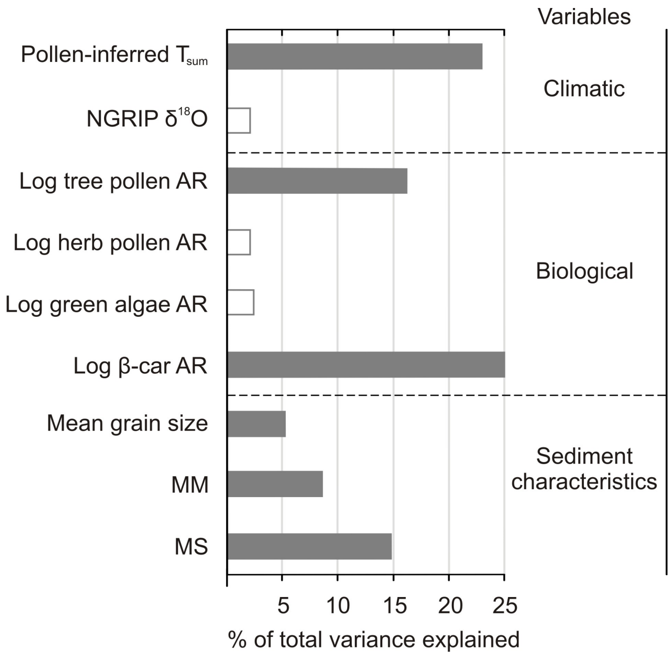

Figure 4. Results from hierarchical partitioning, explaining the C/N ratio in the sediment of Lake Lielais Svētiņu. The variables with significant individual contribution ($p < 0.05$) are indicated with grey bars.

Lake Lielais Svētiņu was released from the embrace of Scandinavian Ice Sheet at least by 14,560 cal yr BP (Veski et al., 2012) when, due to the global climate warming, the ice masses started to retreat. Deglaciated areas were, at first, flooded by a large proglacial lake Lubāna (Paper I, Fig. 1a; Zelčs and Markots, 2004) and although the North Greenland ice core (NGRIP) oxygen isotope ($\delta^{18}O$) data suggest an overall global warming (Fig. 5), the reconstructions of pollen-based T_{sum} (Fig. 5), winter temperatures (T_{win}; Veski et al., 2015), and vegetation history (Veski et al., 2012) of this area suggested that local climate was still rather cool due to the proximity of the ice margin. The overall low C/N ratio (Fig. 5), fluctuating around 8, indicates that during the start of the Bølling–Allerød interstadial (from 14,560 cal yr BP), the surroundings of the lake had virtually no vegetation, which could raise the C/N ratio if any kind of wash-in events had occurred. Instead, the low C/N ratio suggests that an aquatic environment existed and, even though lacustrine phytoplankton productivity was extremely low, as indicated by β-car and green algae AR (Fig. 5), it was the predominant source of OM to sediments in Lake Lielais Svētiņu.

*Table 5. Correlations (Pearson's product-moment correlation coefficients) among the variables. Significances are given as follows: *** P < 0.001, ** P < 0.01, * P < 0.05, n.s P > 0.05.*

	C/N ratio	**T_{sum}**	**NGRIP**	**log tree pollen AR**	**log herb pollen AR**	**log green algae AR**	**log β-car AR**	**Mean size**	**MM**
T_{sum}	0.76 ***								
NGRIP	0.27 *	0.16 n.s							
log tree pollen AR	0.69 ***	0.9 ***	0.32 **						
log herb pollen AR	0.22 n.s	0.34 **	−0.12 n.s	0.56 ***					
log green algae AR	0.29 *	0.36 **	0.06 n.s	0.55 ***	0.76 ***				
log β-car AR	0.76 ***	0.88 ***	0.24 *	0.87 ***	0.45 ***	0.54 ***			
Mean size	0.41 ***	0.37 ***	0.32 **	0.47 ***	0.38 ***	0.29 *	0.48 ***	1 ***	
MM	−0.49 ***	−0.51 ***	−0.58 ***	−0.44 ***	0.29 *	−0.05 n.s	−0.49 ***	−0.04 n.s	1 ***
MS	−0.67 ***	−0.8 ***	−0.18 n.s	−0.66 ***	−0.16 n.s	−0.24 *	−0.73 ***	−0.43 ***	0.45 ***

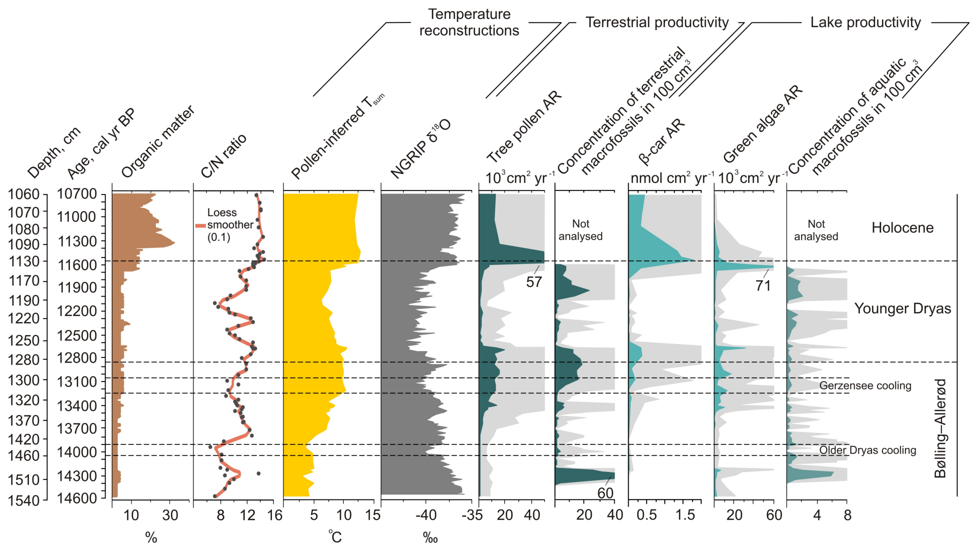

Figure 5. Lake Lielais Svētiņu sediment profiles of organic matter (%), C/N ratio, pollen-inferred summer temperature (T_{sum}, °C), North Greenland ice core $\delta^{18}O$ record (NGRIP $\delta^{18}O$, ‰) data (Rasmussen et al., 2006), AR (cm^2 yr^{-1}) of sum tree pollen, concentration of terrestrial macrofossils (in 100 cm^3 sediment), AR (cm^2 yr^{-1}) of beta carotene (β-car), sum green algae, and concentration of aquatic macrofossils (in 100 cm^3 sediment); grey areas show ten-fold multiplication.

The cold sub-event known as the Older Dryas (14,050–13,900 cal yr BP) was registered in both the NGRIP ice core data and in the Lake Lielais Svētiņu pollen-inferred T_{sum} curve (Fig. 5). In this period, the C/N ratio showed its all-time low values of around 7 (Fig. 5) and indicated that OM originated predominantly from phytoplankton. The cold climate interval is also well reflected in the paleobotanical record of Lake Lielais Svētiņu (Fig. 5; Veski et al., 2012).

The return to warmer climatic conditions was recorded by NGRIP $\delta^{18}O$ data and in the Lake Lielais Svētiņu pollen-inferred T_{sum} values after 13,900 cal yr BP (Fig. 5). The abrupt increase in C/N ratio to values as high as 13 (Fig. 5) reflects the idea that the lake OM, which was previously formed solely by aquatic production, has now received supplemental OM from terrestrial sources. Vegetation development in the surroundings of Lake Lielais Svētiņu would presumably favour nutrient-rich, allochthonous OM input into the lake (higher C/N ratio). Added nutrients enhanced phytoplankton growth, which is reflected by the rising values of green algae and β-car AR ca. 13,600 cal yr BP (Fig. 5). This type of concurrent effect, whereby a higher C/N ratio appears together with enhanced aquatic primary productivity, has been noted in several studies (Lücke et al., 2003; Watanabe et al., 2003; Wagner et al., 2004; Wohlfarth et al., 2004, 2006). For example, a study by Lücke et al. (2003) regarding late-glacial and Holocene lacustrine paleoproductivity and climatic change of Lake Holzmaar, Germany, stated that on millennial time-scales, the primary production of lacustrine algae strongly depends on the delivery of nutrients from the catchment and will be triggered when nutrient supply increases. This clearly supports the above-mentioned statements.

The overall Bølling–Allerød climate warming trend was once again interrupted by a cold sub-event known as the Gerzensee oscillation ca. 12,850 cal yr BP (Fig. 5). While this sub-event was noted in the NGRIP $\delta^{18}O$ data (Fig. 5), it was unnoticed in the pollen data of Lake Lielais Svētiņu (Veski et al., 2012) and nearby Lake Kurjanovas (Heikkilä et al., 2009). At that time, the C/N ratio of Lake Lielais Svētiņu had low values, around 9, indicating that lacustrine phytoplankton was the main source of OM during that period. After this cold sub-event, warmer conditions prevailed again, and the C/N ratio started to rise gradually (Fig. 5).

Following ca. 1100-yr-long cooling event (Younger Dryas, ca. 12,850–11,650 cal yr BP) left strong signals into the sediments of Lake Lielais Svētiņu (Fig. 5; Veski et al., 2012) and elsewhere in Latvia (Heikkilä et al., 2009). The landscape around Lake Lielais Svētiņu became dominated by treeless shrub tundra (Veski et al., 2012). The C/N ratio shows high variability where values around 13 are repeatedly followed by abrupt declines to a value of 7. Variations in MS and grain size throughout the Younger Dryas (Fig. 5; Paper I, Fig. 4) and a shift in OM content from overall low values of 4% up to 8% in the middle of the period confirms that the environment in and around the lake was far from being stable. The earliest findings of *Picea* stomata and needles (Heikkilä et al., 2009; Veski et al., 2012), and the amount of aquatic plant macrofossil remains (Fig. 5; Veski et al., 2012) in the eastern Baltic region within this cold period support the speculations of warming episodes. Possibilities of warmer windows inside this cold spell are also noted by several other authors (von Grafenstein et al., 1999; Isarin and Renssen, 1999; Schmidt et al., 2002; Schwark et al., 2002; Magny et al., 2006; Lane et al., 2013;). Furthermore, a recent study by Schenk et al. (2018) speculated about short-lived warming episodes in Europe at that time and concluded that summers during the Younger Dryas were short but warm, and possibly warm enough to favour in-lake and terrestrial production.

The Younger Dryas cooling event ended with an abrupt warming of the Holocene, which is clearly identified both regionally and locally (Fig. 5; Veski et al., 2012; Stivrins et al., 2015). Rapid ecosystem response to climate warming is corroborated by a high abundance of pollen, macrofossils, and paleopigments in Lake Lielais Svētiņu (Veski et al., 2012; Stivrins et al., 2018) and its nearby surroundings (Heikkilä et al., 2009). Abrupt increases in β-car and green algae AR (Fig. 5) also point to a rapid enhancement in aquatic productivity. However, a gradual increase in the C/N ratio to a value around 14 (Fig. 5) had already commenced by the end of the Younger Dryas ca. 11,900 cal yr BP, which may indicate that environmental conditions were suitable for supporting the growth of terrestrial vegetation and aquatic life forms even earlier than suggested.

Rapid climate oscillations in the eastern Baltic area throughout late-glacial and early Holocene (14,600–10,700 cal yr BP) can be clearly distinguished with the results of C/N ratio analyses. Higher ratios characterized warmer climatic periods and lower ratios characterized colder ones. Furthermore, the C/N ratio data of Lake Lielais Svētiņu sediments detected several climate events that the other proxies or other studies have failed to identify. For example, a paleoclimate study of Kylander et al. (2013) from the late-glacial sediment sequence of Lake Hässeldala Port, southern Sweden, detected no clear geochemical signal from the Older Dryas. Furthermore, a cold sub-event known as the Gerzensee oscillation (ca. 12,850 cal yr BP) was unnoticed in pollen data of our study lake (Veski et al., 2012) and nearby Lake Kurjanovas (Heikkilä et al., 2009). However, the signal of low C/N ratio during these time periods detected the cooling events as well as pin-pointed other major climate oscillations noted in the NGRIP $\delta^{18}O$ data (Fig. 5).

As in Lake Lielais Svētiņu, similar associations of the C/N ratio with climate have been found (Kashiwaya et al., 1997; Wagner et al., 2004; Ji et al., 2005; Striberger et al., 2012). Kashiwaya et al. (1997), who looked at much a broader scale, studied orbital signals in the physical and chemical properties of bottom sediments from Lake Baikal, a sediment core about 100 m long, spanning about 400,000 yr, and found a comparatively higher C/N ratio during the interglacial periods and a lower C/N ratio during the glacial periods. Wagner et al. (2004) examined late Pleistocene and Holocene climatic history of Antarctica through the sediment core of Lake Terrasovoje and also documented low C/N ratio caused by the sparse vegetation in the lake surroundings during cold conditions when input of allochthonous OM was low and most of the OM was aquatically produced, whereas higher C/N ratios prevailed during warmer periods, when vegetation in the surrounding areas became denser and allowed more terrestrial plant material to enter the lake system. Furthermore, Ji et al. (2005), who studied paleoclimate changes over the last 18,000 yr in the area around Qinghai Lake, China, found that warmer and more humid climatic phases are reflected in higher C/N ratios, whereas colder and drier phases are characterized by the decrease of this proxy. On the other hand, Parplies et al. (2008), who examined sediments from Lake Sihailongwan, north-eastern China, covering the time span between 16,500–9,500 cal yr BP, suggested that the low C/N ratio, which indicates high autochthonous productivity, reflects warm climate stages. Axford et al. (2009) argued that over the past 2000 yr, increase in allochthonous sediment input with high C/N ratio in the sediments of Lake Stora Viðarvatn, northeast Iceland, generally tracks cooling phases. Although Parplies et al. (2008) obtained contradictory results, it is possible that the relationship between the C/N ratio and the change in climate found for Lake Lielais Svētiņu is valid under cold conditions when terrestrial vegetation is not well-developed and the overall OM content in the environment is low, e.g., for late-glacial or arctic areas. Comparing the sediment TOC values of different studies revealed that when associations of the C/N ratio with climate change similar to that for Lake Lielais Svētiņu were found, the TOC concentrations were comparably very low, around 0.2–0.6%, as in Lake Lielais Svētiņu (Paper I, Fig. 2). Parplies et al. (2008), who also studied the late-glacial period but found opposite conclusions, reported much higher TOC values, 3–11%, in the sediments of the analysed Chinese lake.

According to the study of Lake Lielais Svētiņu, we can conclude that the C/N ratio is a good indicator of paleoclimate changes, at least for late-glacial cold conditions, when the OM content in sediments is low. However, further research is needed to test the applicability of the C/N ratio as a paleoclimate proxy in different climatic and environmental conditions.

4.2 Application of the C/N ratio in reconstructing kettle-hole lake development

Continuous climate warming forced the ice sheet to completely retreat from the Baltic areas; however, a part of its legacy, in the form of blocks of dead-ice in the ground, remained. Further melting of these buried ice-blocks created thermokarst depressions, some of which formed into lakes (also known as kettle-hole lakes).

We analysed thermokarst features in Lake Ķikuru (Paper II), western Latvia, by means of a multi-proxy approach (pollen, non-pollen palynomorphs, plant macrofossils, diatoms, LOI, MS, C/N ratio, C AR, and radiocarbon dating). Due to the scarcity of paleo-data in that particular region, Lake Ķikuru was at first chosen as a possible study site for reconstructing long-term farming activities. However, during coring, the basal peat layer was discovered, which led to the assumption that it might be a lake with a thermokarst background. While its discovery was a matter of "blind luck" and its identification, at first, only a speculation, the thermokarst origin was evident from the topography map of the studied site. Lake Ķikuru lies in the middle of a ridge that was most likely originally one ridge and not split into two parts, which is the current topography (Paper II, Fig. 2). The ridge is 2.8 km long and 0.6 km wide and, according to its shape, is reminiscent of a drumlin that has been split into two parts by the lake (Paper II, Fig. 2). The surrounding undulating landscape was shaped by the deglaciation of the Apriķi glacial tongue approximately 18,000–15,000 cal yr BP (Zelčs and Markots, 2004; Saks et al., 2011). Saks et al. (2011) imply that a glacial ice tongue was active in the study area until approximately 15,000 cal yr BP, therefore, we can assume that deglaciation took place since then.

It is commonly assumed that the majority of Central and Northern European dead or buried ice-blocks melted during the warmest phase of the late-glacial period and in the early Holocene (Stančikaitė et al., 2009; Błaszkiewicz, 2011; Gałka and Sznel, 2013; Michczyńska et al., 2013; Terasmaa et al., 2013; Błaszkiewicz et al., 2015; Słowiński et al., 2015). However, the study of Lake Ķikuru (Paper II) showed that a block of dead-ice was preserved in the ground until the Holocene Thermal Maximum (8500–7400 cal yr BP). Given that thermokarst arises when the mean summer air temperature gradually increases to a value above the present-day temperature, we must assume that the local conditions must have been exceptional to secure ice-block from the meltdown for so long.

Lake Ķikuru can be considered a "textbook" example of a kettle-hole lake formation (Paper II, Fig. 7), where a basal-peat layer occurs before gyttja accumulation (Maizels, 1977; Fig. 6). Our study shows that after deglaciation, the remaining dead ice started to melt beneath a cover of till and glacial outwash. Soil, which rests directly on till, includes terrestrial plant macrofossils (e.g., undefined wood, Paper II, Table 2) and probably represents the floor of a forest, which began to grow in glacially melted sediment on top of buried ice-block (mixed broadleaved and conifer tree composition, Paper II, Fig. 7). Succession from soil to peat in the Lake Ķikuru basin during 8400–8000 cal yr PB infers the initiation of melting of the subsurface ice-block, which increased the moisture conditions of above-lying soil and created a fen-type plant community, characteristic to wetter site conditions (e.g. *Carex pseudocyperus*, *Typha* sp., and *Nymphaea alba*) (Paper II, Table 2; Fig. 6). A thin peat layer accumulated, and due to the continuous meltdown of the ice-block, it gradually lowered to the bottom of the kettle-hole (Paper II, Fig. 7). Around 8000 cal yr BP with the continuous deepening of the kettle-hole, the coarse-detritus gyttja began to accumulate, which indicated that lake had been formed. The transition to the lake was confirmed with the presence of diatoms, whose composition was dominated by *Stephanodiscus parvus* and other eutrophic planktonic diatoms, suggesting a nutrient-rich environment. Eutrophic conditions characterized Lake Ķikuru for only a relatively brief period, ca. 8000 to 7400 cal yr BP, after which an increase in diatoms, which do not tolerate a high-nutrient content, took place, and the lake underwent rapid oligotrophication. Furthermore, findings of fish remains since 7820 cal yr BP were also a clear indication of the existence of the lacustrine environment (Fig. 6).

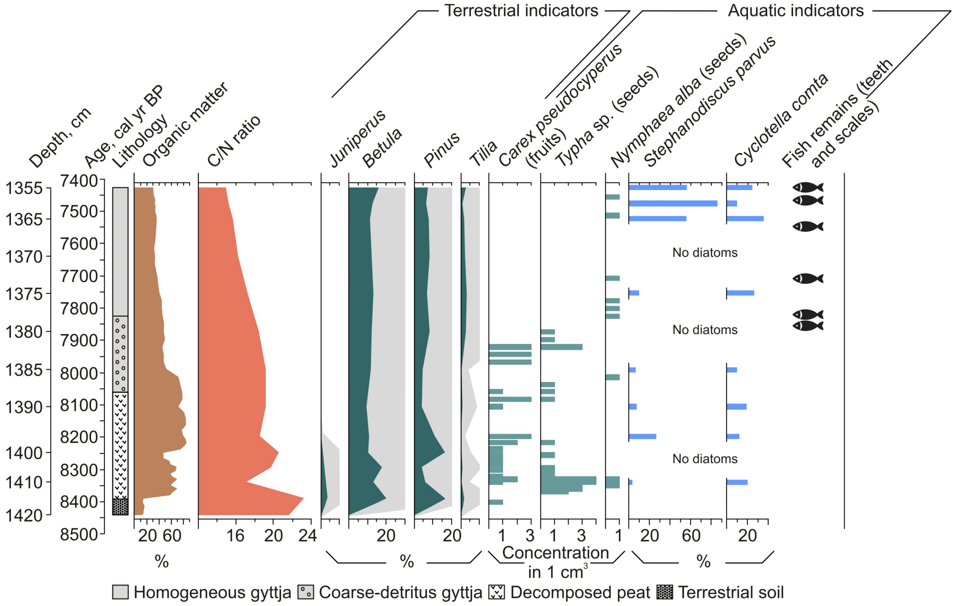

Figure 6. Lake Ķikuru sediment profiles of lithology, organic matter (%), C/N ratio, percentages of selected tree pollen, concentration of aquatic macroremains (in 1 cm^3), percentages of selected diatom taxa, and detected fish remains; grey areas show ten-fold multiplication.

The process of the ice-block meltdown, peat accumulation, and afterward transition into a lake was confirmed in visual and analytical analyses of the sediment sequence, which confirmed that there were no abrupt changes in the lithology, therefore eliminating the presence of a possible hiatus.

The highest C/N ratio values (from 23 to 19) combined with undefined wood material, decayed wood periderm, and other terrestrial macrofossils (Paper II, Fig. 6; Fig. 6) were detected at the base of the core in the succession from soil to peat sequence during 8400–8000 cal yr BP (Fig. 6). The documented high C/N ratio in these bottom layers of the core were expected, confirming the presence of material with C-rich tissues, e.g., material derived from allochthonous sources such as trees and peat (Meyers et al., 1984; Meyers and Ishiwatari, 1993). Moreover, the C/N ratio results from this sequence are also roughly comparable to the reported values for permafrost soil and buried peat samples from the Siberian Yedoma region (Weiss et al., 2016) and peat originating from kettle-hole formations in north-central Poland from Dobrzyń Lake District (Karasiewicz et al., 2017). Results of pollen and non-pollen palynomorph analyses showed that parasitic fungal spores of *Kretzschmaria deusta* were present in the bottommost soil layer (Paper II, Fig. 5a). These spores are evidence of the existence of broadleaf trees, *Fagus* and/or *Tilia*, which have been growing in Latvia since 8500 cal yr BP (Latałowa et al., 2013; van Geel et al., 2013). This provides additional evidence that we are dealing with early-Holocene terrestrial material. In addition, the presence of macrofossils such as *Viola palustris*, *Moehringia trinervia*, *Stachys palustris*, and

Urtica dioica in a soil layer suggest a wet meadow community type at the coring site at that time (Ellenberg et al., 1991; Zarzycki et al., 2002; Paper II, Fig. 6).

The transition from soil to peat (8400–8000 cal yr BP) to coarse-detritus gyttja (8000–7850 cal yr BP) implies further melting of the buried ice-block and, eventually, the formation of a kettle-hole depression and development into a lake. The diatom stratigraphy supports the formation of a lake depression with relatively deep water at the onset of the Holocene Thermal Maximum (8000 cal yr PB) (Paper II, Fig. 5b), followed by the findings of fish remains since about 7820 cal yr BP, as stated previously. The deepening of the kettle-hole depression that concurrently was filled with water and organic sediments during 8000–7400 cal yr BP is also reflected by an overall gradual decreasing trend in the C/N ratio (Fig. 6), suggesting that the OM originating from lacustrine sources (low C/N ratio) grew more important over time. At the end of the studied period (ca. 7400 cal yr BP), the C/N ratio had been reduced to 15, indicating the development of the kettle-hole into a lake, where the sediment OM is a mixture of both vascular and non-vascular plants (Meyers and Ishiwatari, 1993; Meyers, 1994; Meyers and Lallier-Vergès, 1999).

The results of the Lake Ķikuru sediment analyses confirm that ice-block melting was not synchronous over central and eastern Europe. Several different factors may have played role in determining the ice-block meltdown speed and OM sedimentation, which may include hydrology, permafrost, presence of vegetation, local geomorphology, and thickness of the mineral cover. Concerning Lake Ķikuru, the most probable case scenario was that the local geomorphological conditions were exceptional, securing the ice-block from the surficial landscape transformation and environmental processes. As noted previously, Lake Ķikuru lies in the middle of a ridge that was, in the past, most likely one ridge. There is almost a 13-m difference from the highest point of the ridge to the lake water level; therefore, we can assume that the overlay material must have been of a similar thickness, at least. The basal material in the core suggests till as the overlying material over the buried ice-block. Till, consisting mainly of clay and silt fractions, has poor thermal conductivity (Östrem, 1959; Farouki, 1981; Schomacker, 2008), which in combination with the lower geothermal heat in the study area (Kalm et al., 2011) and overall heat-shielding effects of the thick sediment cover above, may have prolonged the survival of buried ice-block.

4.3 Extreme *vs* millennia long gradual human impact on lake ecosystems

Lake eutrophication takes place due to excessive nutrient input, which is usually caused by drastic changes in land-use practices in the lake catchment areas, e.g., agricultural run-off and rapid urbanization with sewage and industrial waste disposal. Added nutrients start to stimulate algae growth, which in turn, begins the conversion of the pristine environment into a eutrophic one. Concurrently with previous descriptions, natural lake eutrophication can also occur. These processes have been observed in newly deglaciated landscapes where the development of the soils and vegetation were the main cause of lake nutrient enrichment (Engstrom et al., 2000; Battarbee and Bennion, 2011). However, direct human activity has notably accelerated nutrient input rates to aquatic ecosystems. Due to this, a large number of freshwater lakes experience a wide range of responses, such as algal blooms, oxygen depletion, loss of biodiversity, and reduced light transparency. Finding the "natural" or "baseline" state enables the setting of reference conditions for lakes, i.e., the conditions expected with only minimal human impact on water bodies (European Union, 2000; Heinsalu and Alliksaar, 2009). The pre-disturbed ecological conditions of lakes allow the determination of the current ecological status of the lake ecosystem, the assessment of the amplitude of environmental change, and the identification of the causes of change, as well as comparison of the course of present and further changes taking place in the lake (Bennion and Battarbee, 2007).

A sedimentary C/N ratio around 14–16 is considered typical for a lake in its natural state, consisting of an equal mixture of algal and vascular plant OM (Meyers and Ishiwatari, 1993; Meyers, 1994; Brenner et al., 1999; Meyers and Lallier-Vergès, 1999; Choudhary et al., 2009a). Paleolimnology can play a crucial role in defining the timing and extent of human impact and its progressive influences on the nutrient status of lakes (Battarbee and Bennion, 2011).

The distinct relationship between the composition of deposited OM and the history of environmental changes in the lake ecosystem and in the surrounding areas is reconstructed from the sediments of Lake Kooraste Linajärv, southern Estonia (Paper III) and from Lake Trikātas, northern Latvia (Paper IV). Lake Kooraste Linajärv was chosen for this study as it has a known history of intense flax retting. According to the remembrance of the local inhabitants, the Lake Kooraste Linajärv was used for flax retting until AD 1955 (Ott pers. comm.), when retting was banned. Also, the word "lina" in the lake name means flax in Estonian, thus, referring to its use for retting purposes. Lake Trikatas is surrounded by many historic buildings that indicate an early human presence—the ruins of Trikātas castle and former manor (Fig. 1 in Stivrins et al., 2016a). The earliest evidence of human presence is a brooch from the 3rd century AD. Furthermore, previous land-use reconstructions from 1200 BC–present (Stivrins et al., 2016a) have created good background information to evaluate the long-term anthropogenic land-use impact on the lake ecosystem.

Nevertheless, contemporary conditions of Lake Kooraste Linajärv and Lake Trikatas also suggest that these lakes have experienced some type of nutrient enrichment in their past. This is clearly reflected by their current trophic state—both lakes are classified as eutrophic/hypertrophic.

Before AD 1780, the sediment C/N ratio of Lake Kooraste Linajärv varied between 14 and 16 (Fig. 7), thus indicating a mixed composition of OM. This natural, unaltered state is supported by high and stable OM, and low MM values in the sediments, suggesting a forested catchment with stabilized vegetation and minimal discharge from the surrounding slopes of the lake (Figs. 7, 8a). A well-illuminated water column, low nutrient level, and overall oligotrophic environment was indicated by the taxonomic composition of the algal community (Paper III, Figs. 6, 7). As tree pollen constitutes about 85% of the total trees/terrestrial herbs relationship (Fig. 7), its presence suggests that the landscape around the study area was mainly dominated by forest. However, the presence of cereal pollen (e.g., *Secale* and *Triticum*), which were documented throughout the studied sediment sequence from AD 1200 (Fig. 7), infers that crop cultivation already occurred in the study area at that time but not necessarily in the direct vicinity of the lake. As a matter of fact, cultivation of *Secale* started around AD 500–600 throughout Estonia (Poska et al., 2004). This suggests that while the human activity was present in the surrounding areas, its impact was evidently low and, for that reason, Lake Kooraste Linajärv showed no response to it. Furthermore, the first macroscopic fragments and pollen grains of *Linum usitatissimum* occur in the

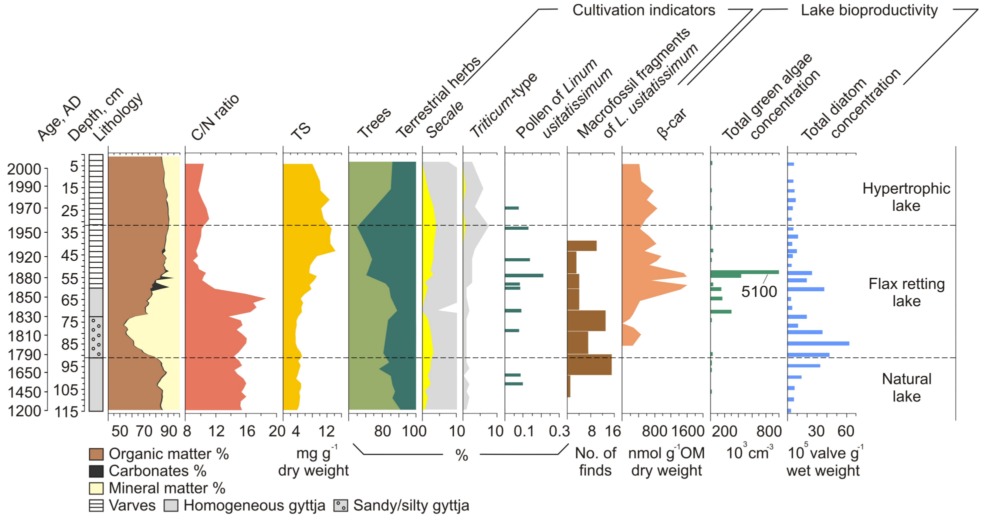

Figure 7. Lake Kooraste Linajärv sediment profiles of lithology, organic matter (%), C/N ratio, TS (mg g^{-1}), percentages of selected pollen types, number of macrofossil finds of Linum usitatissimum capsule fragments, fossil pigment β-car concentration (nmol g^{-1}), total green algae concentration (10^3 cm^{-3}) and total diatom concentration (10^5 valves g^1); grey areas show ten-fold multiplication.

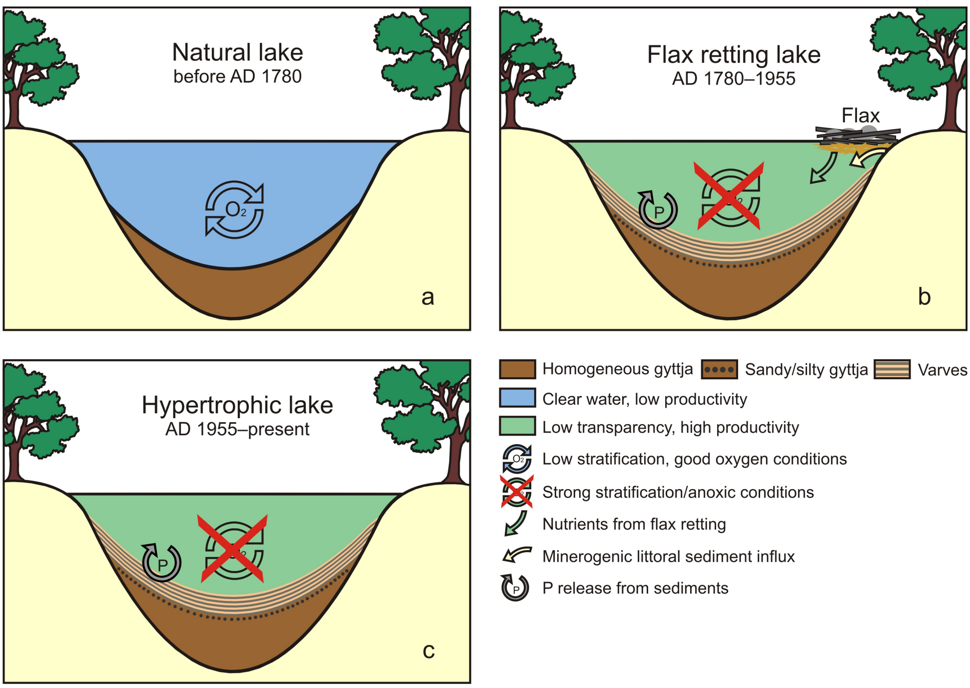

Figure 8. Illustrations of subsequent changes in Lake Kooraste Linajärv, as described in the text.

sediments dated to the beginning of the 16th century AD and suggest that flax retting have been present far back into the lake's history (Fig. 7). However, the early retting seemed to have been chaotic and modest with no far-reaching consequences on the ecological conditions of the lake.

Although the Lake Trikātas sediment core covers a remarkably longer time interval (1200 BC–present) than the Lake Kooraste Linajärv core (AD 1200–present), they both show the presence of an unaltered environment in the lowermost part of the core, but changes in Lake Trikātas occurred much earlier than in the case of Lake Kooraste Linajärv. Before ca. 500 BC (Bronze Age), the sediment C/N ratio of Lake Trikātas remained on a constant level around 16, suggesting that lake was in its natural state, with sediment OM originating from both vascular and non-vascular plants (Meyers et al., 1984; Meyers and Ishiwatari, 1993; Meyers and Lallier-Vergès, 1999). Stable OM content (Fig. 9) and indications of negligible soil erosion, e.g., the occurrence of low calcium (Ca) (Fig. 9) and titanium (Paper IV, Fig. 4) in the lowermost part of the Lake Trikātas sediment core, confirms that there was little evidence for human interference in the surrounding landscape before that time. Few sporadic finds of aquatic macroremains in the lowermost part of the Lake Trikātas sediments (Fig. 9; Fig. 5, in Stivrins et al., 2016a) combined with a C/N ratio of 16 allows us to speculate that some of the OM probably originated from aquatic macrophytes, as similar values of C/N ratio from aquatic plant remains have been reported in several other studies (Lamb et al., 2004; Panizzo et al., 2008; Pu et al., 2013). Therefore, it is speculated that the natural state of Lake Trikātas could possibly be a complex of oligo-mesotrophic conditions.

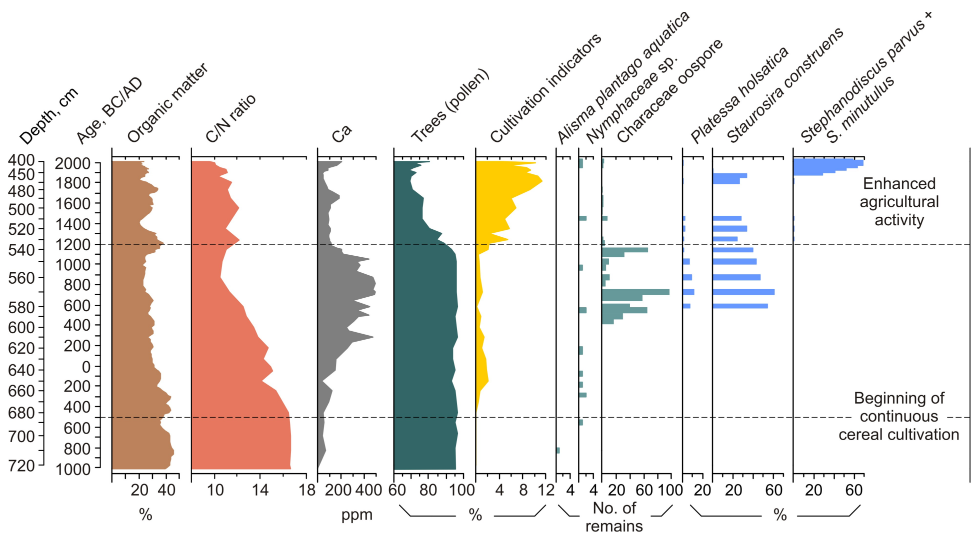

Figure 9. Lake Trikātas sediment profiles of organic matter (%), C/N ratio, concentration of calcium (Ca, parts per million), pollen percentages of trees and cultivation indicators, number of macrofossil finds per sample and percentage values of selected diatom taxa.

First, but modest human activity was starting to take place in the surroundings of Lake Trikātas after 500 BC when the first cereal grains of *Avena-Triticum* and *Hordeum* were recorded (from 500 and 100 BC, respectively) (Fig. 4, in Stivrins et al., 2016a). This indicated the beginning of cereal cultivation (Fig. 9). The C/N ratio immediately started to decrease ca. 500 BC (Fig. 9), which is in contrast with the findings of Lake Kooraste

Linajärv, in which the C/N ratio showed no response to cereal pollen nor to earliest findings of *Linum usitatissimum* fragments in the sediments. The different ecosystem reaction of these lakes may be due to the study site location, its specific peculiarities, and pollen distribution abilities. As the highest elevated lake in the region, with a particularly small catchment area and no inflow/outflow, Lake Kooraste Linajärv eliminates the possibilities of major discharges from the surrounding areas. However, Lake Trikātas is quite the opposite; it is located in a valley, has inflow/outflow, and therefore, is open to material transportation from the catchment area to the lake. In addition, examination of the maps from the Estonian Historical Archives of parishes in the Kooraste region from AD 1685 and a plan of Karste Manor, originating from AD 1903 (Fig. 5, in Alliksaar and Heinsalu, 2012), did not show any arable fields around the Lake Kooraste Linajärv, and the direct surroundings of the lake have always been covered with forests, with the nearest fields more than 300 m away. Therefore, the presence of cereal *Secale* pollen in the Lake Kooraste Linajärv sediments (Fig. 7) was most likely caused by wind-transport from the surroundings, without reflecting any direct consequences from the lake ecosystem due to land-use practices. Furthermore, *Secale* pollen is the most common cereal pollen in Estonian pollen diagrams (Poska et al., 2004), and its good distribution abilities allow us to claim that its number in Lake Kooraste Linajärv sediment is nothing extraordinary. In the case of Lake Trikātas sediments, concurrent reaction of the C/N ratio to the first cereal grains most probably indicates that while the intensity of cereal cultivation was low and human-derived changes in the local landscape were relatively minor, agricultural practices were taking place in the lake catchment area, in the immediate vicinity of the water body, and were powerful enough to affect the lake and change its sediment OM composition.

The continual reduction of the Lake Trikātas sediment C/N ratio throughout 500 BC–AD 800 (Early to Middle Iron Age) (Fig. 9) reflected a shift in the source of OM, in which contribution from algae relative to aquatic macrophytes/terrestrial plants started to rise. The course of these changes is controversial because, at the same time, dominating periphytic diatoms such as *Sellaphora vitabunda* and *Platessa holsatica* still suggest a shallow hard-water lake with oligo-/mesotrophic conditions (Fig. 9; Stivrins et al., 2018), while the pre-dominance of *Staurosira construens* and S. *venter* suggests unstable conditions and a higher turbidity level (Fig. 9; Stivrins et al., 2018). This type of simultaneous dominance of species that describe different environments could just be a result of the land-derived nutrient addition, which first initiated the growth of diatom species with tolerance for low nutrient concentrations, but afterwards, was the cause of a switch to a more hypertrophic species. During ca. AD 800–1200 the C/N ratio had plateaued at low values around 11 (Fig. 9). Concurrently, the subsequent decline of *Picea* pollen from 40% to 15% (Fig. 4, in Stivrins et al., 2016a) may reflect regional forest clearance. This could favour erosion within the lake catchment and could add nutrients into the lake system (Fig. 9), which, in turn, could cause enhanced aquatic productivity in the lake (Litt et al., 2003), resulting in lower C/N ratios (Enters et al., 2006). The peaking of Ca (Fig. 9), an indicator of soil erosion, supports the overall lake catchment instability. This scenario was the probable case for green macro-algae *Chara* spp. domination (range of Characeae species), which is usually considered to be nutrient-sensitive, but our study indicates that land-use with soil erosion most likely initiated *Chara* spp. growth, in the first place. Significant negative correlation between the C/N ratio and *Chara* spp. domination (Paper IV, Fig. 6) confirms this statement. Furthermore, in the current study, sediment C/N ratio results are comparable to previously reported C/N values for *Chara* species and *Chara* spp.-dominated sediment records, which fluctuate between 6.5–19.0 and indicate that the *Chara* species may grow in a wide range of nutrient concentrations (Song et al., 2012; Carlos et al., 2013).

While Lake Trikātas experienced the continuous decline in the C/N ratio, reflecting the cumulative effect of anthropogenic land-use (Fig. 9), Lake Kooraste Linajärv experienced an extremely abrupt reaction. Significant changes in the composition of Lake Kooraste Linajärv sediments started to occur at the end of the 18th century, where a distinct increase in the MM content occurred from around 12% up to 47% (Fig. 7). Considering that the lake has a closed water system without any inflow and outflow, this high level of MM may originate from the littoral area. Furthermore, Lake Kooraste Linajärv is fairly deep, while for flax retting, much shallower lakes were usually chosen. Therefore, to create better conditions, the lake littoral area was probably reworked, which, in turn, raised the MM content in the lake sediments. The intensive flax retting process is detected by changes in the C/N ratio (Fig. 7). The sudden increase in the C/N ratio to a value of 19 is associated with the evident input of carbon-rich flax plants into the lake. The C/N ratio of the *Linum usitatissimum* plant and stems vary in the range of 32–133 (Bruun et al., 2006); therefore, high C/N ratio in lake sediments and fragments/pollen finds confirmed that intensive flax retting activities occurred in Lake Kooraste Linajärv from at least AD 1830. Added nutrients, originating from the flax decomposition process, were also responsible for the changes in the size, abundance, and structure of the phytoplankton community (Fig. 7; Paper III, Fig. 6, 7). Rise in the abundance of phytoplankton is clearly supported by the sharp increase in paleopigments (Fig. 7; Paper III, Fig. 8), which indicate that the trophic state of the lake was changing (Fig. 8b). Also, the study by Jinglu et al. (2007) observed the same type of C/N ratio reaction when studying human-induced changes in Lake Taihu, China, and in its catchment since the early to middle part of the 20th century. The study revealed that the first evidence of eutrophication in Lake Taihu was recorded by an increase in C/N values. This type of shift was related to the development and intensification of agricultural activity in the surroundings of the lake. Consequently, it caused soil erosion (rise in C/N ratio), which, in turn, accelerated the nutrient input into the lake. Addition of the nutrients was eventually the reason for the elevated phytoplankton productivity, which was reflected by the reduction in the C/N ratio. Ongoing flax retting in Lake Kooraste Linajärv led to the same outcome, in which the previously observed high C/N ratio decreased abruptly from 19 to 9 during the AD 1860s (Fig. 7), suggesting a compositional change in the sediment OM and a shift in the lake trophy. Overall, an unstable ecosystem was characterized by the distinct succession of phytoplanktonic communities, their cyclic appearances, sub-domination, and declines (Paper III, Fig. 6, 7). The water column became strongly stratified, meromictic conditions developed, and annually laminated sediments i.e., varves, started to form from the AD 1860s. Increasing quantities of TS (Fig. 7), which directly refer to anoxia (Enters et al., 2006), and greater internal P loadings (Paper III, Fig. 3) suggest that the lake was far from its natural state. Although flax retting continued, demonstrated by the presence of *Linum* fragments, seeds, and pollen grains (Fig. 7), the ongoing release of the nutrients accelerated algae growth even more. This eventually overpowered the terrestrial signal and was the cause of low C/N ratios (Fig. 7).

Palynological analyses from Lake Trikātas sediments indicated major changes in vegetation after ca. AD 1200, where a massive opening of the woodland in the lake surroundings was registered (Fig. 9). This was most probably the outcome of intensifying land use within the lake catchment due to the conquest of Latvia by the Order of the Sword Brothers (AD 1209–1227). Levels of cultivation indicators rise and remain high, suggesting continued intensive agrarian activity (Fig. 9). The lack of tree macrofossils (Fig. 5, in Stivrins et al., 2016a) additionally indicate open lake shores, which, in turn promote soil erosion and increase the share of MM while raising MS values (Fig. 3, in Stivrins et al., 2016a). The C/N ratio with minor fluctuations continues to decrease, suggesting that added nutrients *via* continuous agricultural land use practices have further affected lake trophy, changing it into more eutrophic conditions (Fig. 9).

While extensive land use decreased after AD 1930 at Lake Trikātas, as reflected by woodland recover, lower values of cultural indicators, MM content, MS, and quartz grains (Fig. 9; Fig. 3, in Stivrins et al., 2016a), the C/N ratio continued to decline, showing its all-time low values around 9 in the recent sediments. This confirms the deterioration of the water ecosystem in which the lake OM source was irreversibly changed to solely algal origin (Meyers and Ishiwatari, 1993; Meyers and Lallier-Vergès, 1999). Furthermore, Stivrins et al. (2018) stated that, due to human impact, the overall diatom community has changed by more than a half compared with its reference conditions, and restoring the water quality to its former status could be challenging. Considerable expansion of eutrophic planktonic diatoms, such as *Stephanodiscus parvus* and S. *minutulus* (Fig. 9), only confirm the above-mentioned statements. The same scenario took place in Lake Kooraste Linajärv. While flax retting declined sharply during the early 20^{th} century AD and was abandoned during AD 1950s, when retting in natural water bodies was forbidden in Estonia, Lake Kooraste Linajärv still experiences intensive water blooms over the entire growing season, due to internal nutrient loading, which prevents its recovery up to the present day (Fig. 8c).

Overall, Lake Kooraste Linajärv (Paper III) and Lake Trikātas (Paper IV) followed a similar impact path—a once natural lake with a C/N ratio around 16 was turned into eutrophic/hypertrophic lake due to human activity. However, some distinctions can be drawn by comparing the length of the time necessary to exhaust the lake buffering capacity. Lake Trikātas (Paper IV) responded even to the slightest external disturbance. The C/N ratio showed great sensitivity and reflected the cumulative effect of anthropogenic land-use on the lake ecosystem. Meanwhile, Lake Kooraste Linajärv (Paper III) had a larger tolerance capability and showed minimal reaction to moderate human impact. However, abrupt and intensive human impact caused major changes in the lake ecosystem in a short period of time by completely destroying its previous state. As discussed earlier, study site location and its peculiarities also play large role in defining the susceptibility of the lake ecosystem to external influencers. However, regardless of the previously mentioned differences between Lake Kooraste Linajärv and Lake Trikātas, the outcome of the human-related disturbance to the lake environment was still the same—increase in nutrient input led to enhanced primary productivity, which eventually permanently changed the trophic state of the lake.

5 Conclusions

The dissertation explores the potential of post-glacial paleoclimatic and paleoenvironmental reconstructions in the Baltic area using multiple biotic and geochemical proxies, with special emphasis on sediment C/N ratio. The versatile nature of lakes often complicates the correct interpretation of sediment C/N ratio outcomes; a multi-proxy approach helps to reveal the true capability of the C/N ratio in reconstructing the unique history of each individual lake and its surrounding area. Focusing on climate change, lake development, and human impact, the main results of the current work can be summarized as follows:

- the study of the Lake Lielais Svētiņu sediment sequence covering the post-glacial period between 14,600–10,700 cal yr BP shows that under colder climates, the C/N ratio values are low, indicating that the OM originates predominantly from phytoplankton. Under warmer conditions, in which there is more phytoplankton biomass in the lake, higher C/N values prevail, showing that terrestrial vegetation biomass around the lake developed and increased the input of nutrient-rich terrestrial OM into the lake. Furthermore, the indication ability of the sediment C/N ratio was demonstrated through the detection of the Gerzensee cold event (centred at 13,150 cal yr BP), which was left unnoticed from the pollen data of Lake Lielais Svētiņu and Lake Kurjanovas nearby and highlighted other major climate oscillations noted in the NGRIP $\delta^{18}O$ data;
- C/N ratio tracked the successive gradual development process of the thermokarstic lake depression in western Latvia from the melting of the dead-ice-block stadium until the formation of a kettle-hole lake;
- C/N ratio proved to be an excellent proxy as a part of paleolimnological analyses, facilitating the placement of natural baselines for lakes and detection of the impact magnitude of changing human activity on the well-being of lakes. Reaction to intense human impact in Lake Kooraste Linajärv (due to flax retting) was detected by the extreme fluctuations in the C/N ratio, showing that the lake underwent irreversible changes in the origin of OM and in trophy. Reaction to the ca. 2500-year gradual human impact on the Lake Trikātas ecosystem was detected by the relatively constant reduction in the C/N ratio. Development of farming activities in the catchment area of the lake gradually increased lake-water nutrient loadings and challenged the tolerance of the trophic state of the lake ecosystem;
- multi-proxy approach proved to be an effective tool in C/N ratio studies because it exploits the complementary strengths from each of the proxies to investigate past environmental changes in lakes and their catchments.

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Abstract

Application of lake sediment carbon/nitrogen ratio in post-glacial paleoenvironmental reconstruction

In the light of the current knowledge of global climate and subsequent environmental changes, understanding of the past ecosystem dynamics has become very important in comprehending present-day processes and predicting the future response of an ecosystem. Paleoecological records, preserved in various sedimentary deposits, including lake sediments, can provide a unique insight into the nature of the past.

This dissertation focuses on the composition and origin of lake sediment organic matter during a 14,600-year post-glacial period and assesses the response of organic matter to climate change, lake development, and human impact. The organic matter content of lake sediments comprises a complex mixture of biochemicals contained in the tissues of living and formerly living organisms from the lake itself and its catchment area. In this way, organic material may originate as particulate detritus of phytoplankton, from water plants growing in the shallower areas of the lake, and from terrestrial plants inhabiting the catchment area. The distinction between organic matter sources depends on their biochemical differences; nitrogen-rich non-vascular aquatic algae lack woody cellulosic tissues, whereas terrestrial vascular plants have tissues that contain carbon-rich cellulose. Thus, the carbon/nitrogen (C/N) ratio of lake sediments provides a means to distinguish between in-lake and catchment-derived organic matter.

The specific objectives of this dissertation are: (1) to evaluate the response of sedimentary C/N ratios to extreme climatic variability during the late-glacial and early Holocene period; (2) to evaluate the usability of C/N ratios in reconstructing kettle-hole lake development; and (3) to assess the lake ecosystem reaction to human impact by using C/N ratios.

The research is based on lake sediment sequences from three Latvian lakes (Lake Lielais Svētiņu, Lake Ķikuru, Lake Trikātas) and one Estonian lake (Lake Kooraste Linajärv). In addition to sediment C/N ratio analysis, several other lithological, geochemical, and paleobotanical proxies are used. The chronology of sediment sequences is based on radiocarbon dates, varve counts, and tephra shard analysis.

In the Lake Lielais Svētiņu sediments, which covered the post-glacial period between 14,600–10,700 years ago, the results reveal that the C/N ratio integrates the signal of several environmental variables and is closely related with an evolving climate, vegetation development, and hydrological conditions. The C/N ratio captures the pattern of climate fluctuations and is significantly positively correlated with pollen-inferred mean summer temperature: C/N is lower under colder conditions, indicating that organic matter originated predominantly from aquatic phytoplankton and is higher during warmer conditions, when both phytoplankton biomass and terrestrial biomass around the lake increase.

It is commonly assumed that the majority of buried ice-blocks in Europe melted at the end of the late-glacial period and during the first part of the early-Holocene. This dissertation shows that scattered dead-ice-blocks in the Baltic area may have been preserved in the ground until the Holocene Thermal Maximum ca. 8500 years ago. The development process of the thermokarstic lake depression formation in western Latvia is reconstructed: successive gradual changes from a terrestrial to an aquatic

environment took place due to ice-block melting; terrestrial soil development was followed by fen peat formation, resulting in a subsequent kettle-hole lake.

Lake Kooraste Linajärv sediment sequence studies suggest abrupt and drastic consequences of flax retting since the 19th century, as a clear and soft-water oligotrophic lake with limited sedimentation switched into a hypertrophic high-sedimentation lake with anoxic bottom water, strong stratification, and intense phytoplankton blooms. The research also shows that although flax retting stopped 60 years ago, phosphorus release from the sediments is still so significant today that it hinders the improvement of the water quality of the lake.

The Lake Trikātas paleolimnological study presents a synthesis of the long-term evidence of human impact in the catchment and lake ecosystem over ca. 2500 years and links the development of farming activities and lake-water quality.

The results of this research demonstrate the power of multi-proxy paleolimnological analyses together with sediment C/N ratio for investigating past climatic and environmental changes in lakes and their catchments.

Lühikokkuvõte

Järvesetete orgaanilise aine süsiniku ja lämmastiku suhte kasutusvõimalused pärastjääaegsete keskkonnamuutuste rekonstrueerimisel

Globaalsed kliima- ja keskkonnamuutused on tänapäeval inimkonna ees seisvatest probleemidest üks tõsisemaid. Tulevikuprognoosid saavad toetuda looduslikele teguritele ja protsessidele, mis kujundasid maakera kliimat ja keskkonda geoloogilises minevikus. Järvesetetesse on talletunud informatsioon pärastjääaegsete kliima-, keskkonna- ja inimtekkeliste muutuste ning nende põhjuste kohta.

Doktoritöö käsitleb järvesetetesse akumuleerunud orgaanilise aine koostist ja päritolu, hinnates neid näitajaid kliimamuutuste, järve arengu ning inimmõju seisukohast pärastjääaegsel perioodil. Järves settinud orgaaniline aine on erinevate orgaaniliste ühendite segu, mis on moodustunud veekogus ja tema valglal elanud organismide elutegevuse tagajärjel. Orgaanilise aine elementkoostise süsiniku ja lämmastiku (C/N) suhe on paleouuringutes senini laiemat kasutust leidnud orgaanilise aine päritolu määramisel. Suhte väärtus võimaldab identifitseerida, kas aine pärineb veekogu vetikatest või maismaataimedest – taimhõljum on tänu tselluloosi puudumisele lämmastikurikas, samas kui maismaataimede puitjad koed on süsinikurikkad.

Doktoritöö eesmärgiks oli uurida: (1) äärmuslikke kliima- ja keskkonnamuutusi hilisjääajal ning Vara-Holotseenis ajavahemikul 14,600–10,700 aastat tagasi; (2) glatsiokarstilise järvenõo geneesi arenguetappe ning (3) hinnata nii primitiivse eelajaloolise maaviljeluse kui ka tänapäevase inimtegevuse mõju järve ökosüsteemile, tuginedes peamiselt muutustele järvesetete orgaanilise aine C/N suhte väärtustes.

Uuriti kolme Läti (Lielais Svētiņu, Ķikuru, Trikātas) ja ühe Eesti järve (Kooraste Linajärv) setteläbilõiget. Lisaks C/N suhtele hõlmasid kompleksed uuringud erinevaid litoloogilisi, geokeemilisi ja paleobotaanilisi näitajaid. Radiosüsiniku dateeringute ning varvo- ja tefrakronoloogia põhjal määrati uuritud setteläbilõigete vanus.

Lielais Svētiņu setete uuringutulemused näitavad, et C/N suhte väärtustes talletub kompleksne informatsioon nii kliimamuutuste, taimestiku arengu kui veekogu hüdroloogiliste tingimuste kohta. Uuritud ajalõik hilisjääajal ja Vara-Holotseenis 14,600–10,700 aastat tagasi on tuntud oma äärmuslike kliima- ja keskkonnamuutuste poolest. Leiti tugev positiivne korrelatsioon setete C/N suhte ja vetikate bioproduktsiooni ning õietolmust tuletatud keskmise suvetemperatuuri vahel. C/N suhe oli madalam külmematel perioodidel, millal vaatamata väiksemale vetikate produktsioonile oli sette orgaaniline aine valdavalt pärit fütoplanktonist. C/N suhe oli kõrgem soojematel perioodidel, millal domineeris maismaalt pärinev orgaaniline aine. Kliima soojenedes suurenes küll järve taimhõljumi biomass, kuid sellega kaasnes ka järve ümbritseva taimkatte laialdasem levik.

Seniste teadmiste põhjal eeldati, et enamik jääliustiku taganemisest allesjäänud mattunud irdjääpankadest sulas Euroopas hilisjääaja lõpus või Vara-Holotseeni alguses. Doktoritöö tulemused näitavad, et üksikud mattunud irdjääpangad olid Baltikumis alles veel ka Holotseeni kliimaoptimumi ajal 8500 aastat tagasi. Termokarstilise Ķikuru järve setteuuringud kinnitavad selle järk-järgulist arengut maismaast järveks. Mattunud irdjää sulamisel moodustus jääpanga kohal olevale mullakihile madalsoo, jääpanga edasisel sulamisel ning pinnase vajumisel tekkis aga järvenõgu.

Kooraste Linajärve setteuuringud viitavad linaleotusest põhjustatud äärmuslikele keskkonnamuutustele järve ökosüsteemis alates 19. sajandist. Endine läbipaistev ja pehmeveeline, aeglase settimiskiirusega vähetoiteline järv muutus intensiivse linaleotamise tõttu suure settimiskiirusega rohketoiteliseks järveks, kus veesammas oli tugevalt kihistunud, põhjakihtides valitses hapnikuvaegus ning pea aastaringselt leidsid aset veeõitsengud. Vaatamata sellele, et linaleotus järves lõpetati juba üle poole sajandi tagasi, takistab fosfori sisekoormus tänaseni järvevee kvaliteedi paranemist.

Trikātas järve paleolimnoloogiline uuring käsitleb pikaajalist, umbes 2500 aastat kestnud inimmõju järve ökosüsteemile. Tulemused kinnitavad, et põllumajandusliku tegevuse järk-järguline intensiivistumise ja järvevee kvaliteedi halvenemise vahel on tugev seos.

Käesoleva doktoritöö tulemused rõhutavad interdistsiplinaarse lähenemise olulisust järvede ja neid ümbritsevate alade keskkonna- ja kliimamuutuste rekonstrueerimisel.

Appendix

Paper I

Liiv, M., Alliksaar, T., Amon, L., Freiberg, R., Heinsalu, A., Reitalu, T., Saarse, L., Seppä, H., Stivrins, N., Tõnno, I., Vassiljev, J., Veski, S. (2018). Late glacial and early Holocene climate and environmental changes in the eastern Baltic area inferred from sediment C/N ratio. Journal of Paleolimnology: available online 28. June 2018, https://doi.org/10.1007/s10933-018-0041-0

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ORIGINAL PAPER

Late glacial and early Holocene climate and environmental changes in the eastern Baltic area inferred from sediment C/N ratio

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Abstract We assessed the utility of using the sediment total organic carbon/total nitrogen (C/N) ratio as an indicator of paleoclimate changes in the eastern Baltic area during the late glacial and early Holocene. The C/N ratio in sediments from Lake Lielais Svētiņu, eastern Latvia, was compared with other sediment variables that are used as proxies of past climate and environment. Analysis revealed that although the organic matter (OM) content in late glacial sediments was extremely low, the C/N ratio captured information about OM origin, and fluctuations in the ratio tracked climate oscillations. The C/N ratio was significantly positively correlated with pollen-inferred mean summer temperature. Therefore, C/N ratio was lower under colder conditions, indicating a predominantly phytoplankton origin of OM, and was higher during warmer conditions, when there was more vegetation around the lake. A strong positive correlation between C/N ratio and the paleopigment beta carotene suggested that elevated phytoplankton production resulted from higher nutrient availability that was controlled largely by the input of terrestrial OM to the lake during warmer climate episodes. Thus, C/N ratio was a good indicator of paleoclimate changes, at least for the late glacial period, when generally cold conditions prevailed. This study also demonstrates the power of multi-proxy paleolimnological analyses for investigating past environmental changes in lakes and their watersheds.

Keywords Late glacial · Climate change · C/N ratio · Multi-proxy · Paleolimnology · Latvia

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Introduction

Organic matter (OM) in lake sediment contains approximately 50% carbon (C) (Meyers and Teranes 2001). The concentration of total organic carbon (TOC) can be used to describe the abundance of OM in sediments and to study lacustrine paleoproductivity and OM preservation (Schelske and Hodell 1991; Meyers and Teranes 2001; Magny et al. 2006; Routh et al. 2007). Sediment TOC consists of materials derived from both terrestrial and aquatic sources, and the TOC/total nitrogen (C/N) ratio has long been used to assess the origin of lake sediment OM. Large differences between C/N of phytoplankton and higher plants (Meyers and Ishiwatari 1993; Meyers 1994) make C/N a commonly reported variable in paleolimnological studies (Choudhary et al. 2009, 2013; Terasmaa et al. 2013; Kaushal and Binford 1999; Meyers 2003; Enters et al. 2010; Wohlfarth et al. 2006). Low C/N ratios, between 4 and 10, reflect high proportions of phytoplankton OM, whereas high C/N ratios ($\geq$ 20) are typical of terrestrial material (Meyers and Lallier-Vergès 1999; Meyers 1994). Intermediate values suggest a mixture of vascular and non-vascular plant sources, which is expected for most lakes (Meyers and Ishiwatari 1993; Meyers 1994; Meyers and Lallier-Vergès 1999). These characteristic values arise because non-vascular plants such as algae lack woody, cellulosic tissues and are rich in protein, whereas vascular plants, such as grasses, shrubs and trees, have abundant carbon-rich structural tissues (Meyers 1997). This geochemical proxy has also been used to infer past changes in lake productivity, nutrient cycling and OM depositional history in relation to climate (Larsen et al. 2011; Balascio and Bradley 2012; Ji et al. 2005; Kołaczek et al. 2015; Šeirienė et al. 2009; Wohlfarth et al. 2007).

Changes in sediment TOC content, and thus in C/N ratio, are driven by a combination of factors: (1) deposition of OM, which is affected by nutrient availability within the lake, and OM transport from the land around the lake; (2) OM preservation, which is influenced by the quality of OM and its burial rate; and (3) climate and environmental changes, e.g. delivery of nutrients from the surrounding watershed caused by local precipitation variations, deforestation, and soil erosion (Meyers 1997; Gälman et al. 2008). Although TOC and C/N profiles can provide integrated histories of past paleoenvironmental changes, these geochemical variables have not always been used to their full potential as paleoclimate proxies.

The late glacial and early Holocene time periods are useful for exploring the potential utility of climate proxy variables in lake sediments because the time periods involve several abrupt climate shifts. These climate events have been addressed in many studies (Lücke and Brauer 2004; Veski et al. 2012, 2015; Kylander et al. 2013; Stivrins et al. 2015, 2016).

Recent lake sediment studies of late glacial and early Holocene vegetation history (Amon et al. 2014; Veski et al. 2012; Heikkilä et al. 2009; Stivrins et al. 2016) and phytoplankton community response to long-term environmental changes (Stivrins et al. 2015, 2016) in eastern Europe, demonstrated extreme ecosystem changes through time and improved our understanding of how certain environments reacted to specific climate events. Furthermore, pollen- and chironomid-based quantitative temperature reconstructions in the southern Baltic–Belarus area (Veski et al. 2015; Heiri et al. 2014) display clear spatial and temporal patterns. Therefore, the late glacial and early Holocene, which are characterized by well-documented climate shifts, provide us with a reference period against which to test the reliability of the C/N ratio as an indicator of climate change.

We compared the C/N ratio in a core from Lake Lielais Svētiņu to grain size and paleopigment beta carotene (β-car) results, as well as loss-on-ignition (LOI), magnetic susceptibility (MS) values and data on green algae, pollen, plant macrofossil and pollen-based temperature reconstructions from previous studies of the same lake (Stivrins et al. 2015; Amon et al. 2014; Veski et al. 2012, 2015). This study focused on the time period from 14,600 to 10,700 cal year BP. The C/N data were used to complement previous reconstructions of vegetation and climate histories for the eastern Baltic area (Veski et al. 2012; Terasmaa et al. 2013; Heikkilä et al. 2009) and assess how the aquatic environment reacted to climate oscillations.

Site description

Lake Lielais Svētiņu (Fig. 1) is located in eastern Latvia (56°45.5N; 27°08.8E), 96.2 m above sea level (a.s.l.). The oblong, brown-water (humic-stained) lake is relatively small (18.8 ha) and shallow (Z_{max} = 4.9 m) with small surface inlets and outlets. The catchment area covers approximately 19.7 km^2

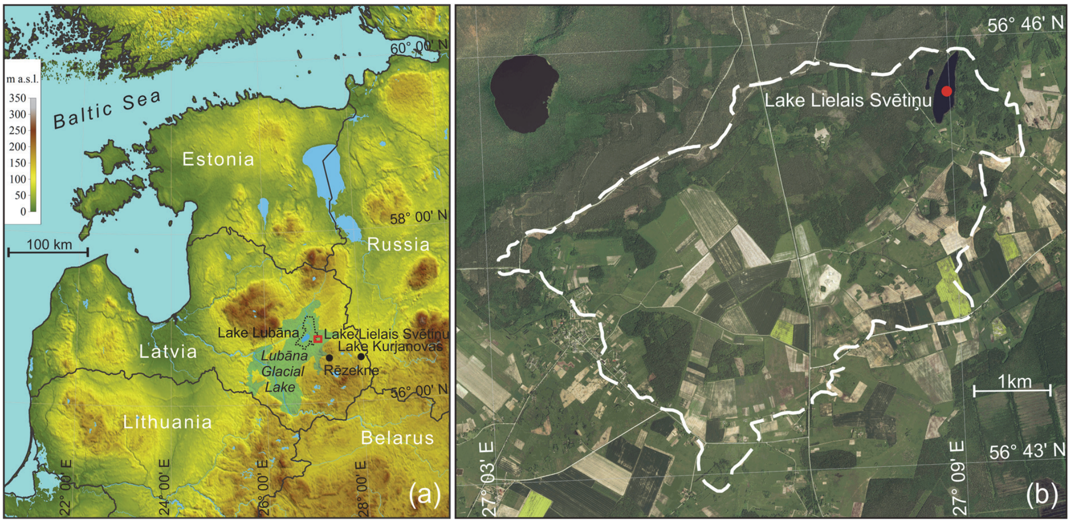

Fig. 1 **a** Overview map of the study area; green area marks the maximum extent of the Lubāna Glacial Lake and black dashed line marks the shoreline ca. 11,000 cal year BP (Zelčs et al. 2011). **b** Lake Lielais Svētiņu catchment area is indicated by the white dashed line. (Color figure online)

(Fig. 1b). The bedrock (Devonian dolomite) is covered by 5–10 m of Quaternary deposits that consist mainly of silts and clays of the Lubāna basin, but also peat, glacial sand and till (Stivrins et al. 2015).

According to reconstructions of late glacial Latvian landscapes (Amon et al. 2014), Lake Lielais Svētiņu was a part of the large Lubāna proglacial lake. Lubāna‘s highest estimated shoreline was 108 m a.s.l. (Zelčs and Markots 2004), and the Lake Lielais Svētiņu study site was located in the eastern part of the basin (Fig. 1a).

Quantitative temperature reconstructions from pollen data show that during the late glacial period, mean winter temperature (T_{win}) was − 18.3 °C and mean summer temperature (T_{sum}) was + 8.6 or + 11.4 °C, depending on the dataset (Veski et al. 2015). Currently, the mean T_{win} in Rēzekne, the closest city to our study site (Fig. 1a), is − 4.1 °C, and the mean T_{sum} is + 16.9 °C (Dauškane et al. 2011).

Materials and methods

Coring and chronology

In 2009, a long core (> 11 m) was collected from Lake Lielais Svētiņu with a Russian corer. The core spanned the entire late glacial and Holocene (Veski et al. 2012; Stivrins et al. 2014, 2015). For this study, we focused on the lowermost part of the core (1535–1060 cm from the water surface), which accumulated in the late glacial and early Holocene.

Radiocarbon dating of terrestrial plant macrofossils was used to develop a sediment core chronology (Table 1). The OxCal 4.1 deposition model (Bronk Ramsey 2008, 2009) and IntCal13 calibration curve (Reimer et al. 2013) were used to build an age-depth model (full description in Stivrins et al. 2015; Table 1). The weighted average ages were used in this paper. Sedimentation rate for late glacial sediments at depths 1535–1498 cm (sand) was 0.09–0.11 cm a^{-1}, at 1498–1268 cm (silt/clay) 0.17–0.19 cm a^{-1} and at 1268–1105 cm (silt) 0.10–0.12 cm a^{-1}. Sedimentation rate for Holocene gyttja (1105–1060 cm) decreased to 0.05–0.06 cm a^{-1}.

Geochemical analysis

Sediment lithology was determined using the LOI method of Heiri et al. (2001). Sediment sub-samples were dried at 105 °C for 24 h or until the weight remained constant. After weighing, samples were combusted at 550 °C for 4 h and OM content was

Table 1 Radiocarbon ages of Lake Lielais Svētiņu sediment core according to OxCal 4.1 deposition model (Bronk Ramsey 2008, 2009) and IntCal13 calibration curve (Reimer et al. 2013)

Depth, cm	Laboratory code	^{14}C date, year BP	Calibrated age, cal year BP at 95.4% probability	Weighted average age, cal year BP	Material dated
1043	Tln-3174	9169 ± 100	10,300–9900	10,070 ± 100	Bulk gyttja
1157	Poz-30426	10,100 ± 60	11,650–11,590	11,620 ± 20	Wood
1185	Poz-36710	10,270 ± 50	12,140–11,810	11,990 ± 90	Twigs
1215	Poz-31768	10,330 ± 50	12,400–12,120	12,290 ± 80	Wood
1261	Poz-31769	10,760 ± 50	12,760–12,560	12,660 ± 50	Twigs, bark
1315	Poz-36711	11,460 ± 60	13,400–13,160	13,290 ± 60	Bark
1355	Poz-36712	11,670 ± 60	13,620–13,400	13,510 ± 50	Stems
1365	Poz-36715	11,630 ± 60	13,660–13,460	13,560 ± 50	Twigs, *Betula nana* leaves, *Potentilla* seed
1400	Poz-36713	11,840 ± 60	13,830–13,640	13,740 ± 50	Twigs
1445	Poz-36714	12,410 ± 60	14,240–13,990	14,110 ± 60	Twigs, *Betula nana* leaf (rejected from model)
1492	Poz-31770	12,380 ± 60	14,440–14,040	14,220 ± 100	Twigs, bark
1510	Poz-29298	12,420 ± 60	14,590–14,150	14,350 ± 110	Wood
1530	Poz-31771	12,350 ± 60	14,950–14,180	14,520 ± 210	Wood

measured as LOI. Carbonate matter (CM) content was estimated as the difference between LOI at 950 °C (for 2 h) and LOI at 550 °C, multiplied by 1.36 to express it as carbonate CO_3^{2-} (Heiri et al. 2001). The non-carbonate mineral matter (MM) content was calculated by subtracting OM and CM from the total dry sample weight. This approach provides a slight overestimate of MM, as the calcium and/or magnesium associated with carbonate are included as part of the MM fraction.

In total, 75 samples, taken at 5- to 20-cm intervals were analysed for TOC and TN content through combustion in a FLASH 2000 Organic Elemental Analyzer. Approximately 15 mg of freeze-dried powdered sediment was put into silver containers. Samples in capsules were initially pre-treated with 4 M HCl to remove inorganic C, and dried on a hotplate at 80 °C for 4 h. Once dry, the capsules were left to cool and carefully wrapped to form granules. Before analysis, the silver containers were packed into tin containers to facilitate combustion. Cystine was used as a standard (ThermoFisher Scientific), and OM-rich sediment was used as a reference material (IVA Analysentechnik e. K). Analyses were done in triplicate. The C/N values are expressed as atomic ratios (Meyers and Teranes 2001). We used a LOESS smoother with span = 0.1 to show long-term trends in the C/N ratio.

Paleopigment analyses followed the recommendations of Leavitt and Hodgson (2001) and are described in detail in Tõnno et al. (2013). All phytoplankton groups contain β-car and although this broadly-distributed pigment is also present in higher plants, it is generally used as a proxy for total phytoplankton biomass (Leavitt and Hodgson 2001; Leavitt et al. 2006; Dreßler et al. 2007).

Grain size and magnetic susceptibility analysis

Grain size of samples was analysed at 5- to 20-cm intervals using a Horiba Partica LA-950V2 laser diffractometer. Prior to analysis, OM was removed with 30% H_2O_2 at 90 °C and samples were washed with distilled water. To avoid grain flocculation, a 0.1% solution of sodium pyrophosphate ($Na_4P_2O_7$) was added to the samples and the built-in ultrasonic probe of the laser diffractometer was utilized. Seventy-five samples were analysed in duplicate and the mean value of the two measurements was used. Results fell into 93 particle-size classes that were grouped into principal granulometric classes following the Udden-Wentworth grain-size scale (Last 2001).

MS was measured with a Bartington MS2E high-resolution scanning sensor. Measurements were made at 1-cm resolution on the cleaned sediment surface that was covered with thin plastic film. Values were expressed in dimensionless SI (standard international) units (10^{-5}).

Biostratigraphic analyses

Procedures and descriptions of methods for analysis of pollen, plant macrofossils and green algae used in this study are described in papers listed in Electronic Supplementary Material (ESM) Table 1.

Statistical analyses

Statistical analyses were performed using results from this study (C/N ratio, granulometry and β-car) and data from previously published studies of Lake Lielais Svētiņu (ESM Table 1).

We used linear models to clarify which of the variables related to climate (pollen-inferred T_{win} and T_{sum}, North Greenland ice core (NGRIP) $\delta^{18}O$ record), biology (accumulation rates (AR) of tree pollen, herb pollen, green algae and β-car) and sediment characteristics (MM content, mean grain size, MS), were significantly associated with the sediment C/N ratio. We built three linear regression models that relate C/N ratio to: (1) climate variables, (2) biologic variables and (3) sediment characteristics. For each model, backward selection of variables was used until only significant ($p < 0.05$) variables remained in the model. AR of trees, herbs, green algae and β-car were log-transformed prior to analysis to achieve uniform distribution of the data. The explanatory variables were standardized to zero mean and unit variance.

To account for temporal autocorrelation in the data, we repeated the analysis with Generalized Least Squares (GLS) models, in which temporal autocorrelation was specified with an autoregressive moving average (Box et al. 1994), and performed the backward selection of variables within each of the three explanatory variable groups until only significant ($p < 0.05$) variables remained in the model.

Hierarchical partitioning (Chevan and Sutherland 1991) was used to estimate the independent contributions of each explanatory variable that appeared significant in the linear models. Randomization tests (based on 499 randomizations) were used to estimate the significance of the independent contributions of each of the explanatory variables. Hierarchical partitioning, in combination with randomization tests enables testing for the influence of each individual variable, after accounting for the influence of the remaining variables. Statistical analyses were carried out using the R programming environment (R core Team 2016). For hierarchical partitioning, we used the R package hier.part (Walsh and Mac Nally 2013). Correlations among the explanatory variables were tested with Pearson's product-moment correlation.

Results

Lithostratigraphy and chronology

The lowermost part of the sediment core (1535–1060 cm), which was analysed in this study, covers the late glacial and early Holocene. The late glacial sediments consist of silt and clay (Veski et al. 2012), whereas silty gyttja and homogeneous gyttja accumulated during the early Holocene (Stivrins et al. 2014).

The sediment core chronology was developed by Veski et al. (2012) and Stivrins et al. (2014, 2015). The sediment sequence in the present study is based on 13 AMS radiocarbon age determinations of terrestrial plant macrofossils and bulk gyttja (Table 1). The studied sediment core covers the time period from 14,600 to 10,700 cal year BP.

Geochemical analysis

The OM content of the sediment (Fig. 2) is low (2–5%) between 14,600 and 11,700 cal year BP, with the exception of 12,350 cal year BP, when OM rises to 8%. Starting at 11,700 cal year BP, the sediment sequence is characterized by slightly higher, but variable OM content and an increase to values around 30% at 11,350 cal year BP.

MM content is high and variable from 14,600 to 11,650 cal year BP, fluctuating between 85–90% (Fig. 2). Between 11,650 and 11,400 cal year BP, MM values are lower and more variable (77–93%). After 11,400 cal year BP, MM content declines abruptly to approximately 64–75%.

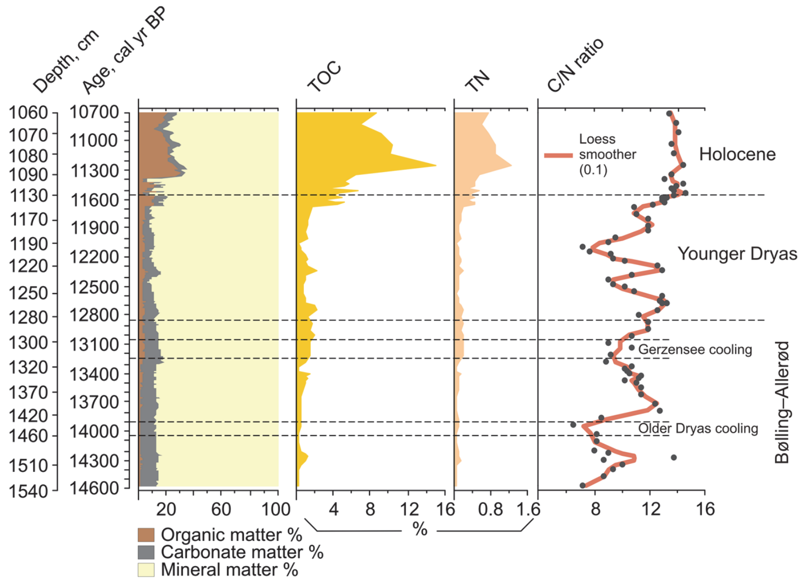

Fig. 2 Sediment organic, carbonate and mineral matter contents estimated by loss-on-ignition (% of dry weight) and profiles of total organic carbon (TOC) %, total nitrogen (TN) % and C/N ratio (dots represent original data, line loess smoother with span = 0.1) in the Lake Lielais Svētiņu sediment core

CM content has elevated values of ~ 12% around 14,600–13,200 cal year BP. CM content decreases steadily towards the topmost part of the studied sediment sequence (Fig. 2).

TOC and TN range from 0.3 to 15% and 0.04 to 1.2%, respectively, tracking one another ($r^2 = 0.99$) and the OM content (Fig. 2). Between 14,300 and 14,250 cal year BP, TOC and TN contents are a little higher (~ 1.1 and 0.1%, respectively), whereas values remain very low during 14,050–13,900 cal year BP (~ 0.4 and 0.07%, respectively). Within the interval 13,900–12,850 cal year BP, TOC and TN contents increase again, reaching values of 1.9 and 0.2%, respectively, though there is a notable drop during the period 13,400–13,300 cal year BP (0.4 and 0.04%, respectively). During 12,850–11,650 cal year BP, TOC and TN values vary, reaching highest concentrations ca. 12,330 cal year BP (2.4 and 0.2%, respectively) and lowest ca. 12,060 cal year BP (0.4 and 0.05%, respectively). Starting at 11,650 cal year BP, TOC and TN contents increase abruptly. In this period, maximum TOC and TN values of the whole studied sediment interval are reached (15 and 1.2%, respectively).

The C/N ratios in the sediment show a relatively wide range of values, from 7 to 15 (Fig. 2). During the interval 14,600–14,050 cal year BP, the C/N ratio remains relatively low (~ 8), but displays a peak at 14,270 cal year BP, reaching a value of 14. The minimum value of the whole core (~ 7) appears during 14,050–13,900 cal year BP. After this low, the C/N ratio increases rapidly to 13 ca. 13,780 cal year BP. Despite a few low values during 13,290–13,080 cal year BP, C/N values are generally relatively high throughout the period from 13,900 to 12,850 cal year BP. From 12,850 to 11,650 cal year BP, the C/N ratio shows high variability. High values (~ 13) are repeatedly followed by abrupt declines (~ 7). After 11,650 cal year BP, the C/N ratio increases and maintains higher values.

Marker pigment β-car, a proxy for total phytoplankton biomass, has two distinctive peak periods and one extremely low, yet still detected rise (Fig. 3). The smallest peak coincides with the time interval 14,330–14,270 cal year BP, a second peak marks the period 13,670–12,540 cal year BP, and a third, which was the most pronounced of the whole studied sediment sequence, occurs during 11,670–11,210 cal year BP.

Grain size

The terrigenous sediment fraction in the Lake Lielais Svētiņu sediment core consists mainly of silt, with smaller proportions of sand and clay. Mean grain size values fluctuate episodically throughout the studied

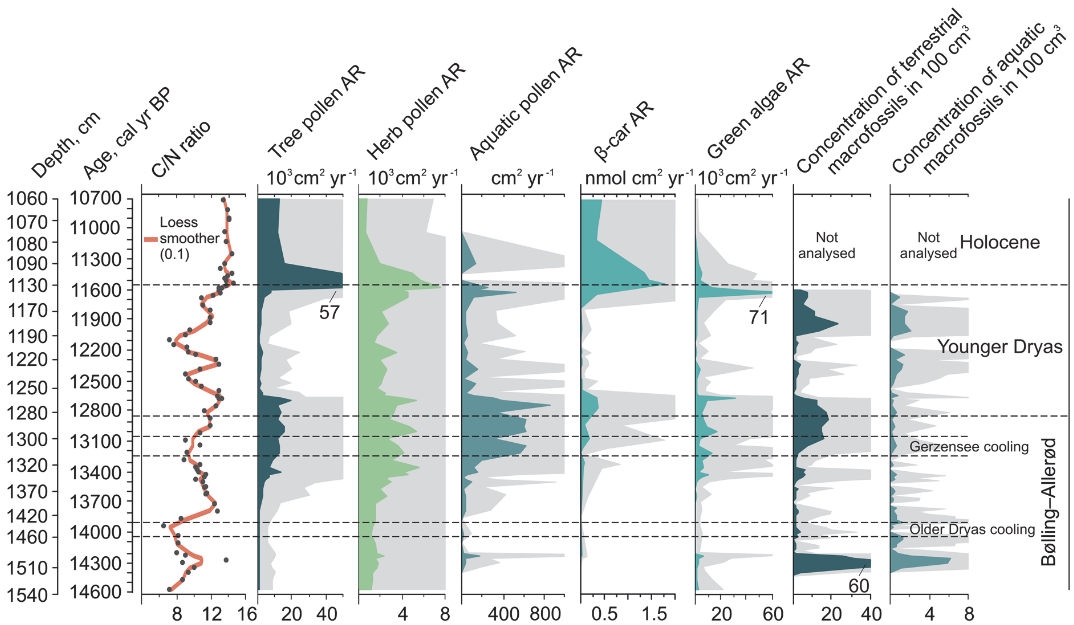

Fig. 3 C/N ratio and accumulation rates (cm^2 year^{-1}) of sum tree, sum herb, sum aquatic pollen, beta carotene (β-car), sum green algae and concentration of terrestrial and aquatic macrofossils (in 100 cm^3) of the Lake Lielais Svētiņu sediment profile; grey areas show ten-fold multiplication

core, between values of 9 and 65 μm (Fig. 4), but overall track the shape of the C/N ratio curve (Fig. 4). There is a shift towards coarser-grain sediments from 13,000 to 11,400 cal year BP. The most significant changes in the composition of grain size fractions occur during 12,850–11,650 cal year BP and 11,650–10,700 cal year BP (Fig. 4). Abrupt compositional shifts are common—a high clay peak (~ 27%) at 12,100 cal year BP is concurrent with a drop in the sand content from ~ 14 to 4% (Fig. 4). The most prominent increase in sand content occurs ca. 11,530 cal year BP, reaching approximately 46% (Fig. 4), while at the same time, the silt content declines to 5% (Fig. 4).

Overall, the median grain size record shows three distinctive peaks, with larger grain size in the basal layer ca. 14,300 cal year BP, in the middle of the studied core (12,800 cal year BP) and ca. 11,500 cal year BP (Fig. 4). Overall, median size remains relatively low and constant, with minor fluctuations between the above-mentioned peaks. Grain size has the greatest standard deviation during 12,600–11,300 cal year BP (Fig. 4). The MS data have three distinct periods of higher values, in the basal layer ca. 14,300 cal year BP, and around 13,300 cal year BP and 12,000 cal year BP (Fig. 4).

Statistical analyses

We explored the associations of the C/N ratio with multiple climatic, biological and geochemical sediment variables. Of the climate variables, pollen-inferred T_{sum} (Veski et al. 2015) is the only variable significantly associated with the C/N ratio, whereas among the biological variables, the β-car AR stands out (Table 2). In hierarchical partitioning, log β-car AR accounts for 25%, T_{sum} for 23% and log tree pollen AR for 16% of the explained variance in C/N ratio (Fig. 5). Of the sediment characteristics, all three variables, mean grain size, MM content and MS, are significant in the linear regression models. After accounting for temporal autocorrelation, however, none of the variables is significant. In hierarchical partitioning, all three variables are significant, with

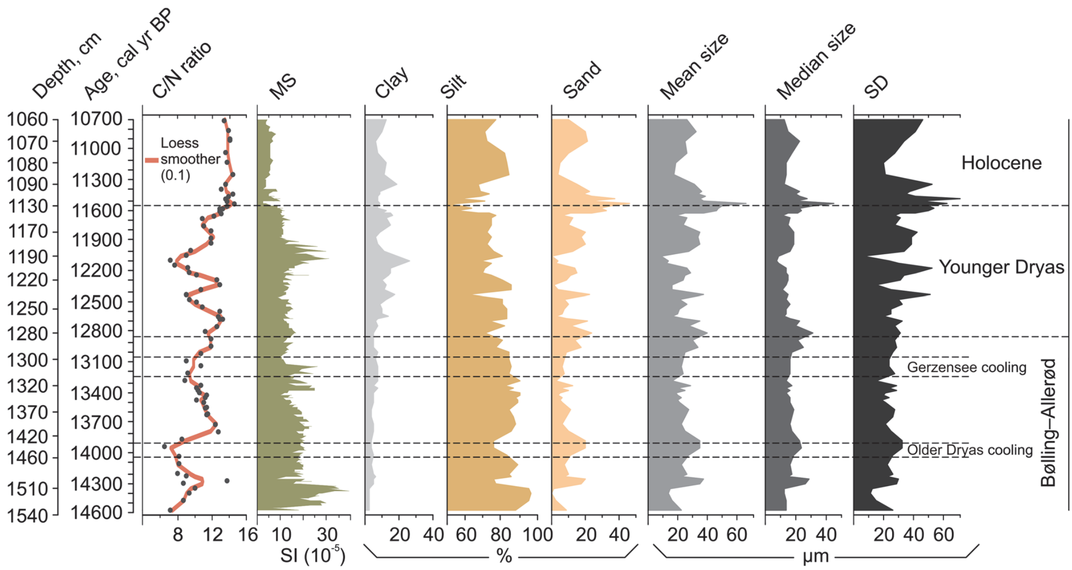

Fig. 4 C/N ratio, magnetic susceptibility (MS, expressed in SI units (10^{-5})), percentage diagrams of grain size distribution (clay, silt, sand); mean size, median size, and standard deviation (SD) expressed in µm for the Lake Lielais Svētiņu sediments

Table 2 Associations of the C/N ratio with biological factors, climate and sediment structure

	Variable	Estimate	*p* value	AIC	R^2
Linear model					
Climate	Pollen-inferred T_{sum}	1.54	< 0.001	261	0.57
Biology	log β-car	1.55	< 0.001	261	0.57
Sediment	MM	− 0.57	0.004	274	0.50
	Mean grain size	0.40	0.037		
	MS	− 0.93	< 0.001		
Generalized least squares with autoregressive moving average					
Climate	Pollen-inferred T_{sum}	1.58	< 0.001	239	0.62
Biology	log β-car	1.44	< 0.001	244	0.62
Sediment	No significant variables				

Results of backward selection with linear models and generalized least squares models, where only significant ($p < 0.05$) variables are kept in the final models. In the generalized least squares (GLS) model, temporal autocorrelation is accounted for by autoregressive moving average. In linear models, temporal autocorrelation is not accounted for. The explanatory variables were standardized to zero mean and unit variance. For each model, variable estimates (Estimate) and their significances (*p* value) are given. The goodness of fit is assessed with the help of Akaike Information Criterion (AIC; smaller values indicate better fit) for all models and with coefficient of determination (R^2) for linear models

MS having the highest explanatory power (15% of the explained variance). Three proxy records—NGRIP, herb pollen AR and green algae AR—were used in the analyses, but were not significantly associated with C/N in any of the models (Fig. 5).

Correlations among the variables confirm a strong positive relation between C/N ratio and T_{sum}, log tree pollen AR, log β-car AR and mean grain size, whereas MM and MS are negatively correlated with C/N ratio (ESM Table 2).

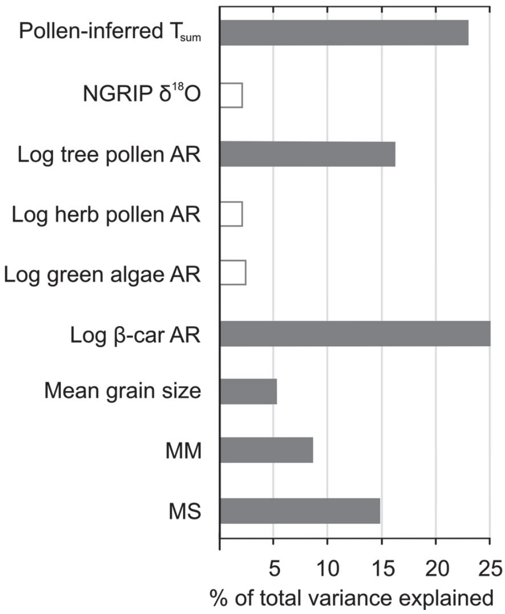

Fig. 5 Results from hierarchical partitioning, explaining the C/N ratio in the sediment of Lake Lielais Svētiņu. The variables with significant individual contribution ($p < 0.05$) are indicated with grey bars

Discussion

Lake Lielais Svētiņu contains well-preserved late glacial sediments (Veski et al. 2012) and is thus a valuable site for paleoecological and paleoclimatological studies. Detailed background information from previous studies of Lake Lielais Svētiņu sediments (Stivrins et al. 2015, 2018; Amon et al. 2014; Veski et al. 2012, 2015) enabled us to evaluate how different sediment variables reflect environmental changes and to assess the potential of C/N ratio as a paleoproxy.

Environmental oscillations (e.g. late glacial climate oscillations) usually leave geochemical evidence in lake sediments (Meyers and Lallier-Vergès 1999; Lücke and Brauer 2004; Wohlfarth et al. 2006; Parplies et al. 2008; Kylander et al. 2013). Although the OM content in the Lake Lielais Svētiņu core is very low (3–4%) throughout the studied late glacial period (Fig. 2), the C/N ratio fluctuates considerably and captures information about the OM origin.

The C/N ratio in lake sediments integrates the signal of several environmental variables and their changes in and around the lake. In this way, C/N is closely related with climate change, vegetation development and hydrological conditions, whose variations are all interconnected. These associations are well confirmed by the statistical analyses of Lake Lielais Svētiņu sediment variables. The strongest positive correlations with C/N ratio are with the fossil pigment β-car AR, a proxy for total in-lake algal production, and with the pollen- inferred T_{sum}, which is a climate indicator (Figs. 3, 6; Table 2, ESM Table 2). Positive associations mean that under colder climate the C/N values are low, indicating that the OM originates predominantly from phytoplankton, although phytoplankton biomass is also very low at these times. Under warmer conditions, when there is more phytoplankton biomass in the lake, higher C/N values prevail, showing that terrestrial vegetation biomass around the lake also had developed and increased the input of terrestrial OM into the lake. As the C/N ratio in lake sediments is also related to watershed hydrological conditions, which in turn are influenced by climate, significant associations with other sediment characteristics were found. Three sediment variables, MS, MM content and mean grain size, were significantly related to C/N ratio (Table 2; Fig. 4), MS having the highest explanatory power (15%). Changes in precipitation regime and overall moisture conditions can cause water-level oscillations and catchment erosion (Balascio and Bradley 2012) that introduce terrestrial MM and OM to the sediments, and as a result, increase the C/N ratio (Xu et al. 2006).

The sediment event stratigraphy of Lake Lielais Svētiņu follows the main climate phases defined by Rasmussen et al. (2014), with the exception that in our chronology, 0 cal year BP corresponds to AD 1950. We use definitions such as "Older Dryas" and "Gerzensee" to describe sub-events within climate-stratigraphic stages, given their widespread use in the literature. The chronology of climate events employed for the current study is:

- Early Holocene (11,650–10,700 cal year BP)
- Younger Dryas (12,850–11,650 cal year BP)
- Bølling–Allerød (14,650–12,850 cal year BP)
  - Gerzensee (13,250–13,050 cal year BP)
  - Older Dryas (14,050–13,900 cal year BP)

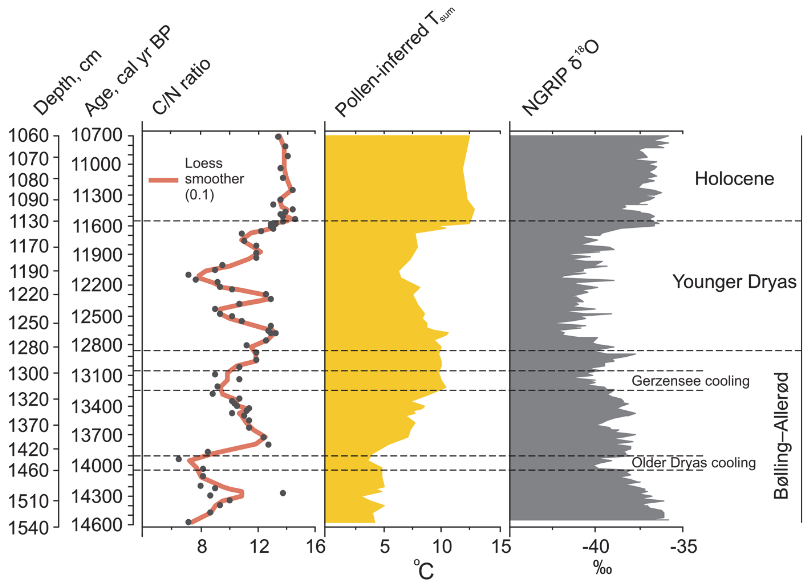

Fig. 6 Lake Lielais Svētiņu sediment profiles of C/N ratio and pollen-inferred summer temperature (T_{sum}, °C) together with North Greenland ice core $\delta^{18}O$ record (NGRIP $\delta^{18}O$, ‰) data (Rasmussen et al. 2006)

Bølling–Allerød (14,650–12,850 cal year BP)

After the retreat of the Scandinavian Ice Sheet from eastern Latvia no later than 14,560 cal BP (Veski et al. 2012), large proglacial Lake Lubāna flooded the area (Fig. 1a; Zelčs and Markots 2004). Although NGRIP data suggest an overall warming (Fig. 6), pollen-based reconstructions of T_{sum} and T_{win} (Veski et al. 2015) and vegetation history (Veski et al. 2012) of this eastern Baltic region suggest that local climate was still cool (Fig. 6) because of proximity to the ice margin. Regression of proglacial Lake Lubāna exposed new land, which at first had virtually no vegetation. The low C/N ratio (Fig. 6) confirms that during the start of the Bølling–Allerød interstadial, an aquatic environment existed and even though lacustrine phytoplankton productivity was very low, as indicated by β-car and green algae AR (Fig. 3), it was the predominant source of OM to sediments in Lake Lielais Svētiņu. The low in-lake productivity can be explained by colder and longer winters, extensive and long-lasting ice cover, delayed melting of ice and a very brief ice-free summer period. Grain-size distribution (Fig. 4) indicates dominance of the fine-grained component, which suggests relatively stable lake-level and depositional conditions. Macrofossil evidence (Fig. 3) points to a shallow-water environment.

An abrupt and short-term increase in the C/N ratio suggests a warmer-episode event ca. 14,300 cal year BP, within an overall cool environmental stage. This is supported by the high amount of plant macrofossils in the sediment interval between 14,400 and 14,200 cal year BP, hinting at a productive macrophyte community. Traces of terrestrial plants such as *Betula nana* Linné, *Salix* Linné, Cyperaceae Juss. and *Dryas octopetala* Linné (Veski et al. 2012) confirm that herb/shrub tundra had replaced pioneer tundra vegetation around Lake Lielais Svētiņu, probably as a consequence of suitable climatic and environmental conditions. Also, slightly elevated green algae AR and first signs of paleopigment β-car presence (Fig. 3), suggest an in-lake productivity rise. Given the relatively open landscape, which favoured catchment instability, allochthonous OM would have washed into the lake easily and raised the C/N value. This assumption is supported by the findings of fungal hyphae (Stivrins et al. 2015), which together with stratigraphic evidence such as a distinct peak in the sand fraction and high MS content (Fig. 4), indicate erosion. Allochthonous OM with higher C/N ratio probably brought nutrients into the lake, which favoured algae growth, but this effect was relatively minor, and was likely overwhelmed by the terrestrial C/N signature.

Higher C/N values, could to a certain extent, be explained by the high abundance of aquatic macrophytes. Highest concentrations of *Potamogeton* spp. in the whole record (Veski et al. 2012), combined with the fact that sediment C/N values are similar to those reported for aquatic macrophytes (C/N 10-20) (Herzschuh et al. 2005; Brenner et al. 2006), support this notion. Nevertheless, we conclude that during the start of the Bølling–Allerød interstadial, although proximity of the Scandinavian Ice Sheet margin should have kept overall climate rather cool, several lines of evidence support the inference for a warmer climate episode.

The sub-event known as the Older Dryas (14,050–13,900 cal year BP) brought even colder climate conditions (Fig. 6), as inferred from the lower pollen-based T_{sum} (Fig. 6). Whereas no clear signal of the Older Dryas was detected in the geochemical record from a sediment core taken in Lake Hässeldala Port, Sweden (Kylander et al. 2013), a short-term decrease of pollen-inferred T_{sum} is reflected in the C/N record of Lake Lielais Svētiņu. During that time, the C/N ratio was at an all-time low (Fig. 6). In that cold climate, the OM originated predominantly from phytoplankton, although bioproduction in the lake was very low, as indicated by β-car AR (Fig. 3). This is confirmed by positive associations between the C/N ratio and both pollen-inferred T_{sum} and β-car AR in statistical analyses (Figs. 3, 6; Table 2, ESM Table 2).

An increase in sand content and rather coarse median grain size during the Older Dryas suggests a higher-energy hydrodynamic environment and thus low water level (Fig. 4). Also, evidence about local vegetation (Veski et al. 2012) suggests a return of treeless tundra, colder climate, dryer soils and lower water level at the Older Dryas.

The shift to Allerød warmer climate conditions after 13,900 cal year BP (Fig. 6) recorded by the NGRIP ice core data, is also registered in the Lake Lielais Svētiņu pollen-derived T_{sum} curve (Fig. 6). In addition, the European chironomid-based paleotemperature reconstruction (Heiri et al. 2014), which uses an independent temperature proxy, confirms the warmer summer conditions in the Baltic region at 13,900 cal year BP.

Elevated C/N ratios, above 10, are seen in the Lake Lielais Svētiņu sediment record after 13,900 cal year BP (Fig. 6). These higher C/N ratio values reflect a mixture of OM from both aquatic and terrestrial sources (Meyers and Lallier-Vergès 1999). With warmer T_{sum}, and thus with a longer ice-free season and a lengthened growing season, there was more opportunity for in-lake algal production (Adrian et al. 1999; Veillette et al. 2011). The increased primary production is also related to nutrient availability (Smith 1986; Salmaso 2010). This increase in C/N ratio is likely linked to soil instability and increased erosion and runoff from the catchment soils (tundra soil C/N ratio > 14; Maslov and Makarov 2016), caused by rapid melting of permafrost in response to higher temperatures. Moreover, increased erosion and inwash of land-derived OM from the catchment would presumably cause an increase in nutrient input to the lake. In Lake Lielais Svētiņu, conditions favourable for lacustrine photosynthetic activity are shown by rising values of green algae and β-car AR ca. 13,600 cal year BP (Fig. 3), with a short delay to warmer T_{sum}. Moreover, Stivrins et al. (2018) showed that in Lake Lielais Svētiņu, all pigment groups originating from diatoms, cyanobacteria, chlorophytes and cryptophytes had low accumulation in the late glacial period, but much higher AR from ca. 13,600 cal year BP, supporting the concept of increasing lake productivity during the Allerød. In brief, we suggest that warmer conditions favoured nutrient-rich, allochthonous OM input into the lake (higher C/N ratio), which in turn enhanced phytoplankton growth, and the lake sediment OM pool was a mixture of these two sources. Several other studies have noted this concurrent effect, whereby higher C/N ratio appears together with enhanced aquatic primary productivity (Lücke et al. 2003; Watanabe et al. 2003; Wagner et al. 2004; Wohlfarth et al. 2004, 2006).

The C/N ratio also confirms its importance as an informative climate proxy during the interval when the NGRIP data recorded a small cold event near the end of the Bølling–Allerød interstadial (Fig. 6). This sub-event, known as the Gerzensee oscillation, is also apparent in the C/N data of Lake Lielais Svētiņu (Fig. 6). The C/N ratio in this study might be an even more informative tool for detecting environmental changes than are reconstructed T_{sum} data from pollen (Fig. 6) (Veski et al. 2015) or pollen/macrofossil changes (Fig. 3) (Veski et al. 2012). The timing of the Gerzensee cold event, centred at 13,150 cal year BP, is clearly recognizable in the lower C/N ratio values, whereas this event is unnoticeable in pollen data from Lake Lielais Svētiņu (Veski et al. 2012) and nearby

Lake Kurjanovas (Fig. 1a; Heikkilä et al. 2009). During the Gerzensee event, Lake Lielais Svētiņu was already surrounded by denser vegetation cover, with a forest community (Veski et al. 2012). Low C/N ratio hints that the return of a short, colder climate period, and probably dryer climate conditions, suppressed the delivery of soil-derived nutrients and supply of land-derived OM to the lake sufficiently to enable the autochthonous C/N signal to dominate (Fig. 6). After this sub-event, warmer conditions prevailed once again, and C/N values began to rise gradually (Fig. 6). Values remained relatively high towards the end of the Bølling–Allerød interstadial, possibly indicating that higher temperatures led to greater inputs of detrital materials of terrestrial origin and aquatic macrophytes, increasing their contribution to lake sediment OM yet again.

The lake sediment mean and median grain sizes display minor fluctuations, but show a rising trend towards the end of the Bølling–Allerød interstadial (Fig. 4). This indicates that, at first, a rather stable environment prevailed, with no major erosion events, and possibly, higher lake water level occurred at the end of the period. Higher water level is also suggested by the study of Goslar et al. (1999) in eastern Poland, where wetter climate is documented by an increase and expansion of species characteristic of environments with more precipitation.

Younger Dryas (12,850–11,650 cal year BP)

The Bølling–Allerød climate warming trend was interrupted by climate cooling ca. 12,850 cal year BP, which is registered in the NGRIP ice core (Fig. 6). Yet, the cooling in the southern Baltic-Belarus area, indicated by the pollen-based T_{sum} and T_{win} reconstructions (Fig. 6; Veski et al. 2015), and changes in the plant composition around Lake Lielais Svētiņu (Fig. 3; Veski et al. 2012) and elsewhere in Latvia (Heikkilä et al. 2009), were not as abrupt as recorded in the NGRIP data, but rather gradual (Fig. 3). Still, the almost 1000-year cooling event left its mark in the Lake Lielais Svētiņu sediment geochemistry and oscillations in C/N ratio values indicate that environmental conditions were quite variable (Fig. 6).

High MS values (Fig. 4) and presence of fungal hyphae (Stivrins et al. 2015) suggest that input of erosional material to the lake was probably a common phenomenon during this time (Magny et al. 2006). Furthermore, fluctuations in granulometric data can be observed throughout the Younger Dryas (Fig. 4). Significant non-homogeneity is indicated by the grain-size standard deviation (Fig. 4) and is supported by changes in the content of the sediment fractions (sand, silt and clay content, mean grain size), which clearly reflect unstable conditions in and around the lake. Sudden appearances and disappearances of clay, silt and sand fraction peaks suggest water-level fluctuations (Henriksen et al. 2003; Punning et al. 2005; Väliranta et al. 2005; Wohlfarth et al. 2006). The presence of telmatic plants throughout the Younger Dryas (Veski et al. 2012) may indicate subsiding or lower water level (Heikkilä et al. 2009; Punning et al. 2005). Similar trends during the Younger Dryas, i.e. dry climate and low lake level, have also been noted by other authors (Wohlfarth et al. 2006; Goslar et al. 1999).

Because of the onset of considerably colder climate conditions, the landscape became dominated by treeless shrub tundra once again (Veski et al. 2012). Although the C/N ratio displays fluctuations, TOC and TN are both low, with only some small peaks (Fig. 2). Furthermore, abrupt decline of green algae and β-car AR confirm that colder climate and possibly prolonged duration of ice cover had a significant effect on aquatic productivity. The lake environment had overall low production during the Younger Dryas and even a minor addition of allochthonous OM to the lake could have affected the C/N ratio. Therefore, fluctuations in the C/N ratio could have resulted from several scenarios, because the sediment geochemical record reflects multiple contemporaneous processes.

Although statistical analyses confirm that during colder climate phases the C/N values are low (Table 2; ESM Table 2), as they generally are in Lake Lielais Svētiņu sediment during the Younger Dryas (Fig. 2), there is a period with higher C/N ratio that could possibly indicate a warmer window inside this 1000-year cold spell. Several studies (Lane et al. 2013; Magny et al. 2006; Schwark et al. 2002; Schmidt et al. 2002; von Grafenstein et al. 1999; Isarin and Renssen 1999) have speculated about short-lived warming episodes and concluded there were warm, short summers during the Younger Dryas (Schenk et al. 2018). The results of the Lake Lielais Svētiņu sediment analysis support those studies with several lines of evidence. The shift in OM content up to 8% in the middle of the Younger Dryas hints that this late glacial period was not constantly cold and stable. The higher C/N ratio at that time shows that environment around the lake may have supported dense vegetation that enabled the input of more detrital terrestrial OM to the lake. Moreover, earliest *Picea* stomata and needles appeared in the eastern Baltic region within the cold Younger Dryas (Veski et al. 2012; Heikkilä et al. 2009). In addition, amounts of aquatic plant macrofossil remains (Fig. 3) (Veski et al. 2012) and the organic geochemical data display similar trends, suggesting that remains of submersed macrophytes were incorporated into the lake sediments, which indicates a suitable environment for aquatic plant growth, and could also explain higher C/N ratios (Fig. 3).

Higher C/N values can therefore be regarded as evidence for the presence of boreal trees and in-lake macrophytes and suggest that a short-term warming event was conducive to terrestrial and aquatic plant growth. Yet, it should be kept in mind that during the Younger Dryas the amount of sediment OM was still scarce and the generally low C/N ratio was vulnerable to change even with the smallest addition of allochthonous OM.

Early Holocene (11,650–10,700 cal year BP)

The Younger Dryas cooling event ended with abrupt warming, which indicates the beginning of the Holocene and has been identified both regionally and locally (Fig. 6). In some studies, warming at the beginning of the Holocene is only weakly reflected in the sediment record (Goslar et al. 1999), whereas in the Lake Lielais Svētiņu core, the response of all studied sediment climate proxies was rapid and pronounced (Veski et al. 2012; Stivrins et al. 2015). Their gradual response, however, had begun by ca. 11,900 cal year BP, which may indicate that environmental conditions were already suitable for supporting terrestrial vegetation and aquatic life forms towards the end of the Younger Dryas (Fig. 6).

Rapid ecosystem response and climate warming is corroborated by a high abundance of pollen, macrofossils and paleopigments in Lake Lielais Svētiņu (Veski et al. 2012; Stivrins et al. 2018) and its nearby surroundings (Heikkilä et al. 2009). The beginning of the Holocene is marked by abrupt increases in β-car and green algae AR (Fig. 3), which clearly point to a rapid enhancement of aquatic productivity. These elevated values indicate that after the harsh environmental conditions of the Younger Dryas, warmer conditions prevailed, and the area around the lake became forested again. This enabled greater input of nutrient-rich allochthonous components to enter the lake, which once again overwhelmed the low algal C/N ratio signal, while at the same time enhancing algal growth. As a result, the lake sediment OM pool was a mixture of these two sources and C/N ratio increased to values around 14.

Warming caused rapid melting of the previously frozen catchment and promoted terrestrial inwash from surrounding slopes to the lake. The abrupt shift to higher values in mean grain size, and in the sand fraction (Fig. 4), also suggests low water level. Such low water-level periods during the early Holocene have been noted in several studies in the region (Šeirienė et al. 2009; Sohar and Kalm 2008).

Conclusions

This analysis of Lake Lielais Svētiņu sediments provided new insights into the late glacial and early Holocene environment and climate of the eastern Baltic area. The C/N ratio turned out to be a good indicator of paleoclimate changes, at least during late glacial cold conditions, when the OM content in sediments was extremely low.

Statistical analysis of Lake Lielais Svētiņu sediment data confirmed that under cold conditions, when the terrestrial vegetation was not yet fully developed, the C/N ratio was low, indicating that OM originated from aquatic algae. Under warmer conditions, when there was more biomass around the lake and winter conditions allowed catchment vegetation to survive, higher C/N values prevailed. Furthermore, the β-car AR, a proxy for total phytoplankton production, had strong positive associations with the C/N ratio. This suggests that elevated phytoplankton growth resulted from higher nutrient availability, which was largely controlled by the input of terrestrial OM into the lake during warmer climate episodes. The C/N ratio also could be used to detect cooler sub-events within the Bølling–Allerød interstadial that pollen data did not register, and thereby reaffirmed its utility as a paleoindicator. Changes in precipitation regime and overall moisture conditions led to variations in erosion intensity and water level oscillations that were associated with changes in sediment grain-size characteristics (sand, silt and clay content, median and mean size) and MS. Inclusion of detailed background information from previous studies of Lake Lielais Svētiņu sediments lends credence to the conclusions presented here, and demonstrates how multiple lines of paleoenvironmental evidence can complement one another.

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Paper II

Stivrins, N., Liiv, M., Heinsalu, A., Gałka, M., Veski, S. (2017). The final meltdown of dead-ice at the Holocene Thermal Maximum (8500–7400 cal. yr BP) in western Latvia, eastern Baltic. The Holocene 27: 1146–1157.

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The final meltdown of dead-ice at the Holocene Thermal Maximum (8500–7400 cal. yr BP) in western Latvia, eastern Baltic

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Abstract

It is commonly assumed that the majority of buried ice-blocks in Europe melted at the end of Late Glacial period and during the first part of the early-Holocene. We show, however, that scattered dead-ice-blocks may have been preserved in the ground until 8500 cal. yr BP. We analysed thermokarst features in Lake Ķikuru, western Latvia, by means of a multi-proxy approach (pollen, non-pollen palynomorphs, plant macrofossils, diatoms, loss-on-ignition, magnetic susceptibility, C:N ratio, carbon accumulation rate and radiocarbon dating). Abiotic and biotic processes following the ice-block meltdown suggests abrupt development of a thermokarst from 8500 to 7400 cal. yr BP. Important changes in local vegetation occurred with the deepening of a kettle-hole during the transition from a fen to a lake that nearly coincided with the appearance of the first fish at 7800 cal. yr BP, thus forming a clear indication of a lacustrine environment. Our study shows that a thin peat layer formed at first and, due to the meltdown of the ice-block, it gradually lowered to the bottom of the kettle-hole, and gyttja begun to accumulate afterwards. Given that thermokarst arise when the mean summer air temperature gradually increases to a value above the present-day temperature, we must assume that the local conditions must have been exceptional to secure ice-block from the meltdown for so long. Therefore, the legacy of the last ice age was still evident even ca. 5500 years after the Weichselian ice retreat from the eastern Baltic.

Keywords

C:N ratio, diatoms, Holocene, macrofossils, non-pollen palynomorphs, thermokarst

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Introduction

Changing climate exerts a strong control on the nature, extent and severity of glacial and periglacial processes (Tweed and Carrivick, 2015). An increase in the global mean surface temperature causes permafrost to thaw, which initiates substantial carbon and methane emissions (Wik et al., 2016) and reintroduces previously frozen stores of micro- and macronutrients into the environment of the Northern Hemisphere (IPCC, 2014; Lougheed et al., 2015; Marushchak et al., 2015; Mathijssen et al., 2014; Serov et al., 2015; Sherwood et al., 2014). Furthermore, a recent study by Legendre et al. (2015) reveals the exciting finding of a pathogenic DNA virus in prehistorical permafrost layers that should be of concern in the context of global climate change (Tollefson, 2015).

During the recession of the ice sheet, the deglaciation of the permafrost, blocks of dead-ice remain in the ground. The following meltdown is a complex process, as ice-block preservation in the landscape depends on various aspects, such as air temperature, hydrology and geomorphological conditions. One widespread thermokarst legacy in the landscape is kettle-holes. Kettle-hole formation, in large part, is associated with the melting of ice partly or fully buried beneath a cover of deposits that accumulated during a period of progressive ice-marginal and proglacial sedimentation (Maizels, 1977). Because these formations are known to be an indication of ice-blocks in the ground, studies of kettle-holes can provide information on ice-block preservation and thermokarst in the landscape since the retreat of the ice sheet.

Thermokarst features in Europe were extensive, particularly in Central and Northern Europe due to the Last Weichselian deglaciation over these areas (Hughes et al., 2016; Kaiser et al., 2012; Michczyńska et al., 2013; Stančikaitė et al., 2009; Terasmaa et al. 2013; van Loon et al., 2012). Corti et al. (2012) advocate that at low elevations, the glaciers retreated more rapidly than at high altitudes, generating larger blocks of ice. Furthermore, stagnant ice melt gradually or immediately formed kettle-hole basins. In

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the first case, peat accumulates on top of a buried ice-block, indicating mire formation in the shallow depressions. Whereas dead-ice-blocks continue to melt, depressions become deeper and are occupied by lakes, and gyttja starts to accumulate above basal-peat. However, there are also a number of examples where gyttja accumulation in these depressions occurs with no prior basal-peat layer (Błaszkiewicz, 2011; Gałka and Sznel, 2013). These differences in meltdown and organic matter sedimentation can be attributed to the hydrology, permafrost, presence of vegetation, local geomorphology and thickness of the mineral cover (Błaszkiewicz, 2011; Błaszkiewicz et al., 2015; Słowiński et al., 2015; Östrem, 1959). Under certain circumstances, dead-ice and permafrost can even survive from earlier glaciations of more than 80,000 years ago (Henriksen et al., 2003; Szewczyk and Nawrocki, 2011). However, in connection with the more recent Weichselian deglaciation, climate and environmental changes (Banderas et al., 2015; Veski et al., 2015) most likely initiated vast areas of thermokarst from the early Late Glacial period until the early-Holocene in Central and Northern Europe (Michczyńska et al., 2013; Słowiński et al., 2015; Terasmaa et al., 2013). However, was this phenomenon of ice-block melting synchronous over Central and Eastern Europe? What was the nature of the biotic and abiotic processes following the ice-block meltdown and what implications can we gain from studying thermokarst in the past? Bearing in mind future climate warming scenarios, it is crucial to seek answers in geological archives that can provide a long-term perspective of the environmental change. In this sense, palaeolimnology has been demonstrated to be one of the most useful approaches to provide objective information about past hydrological conditions (Bennion et al., 2010). For example, in their seminal study, Florin and Wright (1969) use evidence from diatoms to describe the meltdown of dead-ice in Minnesota. They indicate that the terrestrial diatom composition at the base of the sequence and, subsequently, aquatic diatoms in the upper section are in concordance with the process of thermokarst thawing. Regarding the disappearance of permafrost and the meltdown of buried ice-blocks or dead-ice, the time period after the retreat of the Last Weichselian ice sheet provides a prospect to evaluate the temporal and spatial dynamics of thermokarst in the past, thus improving our understanding of future deglaciation under climate warming conditions.

Here, using a multi-proxy approach, we study the dynamics of thermokarst characteristics in western Latvia, where thermokarst occurred exceptionally late at the Holocene Thermal Maximum (8500–7400 cal. yr BP). During this time, the mean summer temperature increased and was 2.5–3°C higher than that of the present in the Baltic (Heikkilä and Seppä, 2010), which affords unique insights to evaluate the thawing processes of buried ice under a gradual climate warming scenario. The objectives of this paper are (1) to evaluate the nature of abiotic and biotic processes following the melting of dead-ice-blocks and (2) to examine possible controlling delay factors of thermokarst areas in western Latvia, eastern Baltic.

Study area

Lake Ķikuru (21.6 ha, 38.7 m a.s.l., water depth 4.3 m) is located in the Apriķi plain, 10 km to the north of the city of Aizpute in western Latvia (56°48′50″N, 21°37′33″E) (Figure 1). The surrounding undulating landscape was shaped by the deglaciation of the Apriķi glacial tongue approximately 18,000–15,000 cal. yr BP, which emerged from the Kurshian lobe during the North Lithuanian phase (Saks et al., 2011; Zelčs and Markots, 2004). Overall, the main glacial landforms in the study area are drumlins, which are surrounded by a chain of marginal moraines. According to Saks et al. (2011), the drumlin field has been altered by a local, proglacial ice-dammed lake, and hence, the drumlins are mostly buried by glaciolacustrine sediments, allowing the drumlins to be visible only in a limited area. Lake Ķikuru lies in the middle of ridge (Figure 2), located within a drumlin field that stretches from northwest to southeast. The relative difference in altitude between the highest point (51.6 m a.s.l.) of the ridge and the lake (38.7 m a.s.l.) is 12.9 m in a distance of 300 m. The ridge is 2.8 km long and 0.6 km wide and according to its shape is reminiscent of a drumlin that has been split into two parts by the lake. The thickness of Quaternary, or in this case, Pleistocene sediments around Lake Ķikuru (Figure 2) varies significantly from 4.4 to 18 m (Takcidi, 1999). Below the till and limnoglacial–glaciolacustrine sediments in the Apriķi plain, there are grey clay and dolomites of the Upper Devonian. Currently, the lake is surrounded by open fields and scarce stands of pine (*Pinus sylvestris*) and birch (*Betula pubescens*). By having two inflows and one outflow, the lake has a flow-through hydrological regime. The mean annual air temperature in the region is +7°C, and the average annual amount of precipitation is 640 mm.

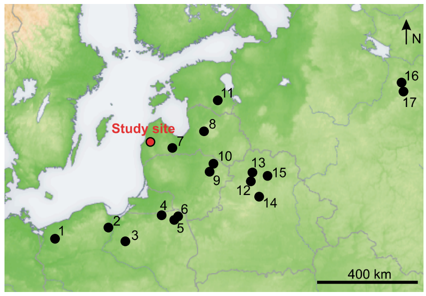

Figure 1. Location of the studied site – Lake Ķikuru and thermokarst sites discussed in the text: (1) River Rega valley (Cedro, 2007); (2) Lake Gniew (Błaszkiewicz and Gruszka, 2005); (3) Lake Retno (Karasiewicz et al., 2014); (4) Lake Czarne (Karpińska-Kołaczek et al., 2014); (5) Lake Linówek (Gałka et al., 2014); (6) Lake Kojle (Gałka et al., 2015; Gałka and Sznel, 2013), Poland; (7) Viki Bog (Kalnina et al., 2015); (8) Lake Ķūžu (Terasmaa et al., 2013), Latvia; (9) Lake Baltys (Šeirienė et al., 2009), (10) Lake Petrašiūnai (Stančikaitė et al., 2009), Lithuania; (11) Lake Juusa (Punning et al., 2005), Estonia; (12) Lake Lozoviki, (13) Lake Mezhuzhol, (14) Lake Sudoble and (15) Lake Krivoe (Novik et al., 2010), Belarus; (16) Lake Chashitsy and (17) Lake Zaozer'e (Wohlfarth et al., 2006), Russia. Source of the map: https://upload.wikimedia.org/wikipedia/commons/b/b7/Europe_topography_map.png; Author: San Jose, modified. The figure is available in colour at online version of this article.

Material and methods

Coring

Sampling of sediments in Lake Ķikuru was performed in March 2013 using a Russian-type corer with a diameter of 10 cm through the ice at the deepest part of the lake. Samples were transformed to 1-m plastic semi-tubes wrapped in plastic film and delivered to the laboratory, where they were kept in a cold room under a constant temperature of 4°C prior to further analyses.

Chronology

The chronology of the whole sediment sequence was based on ^{14}C radiocarbon dates from 12 bulk samples and 4 samples of terrestrial plant remains. Conventional dating was performed at the Institute of Geology at Tallinn University of Technology (Tln), and AMS terrestrial plant remains were measured in the Poznan Radiocarbon Laboratory (Poz). Individual radiocarbon dates were converted to calendar years using the IntCal13 calibration dataset (Reimer et al., 2013) with a 2σ (95.4%) confidence level in Clam

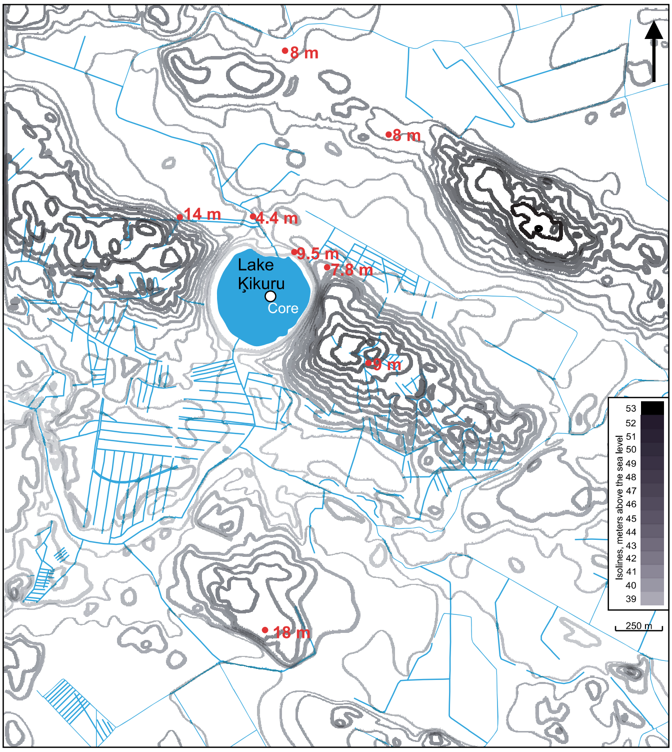

Figure 2. Topography of study area. Elevation isolines from black (higher) to light grey (lower) lines. River/irrigation system and lake indicated in blue colour. Location of coring point in Lake Ķikuru is shown. By red dots marked thickness of Quaternary sediment in vicinity according to Takcidi (1999). The figure is available in colour at online version of this article.

2.2 (Blaauw, 2010), and an age–depth model was produced using Bayesian software Bacon 2.2 (Blaauw and Christen, 2011) because the Bayesian approach provides more robust estimates of uncertainty than classical age–depth methods. For both, we used the R environment (version 3.0.3) (R Core Team, 2014).

Loss-on-ignition and magnetic susceptibility

The dry weight of 1-cm-thick subsamples with a 2-cm^3 volume was determined after oven-drying at 105°C until a constant weight. The organic matter content of the sediment was determined by loss-on-ignition (LOI) at 550°C for 4 h. The bulk density (g cm^{-3}) was calculated on the base of the LOI for all samples. The magnetic susceptibility was measured with a Bartington MS2E meter (Nowaczyk, 2001).

Geochemical analysis

The weight percentages of total organic carbon (TOC) and total nitrogen (TN) in freeze-dried acid-treated sediments were determined through combustion in a FLASH 2000 Organic Elemental Analyser. For the measurements, BBOT ($C_{26}H_{26}N_2O_2S$) or Cystine was used as a standard (ThermoFisher Scientific), and the algae *Spirulina* or a high-organic sediment was used as reference material (IVA Analysentechnik e. K). Analyses were performed in triplicate. The TOC/TN (C:N ratio) values are expressed as atomic ratios and were calculated to estimate the origin of the organic material (Meyers and Teranes, 2001). In addition, carbon accumulation rates (CAR, g C m^{-2} yr^{-1}) were estimated for each depth where C concentration measurements were available according to van der Linden et al. (2014): CAR = $r \times C \times \rho$, where r is the sediment accumulation rate, C is the carbon concentration and ρ is the bulk density.

Pollen analysis

Pollen subsamples were treated with 10% HCl, boiled in 10% KOH and then acetolysed for 5 min using a standard acetolysis procedure combined with a concentrated HF treatment to remove inorganic matter (Berglund and Ralska-Jasiewiczowa, 1986). At least 500 terrestrial pollen grains per sample were counted to the lowest possible taxonomic level using published pollen keys, and the reference collection was stored at the Institute of Geology at Tallinn University of Technology. The percentage of terrestrial taxa was calculated using arboreal (AP) and non-arboreal (NAP) pollen sums (excluding sporomorphs of aquatic and wetland plants). Non-pollen palynomorphs (NPP) were recorded throughout the pollen analysis and identified using the published literature listed in Miola (2012) as well as the descriptions of Jankovská and Komárek (2000) and Sweeney (2004). The counts of spores and NPP were calculated as percentages of the total sum of terrestrial pollen plus the number of spores or NPP. A pollen and NPP diagram was compiled using TILIA 1.7.16. software (Grimm, 2011), but zonation was set according to the changes in the lithology of the sequence.

Plant macrofossil analysis

Plant macrofossils were analysed at continuous 1-cm intervals. The material was rinsed on 0.25- and 0.5-mm mesh size sieves. Macrofossils of the selected plants were studied with the use of a Nikon SMZ800 stereoscopic microscope at magnifications of 10–200 and

Table 1. Radiocarbon dates of Lake Ķikuru sediment.

Laboratory code	Depth (cm)	^{14}C date (yr BP)	Calibrated age (cal. yr BP, 2σ)	Material dated
Poz-53110	525–526	845 ± 30	690–895	Gyttja, bulk
Tln3382	572–578	950 ± 50	740–940	Gyttja, bulk
Tln3383	620–626	1475 ± 70	1290–1520	Gyttja, bulk
Tln3384	660–666	1510 ± 50	1310–1450	Gyttja, bulk
Tln3385	760–766	1900 ± 55	1710–1950	Gyttja, bulk
Tln3386	800–806	2270 ± 55	2150–2355	Gyttja, bulk
Tln3387	900–906	2700 ± 70	2720–2960	Gyttja, bulk
Tln3388	940–946	3385 ± 65	3470–3730	Gyttja, bulk
Tln3389	1050–1056	3990 ± 60	4250–4590	Gyttja, bulk
Tln3390	1090–1096	4370 ± 70	4840–5080	Gyttja, bulk
Tln3391	1200–1206	5170 ± 65	5750–6025	Gyttja, bulk
Tln3392	1240–1246	5540 ± 80	6190–6490	Gyttja, bulk
Poz-48432	1364	6270 ± 50	7150–7290	Wood
Poz-72713	1393–1394	7560 ± 50	8300–8445	*Alnus glutinosa*, 9 fruit+1 cone
Poz-48435	1415	7560 ± 40	8320–8430	Wood
Poz-72714	1418–1420	7690 ± 50	8400–8560	*Stachys palustris* seeds

a transmitted light microscope. Species determination of individual plant macrofossils was performed with the help of the following keys: Velichkevich and Zastawniak (2006, 2008) and Hölzer (2010). The results of plant macroremains were plotted using the graphics program C2 (Juggins, 2003). The results were summarised in diagrams in absolute numbers for vascular plants, while for the vegetative parts of mosses, 'one' represents the presence of remains. The plant nomenclature follows Mirek et al. (2002).

Diatom analysis

For diatom analysis, sediment subsamples with fixed volumes (0.4 cm^3) were subjected to sequential treatment with 30% H_2O_2 and 10% HCl to remove organic matter and carbonates, respectively (Battarbee et al., 2001). The microfossil concentration (diatom valves cm^{-3}) was determined by the addition of a known quantity of microscopic divinylbenzene markers to the cleaned sediment slurry. Subsamples were then dried onto the cover glass, mounted onto slides using a Naphrax medium and analysed under a Zeiss Axio Imager light microscope at 1000× magnification using oil immersion and differential interference contrast optics. Diatoms were grouped according to their habitat into plankton and periphyton, the latter including benthic, epilithic and epiphytic life forms.

Statistical analyses

Principal component analysis (PCA) using CANOCO 4.5 (Ter Braak and Šmilauer, 2002) was performed to explore the general changes in the pollen and plant macrofossil data. A square root transformation was applied to stabilise variances.

Because calibrated dates often have asymmetric probability distributions spanning decades to centuries, the mean age derived from an age model will not always represent the most probable age (Blaauw and Christen, 2011; De Vleeschouwer et al., 2012). To evaluate the chronological uncertainties of proxies, we used a function named *proxy.ghost()* (Blaauw and Christen, 2011, 2013) in Bacon 2.2 software and analysed the pollen and plant macrofossil PCA axis 1 because it represents the general pattern of changes in local and regional vegetation. The proxies analysed along the depths of a core were plotted as graphs against the calibrated age, where chronological uncertainties of age were taken into account. Through this test, we assessed the variability of the proxy signals (indicating the most credible time of changes in vegetation), which is most likely a more accurate way of characterising the chronologies of proxies in a studied sequence.

Results

Lithology

The obtained sediment thickness reached 1050 cm, but in this study, we used the lowermost part of the sequence, 1420–1355 cm (depth indicated from the ice). Lithologically, the cored sequence consists of greyish-brown till, the upper 4 cm darkened with mixed humus (1450–1430 cm); dark-brown to black humic sandy silt resembling a terrestrial soil (1430–1415 cm); dark-brown to black, highly decomposed peat (1415–1388 cm); brown coarse-detritus gyttja (1388–1378 cm) and brown homogeneous gyttja (1378–1355 cm) (Supplementary Material 1, available online). It is important to mention that there were no visually abrupt changes in lithology, and the sediment transitions were gradual.

Chronology

Dating results from the basal part of the sediment core reveal an age of 8400–8560 cal. yr BP (Table 1). Seeds of the terrestrial plant *Stachys palustris* (marsh woundwort) were collected from the soil sediment section. It is known that *Stachys palustris* is a terrestrial near-shore habitant of lakes and damp meadows (Taylor and Rowland, 2011). Because there were no dating offsets, we can argue that the basal sediment started to accumulate from 8560 to 8400 cal. yr BP. Additionally, other AMS dates from the peat layer show reasonably close ages and therefore maintain the timing of the onset of the middle-Holocene. The age–depth model indicates sedimentation changes at approximately 7500 cal. yr BP (Figure 3).

Based on visual and analytical analyses of the sediment sequence, there were no abrupt changes in the lithology at that time, which eliminates the presence of a possible hiatus. The age–depth curve shows projected changes – a higher sedimentation rate for peat and a lower rate for the gyttja section. Finally, the assessment of the proxy chronological uncertainties indicates a narrower uncertainty for the beginning and end of the studied sequence (Supplementary Material 2, available online). In fact, the darker colour in Supplementary Material 2, available online, indicates a smaller modelled age uncertainty, while the grey-pale colour displays a larger uncertainty. Given that the larger uncertainty in the middle section underscores the possible bias of proxy signal differences in timing, there is less uncertainty at the beginning and end of the studied sequence, which indicates the most credible age of the vegetation change. The overall resolution of our chronology and results are reliably high, which allows us to convincingly discuss kettle-hole formation and its filling with organic matter at the onset of the Holocene Thermal Maximum in western Latvia.

Organic matter and magnetic susceptibility

The sediment organic matter values were below 20% until 8390 cal. yr BP, when they rose abruptly to 70% (Figure 4). They remained elevated within peat and decreased starting 8000 cal. yr BP. The magnetic susceptibility decreased from 4×10^{-5} in soil to -2×10^{-5} in peat. Subsequently, it rose steadily in gyttja, reaching 2×10^{-5} (Figure 4f), indicating a minor increase in ferromagnetic mineral inwash from the catchment.

C:N ratio and CAR

The TOC contents range from a minimum of 8.9% to a maximum of 43.2% by weight. The base of the core had the lowest values, followed by a steady increase to maximum values. After the peak values at 1395 cm, the TOC content starts to gradually decrease towards the top of the core. TN values vary between 0.5% and 2.7% by weight and almost mirror the oscillations of the TOC contents' curve (Figure 4b). The calculated C:N ratios vary between 14.9 and 23.2; the highest values characterise the base of the core, and the lowest values characterise the topmost samples (Figure 4d). Meanwhile, CAR reaches 20 g C m^{-2} yr^{-1} at approximately 8300 cal. yr BP (Figure 4e) and decreases to as low as 3 g C m^{-2} yr^{-1} in gyttja, except at 7500 cal. yr BP, when it increases to 8 g C m^{-2} yr^{-1}.

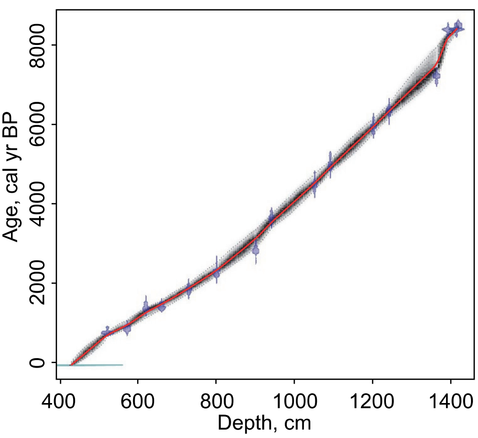

Figure 3. Age–depth model of Lake Ķikuru. Age–depth model based on ^{14}C (purple) dates. The red curve shows the weighted mean ages of all depths, whereas greyscales show uncertainties (where darker grey indicates more certain section). The figure is available in colour at online version of this article.

Biostratigraphic evidence of environmental change

A detailed description of the results of pollen, non-pollen palynomorphs, diatoms and plant macroremains are given in Table 2, but a visualisation is presented in Figures 5 and 6.

In comparison to pollen, which may travel and settle in a sampling point from local to regional areas, plant macrofossils are usually transported short distances and thus indicate a strictly local plant presence. Because there are pollen and plant macroremains that are not preserved over time and give us a partial picture about the temporal vegetation cover, we use both pollen and plant macrofossils to characterise the local vegetation dynamics during the formation of the kettle-hole because their data supplement each other. Overall changes in the pollen PCA axis 1 are shown in Figure 4a and represent local to regional vegetation dynamics. Increased changes occurred during peat formation, and later, the trend of change was gradual. Plant macrofossil PCA1 showing local vegetation changes indicates a principal change at the peat-gyttja boundary (Figure 4h). It is noteworthy that fish remains were found exclusively in gyttja starting at 7800 cal. yr BP (Figure 4h), indicating a lacustrine environment.

Diatoms are beneficial indicators of environmental conditions, especially of aquatic conditions (but not exclusively). In the case of kettle-hole formation, they can provide evidence about changes in water levels or lake trophic states. This aspect is crucial to reveal the time at which more nutrients were entering the water and to determine whether it was a deep or shallow water body. A similar core is for other algae that have been identified during the pollen analyses (Figure 5, Table 2) and are commonly named by palynologists as non-pollen palynomorphs.

Discussion

Evidence of the gradual ice-block meltdown and nature of abiotic and biotic processes

The lithology of Lake Ķikuru, particularly the soil above the till, implies a sedimentation gap between deglaciation and kettle-hole formation. Unfortunately, it was not possible to distinguish possible gleization or to establish the degree of maturity of soil that could be helpful in determining the conditions prevailing between the accumulation of till and of the basal-peat layer. Nevertheless, based on the dating results of terrestrial plant

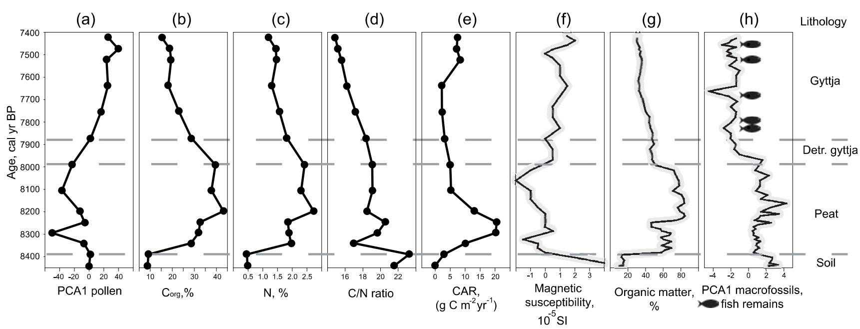

Figure 4. Results of (a) principal component analysis axis 1 of pollen data (PCA 1); (b) C_{org}, %; (c) N, %; (d) C:N ratio; (e) CAR, g cm^{-2} yr^{-1}; (f) magnetic susceptibility, 10^{-5} SI; (g) organic matter, % and (h) plant macroremain principal component analysis axis 1 of plant macrofossil data (PCA 1) and indication of fish remains. Zones are according to lithology.

Table 2. Lake Ķikuru pollen and non-pollen palynomorphs, plant macroremain and diatom results described according to lithological zones.

Depth (cm); age (cal. yr BP); lithology	Pollen and non-pollen palynomorphs	Plant macrofossils	Diatoms
1378–1355; 7850–7450; homogeneous gyttja	Broadleaved trees dominate (*Corylus* 35%, *Ulmus* 15% and *Alnus* 10%). Poaceae values below 10%. Presence of HdV 44, HdV 7, HdV 126, HdV 143. Highest values for HdV 601 around 7600 cal. yr BP. Abundance of microcharcoal at 7650 and 7425 cal. yr BP.	Continues abundance of *Sphagnum* sec. *Acutifolia* and *Sphagnum* cf. *angustifolium*. Two finds of *Pinus sylvestris*. *Chara* sp. at 7900 cal. yr BP. Only find of *Najas marina* at 7450 cal. yr BP. Presence of fish teeth and scales exclusively in this zone.	In the lowermost part of gyttja, diatoms still bear signs of dissolution, and therefore, total diatom concentration is low. Since 7500 cal. yr BP diatom preservation is fine and concentration distinctly increased to >1000 × 10^4 valves cm^{-3}. At around 7500–7400 cal. yr BP eutrophic planktonic *Stephanodiscus parvus* predominate. Thereafter, *Stephanodiscus parvus* undergoes an abrupt decline and is replaced by diatoms like *Cyclotella comta, Fragilaria capucina* and *Tabellaria flocculosa* that grow in the waters with reduced nutrient availability.
1388–1378; 8000–7850; coarse-detritus gyttja	Increase in *Corylus* from 10% to 20% and *Tilia* from 1% to 3%. Decrease of Poaceae from 50% down to 20%. Polypodiaceae stable with 10%. Only find of HdV 263 at 7870. Two charcoal peaks at 7990 and 7870 cal. yr BP. Appearance of *Coelastrum reticulatum* at the end of zone.	Zone is characterised by the presence of *Carex pseudocyperus, Carex* sp., *Typha* sp., *Nuphar lutea* and small amount of *Alnus glutinosa*.	Diatoms are not well preserved and often bear signs of dissolution. The total diatom concentration is low 20 × 10^4 valves cm^{-3}. Periphytic diatoms have the highest relative abundance.
1415–1388; 8400–8000; peat	Decrease of *Betula* from 25% to 10%, *Picea* from 5% to 1%. *Alnus* peak up to 45% at 8200 cal. yr BP. Polypodiaceae values at 50% until 8300 cal. yr BP, then decrease down to 5% and increase up to 10% at the end of the zone. Poaceae values as high as 50% around 8350 cal. yr BP, 15% at 8200 cal. yr BP and 50% at the end. HdV 1103 peak around 8250 cal. yr BP, but absence of HdV 44 at this time. Otherwise HdV 44 is abundant throughout the zone. Presence of HdV 113, HdV 55, HdV 92, HdV 126, HdV 575 and HdV 13. Two points of Pinus stomata at 8300 and 8250 cal. yr BP.	Variety of plant remains including *Carex pseudocyperus, Solanum dulcamara, Urtica dioica, Ranunculus lingua* and *Iris pseudacorus* continues record of undefined wood. Peak distribution of *Alnus glutinosa* from 8200 to 8150 cal. yr BP with a less pronounced concentration around 8080 cal. yr BP. Presence of *Nymphaea alba* and *Typha* sp. at the base of zone.	Siliceous microfossils in the peat are sparse and the total diatom concentration is extremely low <10 × 10^4 valves cm^{-3}. Diatoms found are planktonic centric species, notably *Cyclostephanos dubius, Cyclotella comta* and *Stephanodiscus parvus*.
1430–1415; 8500–8400; soil	Domination of Polypodiaceae. Increase in all trees and herbs. Mixed broadleaved and conifer tree composition. Highest values of *Juniperus* (5%) at the end of the zone. Abundance of HdV 44, HdV 55, HdV 113, HdV 7 and HdV 112. HdV 96A is present only in this zone. Highest values of EMA 7–9.	Continuous record of undefined wood. Presence of fungi remains (*sclerotia*), *Urtica dioica, Moehringia trinervia* and *Stachys palustris* until the 8400 cal. yr BP. One find of *Viola palustris* at 8430 cal. yr BP. Macroscopic charcoal record around 8410 cal. yr BP.	Devoid of diatoms.

macrofossils from a soil layer (Table 1, Figure 3), it is evident that the soil was formed before 8500 cal. yr BP. Succession from soil to peat in the Ķikuru Basin infers the initiation of melting of the subsurface ice-block and points to a gradual transition from terrestrial to wetter site conditions as well as the establishment of a moist swamp with the deposition of the thin basal layer of peat (Supplementary Material 1, available online). The origination date of the basal-peat layer is from 8400 to 8000 cal. yr BP. The transition from peat to coarse-detritus gyttja implies further melting of the buried ice-block, formation of the kettle-hole depression that concurrently was filling with water and organic sediment, and formation of a lake with a rapid deepening of the water depth after 8000 cal. yr BP (Figure 7). This scenario is also supported by the C:N ratio. Expectedly, the highest C:N ratio was at the base of the core, where the sediment sequence consists of soil and peat. The clear terrestrial plant material C:N signal is also confirmed by the presence of terrestrial macrofossils (Figure 6, Table 2). Further limnological development of the lake is reflected by a gradual decreasing trend of the C:N ratio, suggesting that organic matter originating from lacustrine sources grew more important over time. Variations in the C:N ratio suggest that both terrestrial and in-lake production have been important sources of organic matter in Lake Ķikuru (Meyers and Ishiwatari, 1993).

The diatom composition within the peat layer, including planktonic species, such as *Cyclostephanos dubius*, *Stephanodiscus parvus* and *Fragilaria crotonensis*, are not characteristic of sub-aerial habitats (Johansen, 2010) or wetlands (Gaiser and Rühland, 2010). Instead, they imply eutrophic deep-water lake conditions and are rather similar to the diatom composition in the overlying gyttja layer. The infiltration of single diatoms from settling gyttja into the peat matrix with high porosity and vertical downwards penetration deeper into the peat layer might explain the controversial diatom content within the peat. The aforementioned phenomenon is also supported by the very low diatom concentration in peat (Figure 5b).

The diatom stratigraphy supports the formation of a lake depression with relatively deep water at the onset of the Holocene

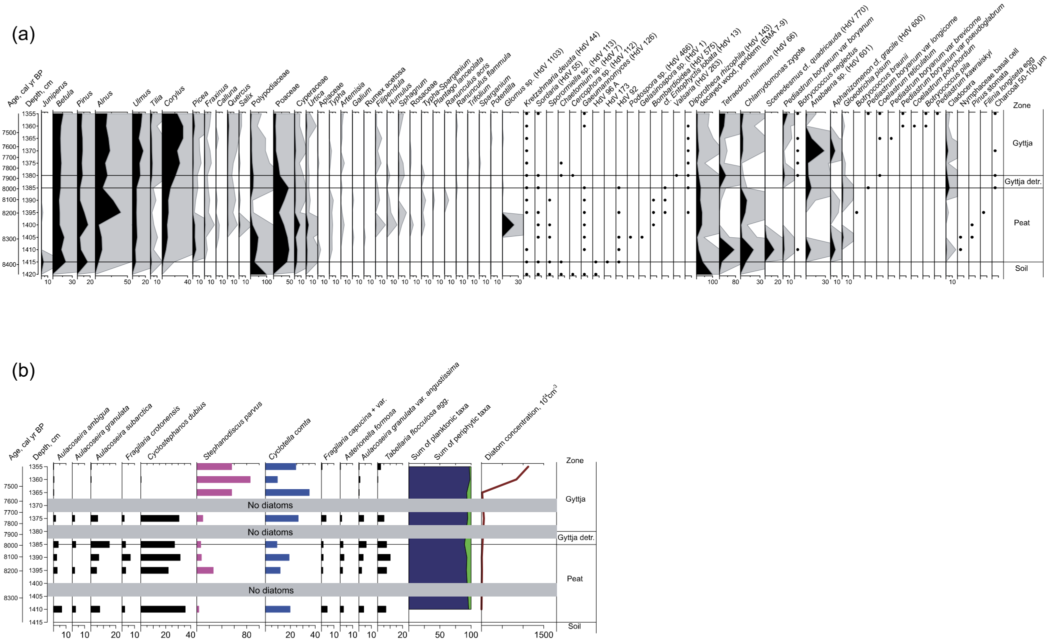

Figure 5. (a) Percentage pollen and non-pollen palynomorphs and (b) diatom diagram from Lake Ķikuru. The grey curves show 10× exaggeration of the pollen and non-pollen palynomorphs percentage values. Ratio of planktonic and periphytic taxa and concentration of diatoms are shown. Zones are divided according to lithology.

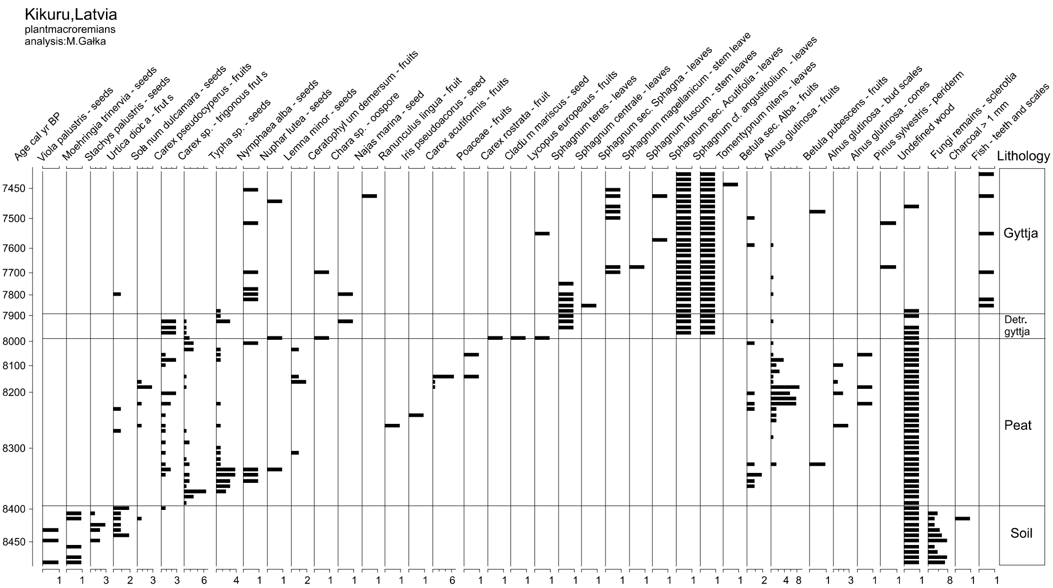

Figure 6. Plant macrofossil concentration diagram. Zones set according to lithology.

Thermal Maximum in western Latvia. Newly formed limnic environments are often eutrophic and become more dilute over time (e.g. Engström et al., 2000). Similarly, *Stephanodiscus parvus* and other eutrophic planktonic diatoms in the lowermost gyttja sequence of Lake Ķikuru sediment suggest a nutrient-rich lake environment. However, within a relatively brief period from ca. 8000 to 7400 cal. yr BP, a decrease in eutrophic diatoms and increase in diatoms that do not tolerate a high-nutrient content, such as *Cyclotella comta*, indicate that the lake underwent rapid oligotrophication.

Meanwhile, the results of pollen and non-pollen palynomorphs analyses showed that parasitic fungal spores of *Kretzschmaria deusta* (HdV 44) were present in the bottommost soil layer (Figure 5a). These spores are evidence of the existence of broadleaf trees (*Fagus* and/or *Tilia*) in the vicinity (Latałowa et al., 2013; van Geel et al., 2013) earlier than 8500 cal. yr BP. In

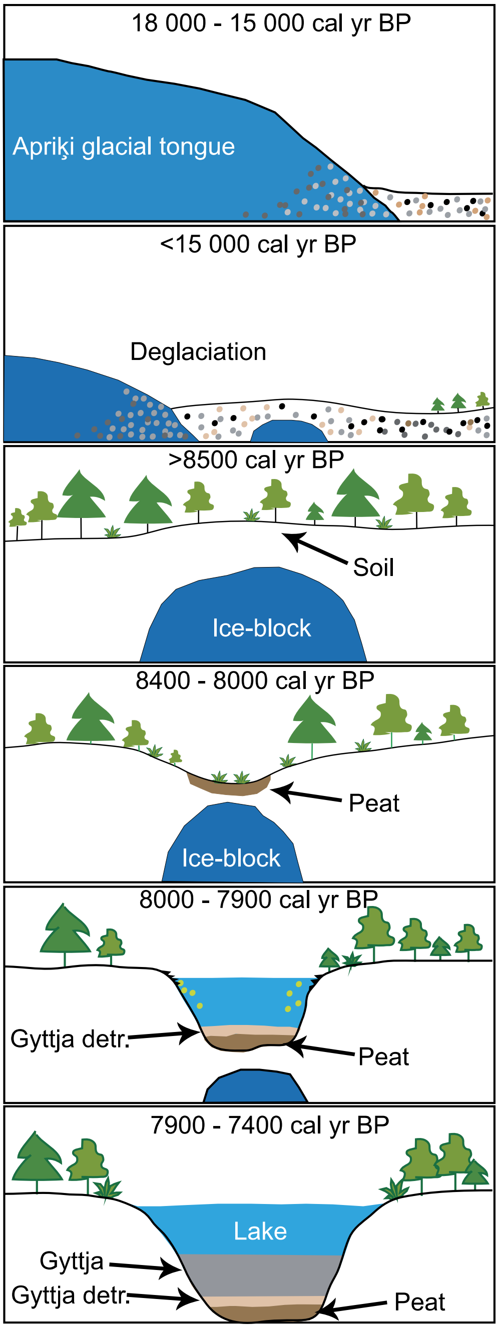

Figure 7. Schematic reconstruction of geomorphological evolution of Lake Ķikuru kettle-hole.

case of *Tilia*, it has been growing in Latvia since 9500 cal. yr BP (Kangur et al., 2009; Stivrins et al., 2014), which provides additional confidence that we are dealing with early-Holocene terrestrial material. In addition, undefined wood material and decayed wood periderm in the soil may indicate a local presence of shrubs or trees (Figure 6). Macrofossils of *Viola palustris*, *Moehringia trinervia*, *Stachys palustris* and *Urtica dioica* in a soil layer suggest a wet meadow community type at the coring site at that time (Ellenberg et al., 1991; Zarzycki et al., 2002).

During the initial phase of peat formation, plants (*Nymphaea alba*, *Nuphar lutea* and *Typha* sp.) typically growing in the near-shore zone or in shallow lakes (Gałka et al., 2015; Hannon and Gaillard, 1997) were present (Figure 5). The presence of *Typha* sp. at approximately 8300 cal. yr BP suggests that the mean July air temperature could be at least 15–16°C (Väliranta et al. 2015). The marked concentration of *Alnus glutinosa* (a tree typical around waterbodies and wet areas) remains from 8240 to 8060 cal. yr BP advocate seasonally relatively wet terrestrial conditions like those of *Alnus* carr. The overall macrofossil PCA first axis shows major changes in local vegetation in the transition zone from a fen to a lake from 8000 to 7950 cal. yr BP, with the first fish existence since 7820 cal. yr BP as a clear indication of the deepening of the kettle-hole and the existence of a lacustrine environment (Figure 4h). In this sense, local vegetation succession displays gradual changes from a terrestrial to an aquatic environment.

In addition to vegetation dynamics, we also track signs of fauna interaction that at some point may influence surface-landscape processes. The presence of large herbivores, for instance, can change vegetation cover and may further effect local hydrology (Bakker et al., 2015; Beach et al., 2015; Salemi et al., 2012), thus also influencing buried ice-block, that is, enhancing the melting of ice-block. The composition of coprophilous fungi spores from soil and peat, such as *Sporormiella* sp. (HdV 113), *Sordaria* (HdV 55), *Podospora* sp. (HdV 466) and *Bombardioidea* (HdV 575), confirm herbivore activity in the local vicinity (Figure 5a). Especially interesting is the record of *Bombardioidea*, a dung inhabiting fungus, which has been linked to the presence of moose (*Alces*) (Bos et al., 2005). A recent study by Bergman and Bump (2015) showed that the abundance of moose in the vicinity of a lake positively correlates to changes in the diversity of macrophyte species in glacial lakes. In addition, moose consume both aquatic and terrestrial vegetation. In fact, the movement of large herbivores between both aquatic and terrestrial habitats can impact the entire fen and lakeside zone, hence affecting the local landscape and surface geomorphological features (Bakker et al., 2016). The soil, but mostly the peat layer from which the coprophilous fungi spores were found, already indicates that the ice-block melting process was initiated, and it is difficult to say whether there was a link between biota and ice-melting or not. Thus, more studies must be performed in the future to test the effect of such aspects on the meltdown of ice-block.

Thermokarst: Implications for CAR

Our results illustrate the increased CAR during the initial phase of peat formation, when values reached 20 g C m^{-2} yr^{-1} between 8300 and 8200 cal. yr BP (Figure 4e). Comparable values have been recorded from a subarctic fen in northern Finland, where during the initiation phase of the fen, the CAR was as high as 17 g C m^{-2} yr^{-1} (Mathijssen et al., 2014). The subsequent results of newly formed moist fen not only show C capture but likewise an increase of emitted CH_4 (Korhola et al., 2010; Swindles et al., 2015). Nevertheless, deglaciation and the subsequent thawing thus cannot only initiate increased emissions of CO_2 and CH_4 but in a case of dead-ice melt-out, certain peat layers can gradually sink to the bottom of newly formed lakes, thus storing C.

Environmental factors behind delayed thermokarst

Our study reveals that although the majority of Central and Northern European dead-ice melted during the warmest phase of the Late Glacial period and in the early-Holocene (Błaszkiewicz, 2011; Błaszkiewicz et al., 2015; Gałka and Sznel, 2013;

Michczyńska et al., 2013; Stančikaitė et al., 2009; Słowiński et al., 2015; Terasmaa et al., 2013), scattered dead-ice-blocks could have been preserved in the landscape until the Holocene Thermal Maximum. There are several climatic, environmental and geomorphological characteristics that could possibly prolong the survival of dead-ice in western Latvia. Saks et al. (2011) imply that a glacial ice tongue was active in the study area until approximately 15,000 cal. yr BP, and we can assume that deglaciation there took place since then. Lake Ķikuru lies within a small drumlin field that is surrounded by a chain of marginal moraines that probably add more complexity and possibilities for dead-ice to be buried by a layer of thicker erratic material. This is also evident from the topography of the studied site. Lake Ķikuru lies in the middle of a ridge that was most likely one ridge at first and not split into two parts, which is the current topography (Figure 2). It is rather difficult to determine the exact thickness of the overlying sediment at the sampling point, but based on the thickness of Quaternary sediment around a lake, it can vary from 4.4 to 18 m (Figure 2). These variations can be seen even within a relatively short distance. There is almost a 13 m difference from the highest point of the ridge to the lake's water level. In addition, the change is quite rapid, as it occurs within 300 m. If we were to consider that this was once one ridge, then we can assume that the overlay material must have been of a similar thickness at least. This aspect could support the idea of thicker material overlay.

Commonly, the waning ice sheet margin would lead to a development of an ice-rich periglacial permafrost landscape and subsequent thermokarst processes. Even today, relict permafrost from the Last Glacial period can be found deep in the ground in Central Europe (Szewczyk and Nawrocki, 2011), showing the complexity of permafrost disappearance. Of course, it would be incorrect to assume a permafrost presence in western Latvia 5500 years after ice retreat given that there is no direct evidence for such conditions in this particular area. In this regard, the overlying material can play a significant role. Basal material in the core suggests till as the overlying material over buried ice-block, which could possibly hold or delay thermal conductivity from fully reaching the ice-block. Till, consisting mainly of clay and silt fractions, has poor thermal conductivity (Farouki, 1981; Schomacker, 2008; Östrem, 1959) which in combination with the lower geothermal heat in the study area (Kalm et al., 2011) may prolong the survival of ice-block. Due to these aspects, it is not excluded that exceptional conditions prevailed until 8500 cal. yr BP that probably also included constantly cold conditions around the ice-block in the ground for a certain time period.

In her study, Maizels (1977) carried out experimental work to find the origin of kettle-holes. In a transparent container filled with fine sediment, several ice-blocks were placed on the surface, partly buried and buried. After melting, the buried ice-block resembled a wide, deep and permanent kettle-hole similar to those observed in proglacial outwash plains (Fay, 2002). In addition, the depth and shape corresponded to the thickness and shape of the buried ice-block. The shape of Lake Ķikuru is circular, and without organic sediment, its depth would reach almost 15 m; thus, it can be assumed that the ice-block could be of a similar size.

Likewise, if compared with the Late Glacial period and early-Holocene when the majority of ice-blocks melted in Europe, significantly different environmental and climatic conditions prevail (Feurdean et al., 2014; Gałka and Sznel, 2013; Kalnina et al., 2015; Muschitiello et al., 2013; Stivrins et al., 2015; Veski et al., 2015). Veski et al. (2015) observed a geographical divergence in the rise of early-Holocene paleotemperatures. Their study shows that winter temperatures reached modern values 1000 years earlier in Belarus (10,000 cal. yr BP), while in Latvia and Estonia, these temperatures were reached at 9000 cal. yr BP. The length and severity of winter limit the growing season for vegetation and, under certain circumstances, can either support the prolongation of cold conditions in the ground or increase thawing. In addition, the temperature simulations of Renssen et al. (2012) expose a delay of the Holocene Thermal Maximum by 2000–3000 years over Europe compared with the insolation maximum. Given that arise when the mean summer air temperature gradually increased by approximately 2°C beyond modern temperatures (Heikkilä and Seppä, 2010) and that there is a low correlation between the ice-block melt rates and climate parameters (Schomacker, 2008), we can argue that the Ķikuru ice-block was deep enough to be secure from surficial landscape transformation processes.

One may argue that what we see is a groundwater increase and that the kettle-hole was actually dry until 8000 cal. yr BP. In this respect, we would like to draw attention to the fact that water level studies from a region indicate a higher water level stand prior to and a lower water level during the middle-Holocene (Gryguc et al., 2013; Hammarlund et al., 2003; Sohar and Kalm, 2008). Additionally, the relatively close Baltic Sea (30 km to west from the study site) does not support rapid changes in the groundwater level due to the rather constant interplay between land uplift and eustatic sea-level rise in Latvia (Grudzinska et al. unpublished).

Hydrological and climatic changes after the last ice retreat have been put forward as the main force behind the disappearance of thermokarst from Europe. By using a comprehensive dataset of basal-peat ^{14}C dates from northern Poland, it has been shown that in particular, the Bølling-Alleröd and early-Holocene warm interglacial periods have a massive disappearance of permafrost and dead-ice meltdown (Cedro, 2007; Michczyńska et al., 2013; Niewiarowski, 2003). Similar observations have been documented in northern Germany, Belarus, Russia, Estonia and Lithuania (Figure 1) (Cedro, 2007; Kaiser et al., 2012; Michczyńska et al., 2013; Niewiarowski, 2003; Novik et al., 2010; Punning et al., 2005; Stančikaitė et al., 2009; Wohlfarth et al., 2006). Numerous studies on river valleys suggest dynamic hydrological network changes with the disappearance of permafrost and dead-ice. A study by Słowiński et al. (2015) regarding hydrological changes of the Wda River valley in northern Poland indicates that discontinuous permafrost was present until the onset of the Holocene. They dated the buried basal-peat layer from this valley to 11,220 cal. yr BP. Another example of the presence of buried ice-block and its meltdown in northern Poland was provided by Błaszkiewicz (2011) and Błaszkiewicz and Gruszka (2005). In this case, the basal-peat layers indicated ages from 10,550 to 15,600 cal. yr BP. Nevertheless, both studies demonstrated evidence of the influence of buried ice-block meltdown on the geomorphological development, hydrological changes and biotic environment. A contrasting explanation of basal-peat formation is given by Novik et al. (2010). In their study of the development of Belarusian lakes during the Late Glacial period and Holocene, the authors suggest that the formation of the basal-peat layer is linked to the position of the low levels of groundwater. The rationale for taking all of the sediment samples in a littoral zone was not clear, that is, closer to the lake shore and not in the middle/deepest part of the lake can cause a possible bias in the results and interpretation. Similar examples of the occurrence of basal-peat layers in littoral zones of lakes were also documented in Poland (Gałka et al., 2015; Marks, 1996). Nevertheless, the dating results provided indicate that the basal-peat formation in the studied kettle-holes took place from 16,600 to 11,700 cal. yr BP (Figure 1). In comparison, in Lithuania, basal-peat in kettle-holes are dated to 12,900 and 11,000 cal. yr BP (Šeirienė et al., 2009; Stančikaitė et al., 2009). It is worth noting that thermokarst kettle-holes can be absent of a basal-peat layer. Such lakes, for example, are known in Russia (Figure 1) and were formed due to thermokarst thawing at 11,650 and 11,200 cal. yr BP (Wohlfarth et al., 2006), in Estonia at

11,550 cal. yr BP (Punning et al., 2005) and in Poland at 14,000 and 12,750 cal. yr BP (Gałka et al., 2014; Gałka and Sznel, 2013; Karasiewicz et al., 2014; Karpińska-Kołaczek et al., 2014). Regarding thermokarst in Latvia, at least two sites are known to have basal-peat formation (Figure 1). Both reveal a relatively close age of formation of 11,300 cal. yr BP for Lake Ķūžu (Terasmaa et al., 2013) and 10,950 cal. yr BP for Viki Bog (Kalnina et al., 2015). In comparison to the aforementioned sites in Europe and Russia, the Ķikuru kettle-hole suggests an exceptionally late formation. Therefore, our finding is significant because it shows that there might have been buried ice-blocks in the ground even at the onset of the Holocene Thermal Maximum – a time when such features at this latitude supposedly should not exist.

Conclusion

Using a multi-proxy approach, we studied the dynamics of thermokarst characteristics in western Latvia, where thermokarst occurred exceptionally late at the Holocene Thermal Maximum. Our results demonstrate gradual changes from a terrestrial to an aquatic environment, with soil development at first and subsequent fen peat formation that was overlain by gyttja due to ice-block melting and kettle-hole formation. Abiotic and biotic processes following the ice-block melt-out suggest a thermokarst active phase that began 8500 cal. yr BP and lasted at least until 7400 cal. yr BP. Given that thermokarst arise when the mean summer air temperature gradually increased ca. 2°C beyond the modern day temperature, we can argue that before that point, the local geomorphological conditions at the study site must have been exceptional to secure ice-block from the surficial landscape transformation and environmental processes.

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Paper III

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ORIGINAL ARTICLE

Drastic changes in lake ecosystem development as a consequence of flax retting: a multiproxy palaeolimnological study of Lake Kooraste Linajärv, Estonia

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Abstract This study demonstrates the power of multiproxy palaeolimnological analyses in investigating environmental changes in the Lake Kooraste Linajärv ecosystem through historical time in response to flax retting. Flax retting history was proven by applying pollen and macrofossil evidence and by using several biotic and geochemical proxies on a sediment core. Continuous findings of flax pollen and macrofossil remains in lake sediments were considered as strong evidence for the occurrence of retting. Analyses of the well-dated sediment core show the consequences of flax retting in the lake. As a result, the once clear soft water oligotrophic endorheic lake with limited sedimentation has turned into a hypertrophic high-sedimentation lake with anoxic bottom water, strong stratification and intense water blooms. Despite the fact that flax retting was forbidden in Estonia around AD 1950s and retting has not occurred over the last six decades, anthropogenic alterations were so pervasive in the past, that they have prevented any lake water improvements until the present-day.

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Introduction

Flax (*Linum usitatissimum*), whose origins as a domesticated plant probably occurred in the Near East approximately 10,000 years ago (Zohary and Hopf 2000), is one of the earliest cultivated plants used for making cloth, nets, ropes and oil. Flax first spread from the Near East to Europe and the Nile Valley and later on had a very wide biogeographical range spanning western Europe and the Mediterranean, North Africa, western and southern Asia and the Caucasus regions (Allaby et al. 2005; Karg 2011). The oldest European archaeobotanical evidence for cultivated flax derives from north of the Alps and is associated with the Early Neolithic Linearbandkeramik period (5400–4900 BC) (Karg 2011; Harris 2014).

In Estonia, the early cultivation history of flax is poorly understood; the first evidence of probable flax cultivation was derived from archaeological material. Small fragments of fine-woven fabric of linen cloth from a hoard, dated to the 6th century AD (Kriiska et al. 2005), could imply flax cultivation during that time. The oldest *L. usitatissimum* pollen find from Estonia was from sediments in Lake Plaani, southern Estonia, dated to ca. AD 1050, suggesting that flax was among cultivated plants in Estonia from at least the 11th century AD (Niinemets and Saarse 2009).

Documentary evidence indicates that a substantial amount of flax was exported from the Hanseatic towns of the eastern Baltic to Western Europe since the 13th century AD (Sherman 2014), however its production peaked in AD 1860s throughout Europe (Friedlaender and Oser 1953; Bielenberg 2009), also including Estonia (Lepajõe 1997). The growth

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in the linen industry was connected with scarcity of cotton, which was induced by the American Civil War during AD 1861–1865. Based on the Estonian statistical yearbooks (from AD 1881 until the present, including also sporadic data from previous years—1819, 1839, 1869 and 1875), the cultivation area of *L. usitatissimum* increased abruptly in the middle of the 19th century AD indicating clearly the rising demand for flax at that time. At about the same time, the enactment of agrarian reforms took place in Estonia, creating peasants the legal right to buy-out farms from manors (Tarkiainen 2008), which also increased flax cultivation in order to pay for the purchased land (Lepajõe 1997; Veski et al. 2005; Ertl 2008).

Since the historic documentary evidence for flax is incomplete, palynological investigations can provide local details about the history of this crop (Huang and O´Connell 2000; Mehl and Hjelle 2016). However, flax pollen is difficult to detect from sediments due to its low pollen production and poor dispersal abilities. *L. usitatissimum* is known to self-pollinate and many insects also distribute its pollen grains (Williams 1988) which explains why flax is palynologically under-represented in pollen diagrams. In fact *L. usitatissimum* is often only detected as a single pollen grain per sediment sample and even these single findings are considered as strong evidence for the presence of flax cultivation in the nearest vicinity of a lake, or even as evidence of the introduction of the plant itself into the waterbody in order to process the fibre (Veski et al. 2005; Niinemets and Saarse 2007).

When flax has been grown for its fibres several processes must be carried out to obtain fine threads for textile production (Andresen and Karg 2011). One of the main processes for extracting the fibres is retting the plant stems. This can be done by field retting or water retting, the latter is taking place in lakes, rivers or retting pits (Andresen and Karg 2011). Flax retting in small and shallow lakes was a common practise in Estonia. There are 32 lakes called Linajärv in Estonia. Being one of the most common lake names, it is often used independently or as a combination with the location of the lake (Tamre 2006). The word “lina” in the lake name means flax in Estonian. Usually this kind of name indicates that lake has been used for flax retting during its history, but also many other lakes without the name were used for the same purpose. Flax processing detrimentally affected the lakes, leading to hypertrophy, and there are known cases where fibre retting was probably the only or most distinct cause of alterations to some lake ecosystems (e.g. Grönlund et al. 1986; Punning et al. 2004; Bradshaw et al. 2005). Many lakes, the history of which includes flax retting activities, are still experiencing after effects of these actions today.

Evidence for *L. usitatissimum* cultivation and retting is consequently difficult to find in the course of palaeoecological studies. Botanical analysis of a bundle of flax from northern Poland (Latałowa 1998) revealed that there are several weeds, which commonly occur with flax cultivation and can therefore be used as a proxy to infer this agricultural activity. In this way, linking of archaeology and palaeobotany can give us additional information about the flax processing history of the area. Moreover, a real multidisciplinary approach, where besides different palaeobotanical analyses palaeolimnological analyses are used additionally showing the effect of fibre retting on the lake ecosystem, can serve as an indicator of this complex agricultural history. Lake Kooraste Linajärv (LKL) was chosen for this study as it has a known history of intense flax retting in the past.

The study has two main objectives: to investigate the palaeobotanical signature of the flax retting in the lake known for this history; and to assess changes in the aquatic environment in connection with the process of flax retting. We also assess whether the conditions have a trend towards recovery, or whether the impact from previous anthropogenic disturbances has remained. In this multiproxy study, we apply palaeobotanical analyses (pollen, macrofossil) to identify the signal of flax retting, and different palaeolimnological methods (biological and geochemical) to determine the consequences of retting in the lake ecosystem.

Study area

LKL (57°57′47″N; 26°39′48″E) is a small kettle-hole lake of thermokarstic origin and is the highest elevated lake in the region at 117 m above sea level. It is located in southern Estonia in a region of nutrient-poor sandy soils with no agricultural activities in its immediate vicinity (Fig. 1). With simple basin morphology—steep slopes and a small flat central part, the almost circular lake (110 m diameter) is small in area (3.3 ha), is deep (maximum depth 12 m), has no surficial inflow or outflow, and is sheltered from prevailing winds. Due to high slopes around the lake its catchment area is very small, only 3.7 ha and surrounds the lake (Fig. 1b). LKL is strongly stratified meromictic lake, supporting a permanent anoxic bottom water layer that has facilitated the preservation of seasonal rhythms in its sediments (evidence of varve formation). Long-lasting human impacts have also contributed to the anoxia of the bottom water layers of the lake. According to the reminiscences of the local people the LKL was used for flax retting until 1955 (Ott pers. comm.), when retting was banned. Also the name of the lake refers to its use for flax retting and furthermore, in the course of the lake monitoring, remnants of flax boons have been found in littoral sediments (Timm 2002).

Today, LKL is classified as a hard-water hypertrophic lake and extreme seasonal changes in nutrient concentrations and phytoplankton taxonomic composition are common

Fig. 1 Study area: **a** location of study site; **b** location of Lake Kooraste Linajärv and Lake Kooraste Kõverjärv. The coring site is indicated by a white dot, the catchment border with a dashed line. Aerial photo from Estonian Land Survey (2017)

phenomena. Occurrence of intensive water blooms over the entire growing season has been observed almost annually. The lake has been monitored intermittently from 1972 to 1998. Despite the scarcity of measurements, the results of water chemistry confirm a high seasonal environmental variability in the epi- and hypolimnion (ESM 1 Table 1) caused by long-term flax retting activities in the lake, which have also triggered meromictic processes. Carbon dioxide, formed during decomposition of flax in the lake water, produced alkalinity. Nowadays, while water in the epilimnion is still soft, the lower layers have hard, or near the bottom even very hard water. Recurring shifts in the composition of the phytoplankton are common in the lake, in that particular phytoplankton species appear and disappear frequently. Small-sized green algae (*Monoraphidium* spp., *Dictyosphaerium* spp., *Chlamydomonas* spp.), dinoflagellates (*Peridinium* spp.) and cryptophytes (*Cryptomonas* spp.) dominate strongly, while cyanobacteria (*Dolichospermum* spp., *Limnothrix redekei*) are less well represented but sometimes also bloom. During intensive water blooms of green algae, infrequently with cyanobacteria in addition, the biomass in the water column is very high (ESM 1 Table 1) and the colour of the lake water is yellow-greenish. The very different water colour of this lake as compared to other lakes, and through this blooming times, is easily seen in orthophotos of the area, e.g. from the years 2009 and 2011 (Estonian Land Survey 2017). However, sometimes in the middle of summer, a brief clear-water period occurs when the epilimnion is clean and oligotrophic indicators dominate.

Materials and methods

Materials and methods for sampling and chronology, and palaeobotanical (diatoms, green algae, micro-charcoal, pollen, plant macrofossil), geochemical [fossil pigments, total organic carbon/total nitrogen (C/N) ratio, loss-on-ignition, total sulphur (TS), total phosphorus (TP), total iron (Fe)] and statistical analyses are given in ESM 2.

Results

Lithostratigraphy, chronology and sedimentation rates

A sediment core with a length of 377 cm was obtained. The basal sand layer (377–370 cm) is overlain by a 7 cm thick peat layer (370–363 cm) and greenish brown-to-brown homogeneous gyttja (363–91.5 cm). At depth 91.5–72.5 cm a visually indistinguishable sandy/silty gyttja section follows, which is overlain by homogeneous gyttja layer (72.5–60.3 cm). The sediment sequence from 60.3 cm to the substrate surface is composed of a monotonous repetition of laminated organic lake sediment, in which couplets (e.g. varves) consist of a greenish-to-brownish light grey layer and a brown-to-black dark layer (Fig. 2). These laminae are assumed to represent annual deposition cycles. The thickness of a single lamina couplet ranges from 20 mm in the upper part of the section to 2 mm in the lower part of the laminated sequence.

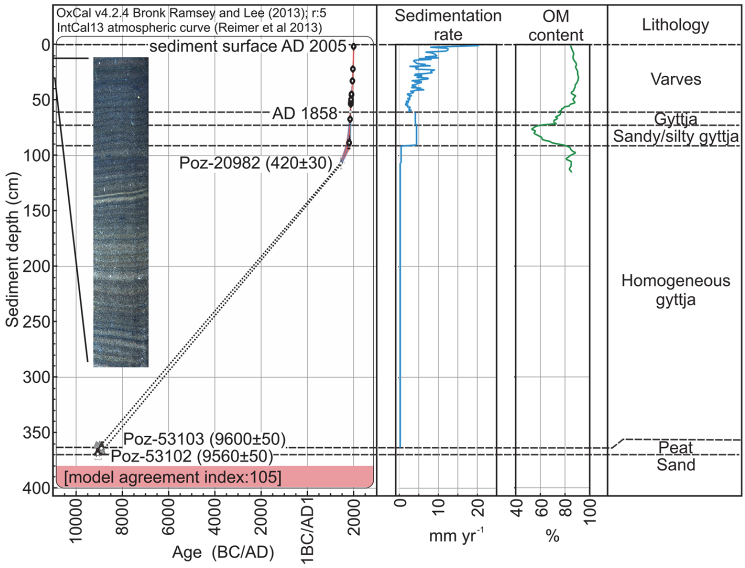


Fig. 2 Age-depth model, sedimentation rate, organic matter (OM) content and lithology for the Lake Kooraste Linajärv sediment core. The graphs on the age-depth curve show the likelihood (grey) and posterior (black) probability distribution of the calibrated radiocarbon dates. The white circles represent the median calibrated ages. Uncalibrated radiocarbon dates are given in brackets. Black dashed lines mark the lithological boundaries. Photograph of varved sediment section covers the 12–30 cm depth interval

The chronology of the LKL sediment (Fig. 2) is based on the combination of AMS ^{14}C measurements on terrestrial plant macrofossils (ESM 3 Table 1) and varve counts. According to the age depth model the peat layer at a depth 370–363 cm accumulated before 9040–8780 BC (median age 8900 BC). Our previous study (Stivrins et al. 2017) in western Latvia, Lake Kikuru, had a similar thermokarstic origin and showed no hiatus on the peat/gyttja border, suggesting/indicating that gyttja accumulation in LKL started at approximately 8900 BC. Homogeneous gyttja (363–91.5 cm) accumulation continued up to AD 1710–1840 (median AD 1780) followed by sandy/silty gyttja (91.5–72.5 cm) that accumulated until AD 1810–1850 (median AD 1830) and homogeneous gyttja (72.5–60.3 cm) until AD 1858. In the upper part of sediment sequence, a total of 140 varves were counted (with the varve counting error estimate of ± 3 varves or ± 2%), with the first complete varve accumulating in AD 1858 (at 60.3 cm depth) and the last forming in AD 2005 (sediment surface).

All proxies of this study were analysed from the upper 115 cm long section of the core, which according to age-depth model (Fig. 2), corresponds to the time interval since AD 1200, i.e. covering the last ca. 800 years. The average sedimentation rate from depth 364–107 cm (8900 BC up to AD 1450) was low, approximately 0.25 mm year^{-1}. From the depth of 107 cm up to 60.3 cm (AD 1450–1858), the average accumulation rate rose to 1.2 mm year^{-1}. Within that interval at a sediment depth from 90 to 70 cm, a high mineral matter (MM) content was observed (Fig. 3), suggesting probably a higher sedimentation rate (ca 4 mm year^{-1}) at this level. The sedimentation rate within lower varves was ca. 2.5 and up to 20 mm year^{-1} in the upper varves.

Geochemistry

MM content is low throughout the studied sequence (10–15%), with an exception in sandy/silty gyttja layer at a depth of 91.5–72.5 cm (ca. AD 1780–1830) (Fig. 3), where it reaches its maximum value of 47%. Carbonate content is below or around 1% for most of the studied core except at the depth 60.3–54 cm (ca. AD 1858–1880), where the first varves form, it is up to 14% in several sub-samples. Organic matter (OM) values are high, 85–90%, apart from the sandy/silty gyttja layer, where they drop below 55%.

Calculated atomic C/N ratio values vary up to ten units in the studied sediment profile (Fig. 3). In homogeneous and sandy/silty gyttja layer at a depth of 115–72.5 cm (prior to AD 1830) the C/N ratio stays relatively stable between values of 14 and 16 but increases markedly to a maximum value of 19 at a depth of 64 cm (AD 1850s). Thereafter an abrupt decline follows (down to 9) up to the surface of the core.

TS content in the lower homogeneous gyttja part is rather constant, 3–5 mg g^{-1} (Fig. 3). Values start to rise and fluctuate from the depth of 63 cm (AD 1850s) upwards to the present, reaching maximum of 14 mg g^{-1} in laminated sediments at the depth of 43 cm (AD 1930s). Continuous low values of TP (~ 2 mg g^{-1}) in the lowermost part of the sediment core start to increase rapidly in the sandy/silty gyttja layer at a core depth of 76 cm (around AD 1820s) (Fig. 3), where a maximum value of 6.1 mg g^{-1} is registered and

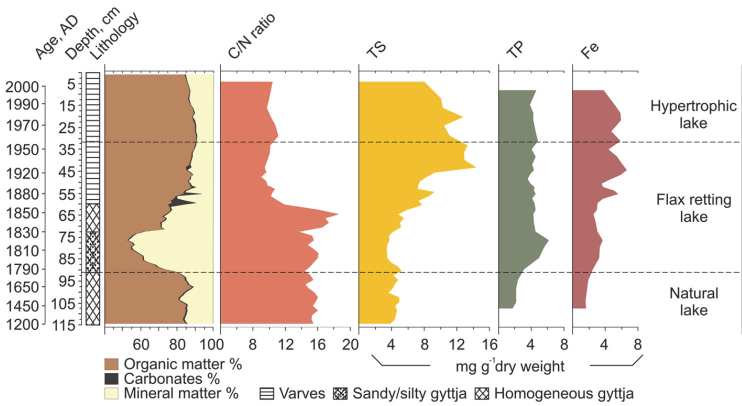


Fig. 3 Lithology, sediment organic, carbonate and mineral matter content estimated by loss-on-ignition (% of dry weight), and sediment profiles of C/N ratio, TS mg g^{-1}, TP mg g^{-1} and Fe mg g^{-1} of Lake Kooraste Linajärv

fluctuate between 4.8 and 3.8 mg g^{-1} up to the topmost sediment sequence.

The content of Fe is stable in the lower homogeneous gyttja part, 1.5 to 1.9 mg g^{-1} (Fig. 3). Fe starts to rise and notably fluctuate between 2.5 and 6.6 mg g^{-1} after the sandy/silty gyttja layer at 89 cm (AD 1800s) towards the upper part of the laminated sediment sequence.

Biostratigraphy

Terrestrial evidence

Tree pollen constitutes about 85% of the total trees/terrestrial herbs relationship below 85 cm (before the 19th century AD; Fig. 4). Terrestrial herb diversity is small. During the interval from 85 to 60.3 cm (first half of the 19th century AD) the proportion of tree pollen rises. At the depth of 60.3–24 cm (ca. AD 1858–1970), with the start of varve formation, the relationship between trees and terrestrial herbs changes in favour of the latter. Thereafter from 24 to 4 cm the tree pollen rises and dominates again.

Evidence of human activities around the lake is present throughout the investigated part of the pollen record, as reflected by the sporadic occurrences of *Triticum* and *Secale* cereal pollen grains (Fig. 4). Ruderals such as *Rumex, Artemisia*, Chenopodiaceae, Lamiaceae, *Urtica* and *Polygonum aviculare*-type occur in low numbers below the sediment depth of 64 cm (before AD 1850) (Fig. 4). The interval 64–32 cm (ca. AD 1850–1955) is characterized by increased evidence of cereal cultivation, ruderals and micro-charcoal.

In the studied sediment core a total of 57 finds of *L. usitatissimum* seeds and capsule fragments were detected (Fig. 5). Macrofossil findings (mostly fruit capsules) occur at the sediment depth of 105–41 cm (ca. AD 1500–1940). Due to the macrofossil sampling strategy we were unable to distinguish the exact sediment layer of their origin, therefore the results on a diagram are presented as a combination of sample vertical thickness and number of finds (Fig. 5). The first pollen grain of *L. usitatissimum* was encountered at 104 cm depth (ca. AD 1500) (Fig. 5) and from this level upwards the pollen evidence has a fairly continuous record until 24 cm depth (AD 1970). Weeds known to be associated with flax crops (*Spergula, Galium*) are present from 93 cm (around AD 1750s), the sandy/silty gyttja layer, but in larger numbers in the interval 64–35 cm (between ca. AD 1850 and 1950) (Fig. 4). Pollen of *Cannabis*-type is present from 74 cm (the 19th and 20th century AD) (Fig. 4).

Aquatic evidence

Diatom analyses were carried out on 27 stratigraphic levels. A total of 114 diatom taxa were identified. Diatom composition indicated a distinct succession with abrupt transitions between intervals of specific sub-dominant diatom species. The homogeneous sediments below 91.5 cm (prior to the 19th century AD) were dominated by soft-water benthic taxa (Fig. 6) and low diatom concentration. A marked increase of small-sized fragilarioid taxa and diatom concentration was observed at the onset of the sandy/silty gyttja layer at 91.5–80 cm (since ca. AD 1780) simultaneously with the peak in MM (Fig. 6). The considerable expansion of eutrophic planktonic diatoms and rapid displacement of dominant taxa one after another characterises the lower laminated sediment part at the depth 60.3–35 cm (AD 1860s–1950s) (Fig. 6). Thereafter the proportion of planktonic diatoms declines and the assemblage is dominated by small-sized benthic diatoms.

The concentration of green algae, such as *Scenedesmus* spp., *Pediastrum* spp. (mostly *P. boryanum*), *Tetraëdron minimum* and *Botryococcus* increases between 64 and 30 cm (AD 1850s–1950s; Fig. 7). Below 64 cm (before AD 1850) the algal component is negligible, except for *Botryococcus* (Fig. 7).

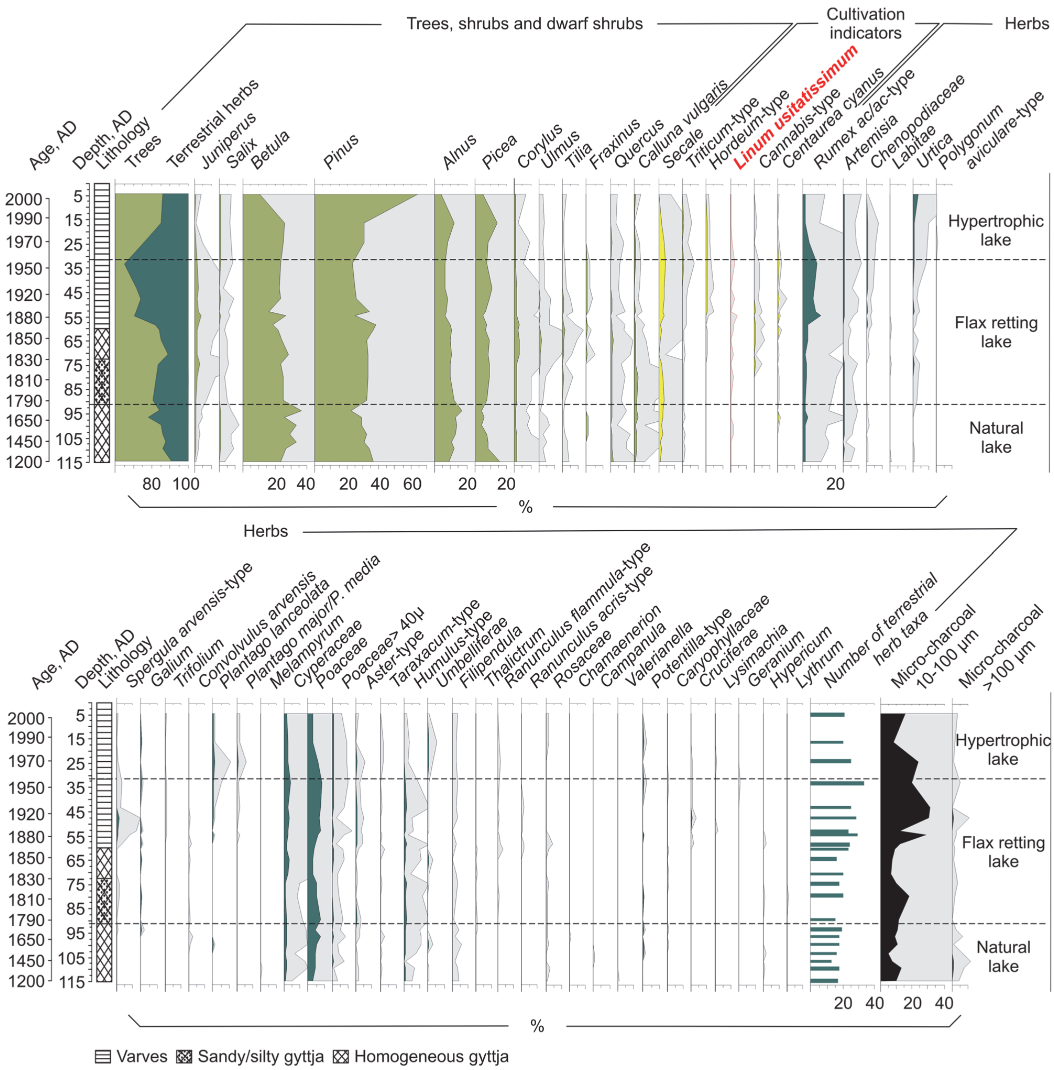


Fig. 4 Lake Kooraste Linajärv sediment profile percentages of selected pollen types and micro-charcoal; grey areas show multiplication by 10

The concentrations of pollen from aquatic plants, such as *Typha, Potamogeton, Nuphar* and *Nymphaea* are high from 64 cm (ca. AD 1850; Fig. 7) and intracellular hairs (branched filament-trichoblasts) of *Nymphaea* are present (Fig. 7).

Palaeo-pigments were measured from the core depth of 86 cm upwards (from ca. AD 1800)(Fig. 8). The content of marker pigments Chl *b* and Echin increases throughout the investigated timespan, while Lut-Zea and β-car have maximum values from 64 to 51 cm (ca. AD 1850–1900). Marker pigment β-car has two distinctive high peaks, one in homogeneous gyttja at around 62 cm (in AD 1850s) and the second in varves at 15 cm (in AD 1980s). The highest values of β-car content, a proxy for total phytoplankton biomass, can be observed in varves at 54 cm (in AD 1880s) and 15 cm (in AD 1980s; Fig. 8).

Statistical analysis

We used segmented regression analysis (Muggeo 2003) of MM content data in relation to sample age to clarify the

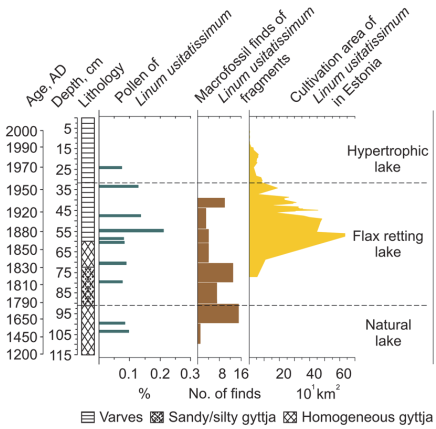


Fig. 5 Evidence of flax: *Linum usitatissimum* pollen% and number of macrofossil finds of *L. usitatissimum* capsule fragments in Lake Kooraste Linajärv sediments, and *L. usitatissimum* historical cultivation area (10 km^2) in Estonia (calculated from detailed data presented in Estonian statistical yearbooks)

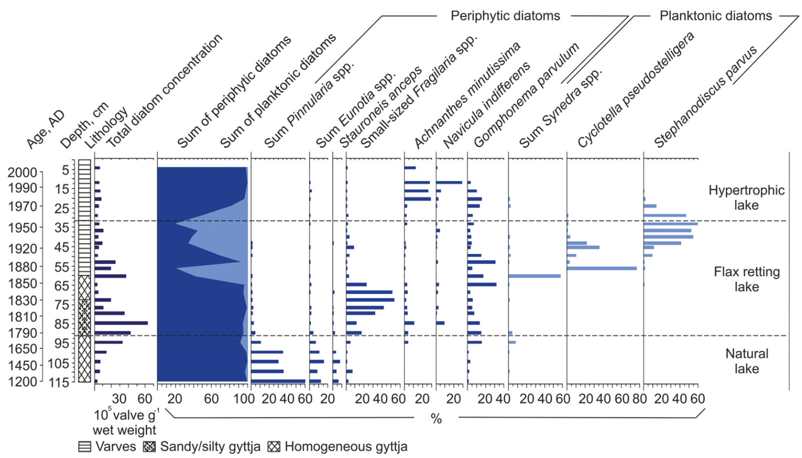
starting point of intensive flax retting in the lake. We chose MM content because it showed a distinct and clear peak indicating severe disturbances directly on the lake shore that could be connected with flax retting activities. The analyses with three break-points indicated a breaking point at a sediment depth of 91.5 cm (ca. AD 1780), which we used as a starting point of intensive flax retting in the subsequent analyses. The end of retting was assumed to be in 1955 (Ott pers. comm.). The time-series was thereafter divided into three time periods: "Natural lake"—below 91.5 cm (before AD 1780), "Flax retting lake"—interval 91.5–32 cm (between AD 1780 and 1955), and "Hypertrophic lake"—above 32 cm (after AD 1955).

The results of PCA and permutational multivariate analysis of variance showed that after the start of intensive retting in AD 1780 the diatom and green algae communities differed significantly ($p<0.05$) from the pre-retting natural communities in the lake (Fig. 9; ESM 3 Table 2). However, the communities of the hypertrophic period (after the retting was stopped in AD 1955) do not differ significantly from the flax retting time. The diatom and algal communities also showed clear gradients in PCA analysis where the first ordination axis explained 42% of the variance in diatom data and 54% of the variance in green algae data (ESM 3 Table 3). The pollen of water plants differs significantly only between the natural and post-retting periods (ESM 3 Table 2) and the PCA analysis indicates great overlap between the time periods (ESM 3 Fig. 1). In the case of land plants, the communities are significantly different in all three periods (ESM 3 Table 2) and the first two ordination axes explain 31 and 22% of the variation, respectively (ESM 3 Table 3).

Discussion

There is sedimentary evidence of flax retting in several Estonian lakes (Punning et al. 1994; Veski et al. 2005; Niinemets and Saarse 2007), though the signal of retting comprises of only one to two pollen grains of *L. usitatissimum*, sporadically and randomly distributed over the sedimentary column. LKL, so far, is the only site in the area exhibiting fairly continuous micro- and macroscopic evidence of flax retting to be used as baseline for other analyses. This palaeolimnological reconstruction revealed the consequences of severe human impact on natural trophic state of the LKL. Due to

Fig. 6 Total diatom concentration (10^5 valves g^{-1} wet weight) and percentage diagrams of selected diatom taxa from Lake Kooraste Linajärv sediments. Diatoms are grouped according to their habitat into periphyton and plankton



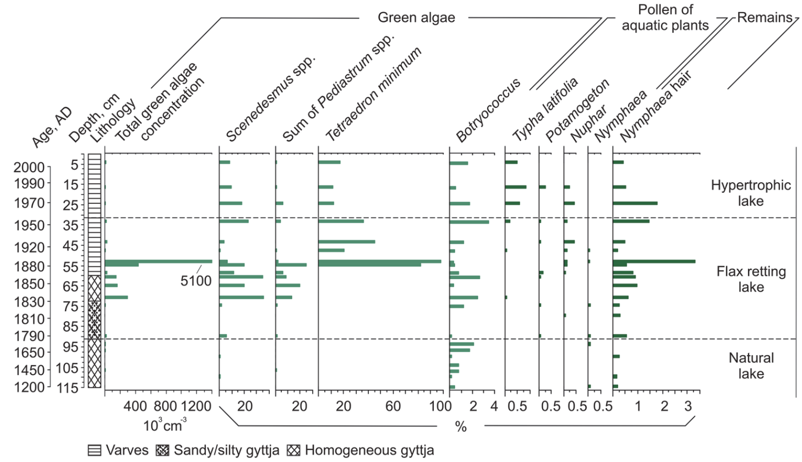


Fig. 7 Total green algae concentration (10^3 cm^{-3}) and percentage diagrams of selected taxa of green algae, pollen of aquatic plants and remains of aquatic macrophytes from Lake Kooraste Linajärv sediments

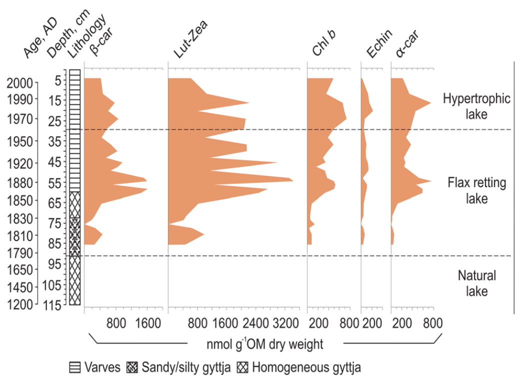


Fig. 8 Concentration (nmol g^{-1} OM dry weight) profiles of the selected fossil pigments in Lake Kooraste Linajärv sediments

intensive flax retting, deterioration of the ecological state of the lake was rapid and major changes occurred in most of the studied palaeoproxies. Based on segmented regression analysis and local historical knowledge, we separated major periods in the lake ecosystem development.

Natural lake

Before AD 1780, LKL was in its natural, unaltered state. Based on the sediment record and reconstruction of the environmental history of Lake Kooraste Kõverjärv (Alliksaar and Heinsalu 2012), the lake located just 100 m north of our study site (Fig. 1b), we can assume that LKL once supported a similarly stable environment and soft clear water. Several lines of evidence support this concept. Low sedimentation rate, with high and stable OM and low MM values in the sediment suggest the existence of a forested catchment with stabilized vegetation and topsoil cover. Low MM (Fig. 3) content hints that this seepage lake had no permanent surface inflow and the discharge from surrounding slopes of the lake was minimal.

A well-illuminated water column and low nutrient level are indicated by the taxonomic composition of the algal community, dominated by epipelic diatoms such as *Pinnularia* spp., *Eunotia* spp. and *Stauroneis anceps* (Fig. 6). A low concentration of green algae and a relatively low abundance of aquatic macrophytes are in good agreement with previous assumptions (Fig. 7). Furthermore, the results of PCA with diatoms and green algae indicate that the natural state of the lake is associated with relatively large and versatile algal taxa (*Pinnularia, Eunotia, Stauroneis, Botryococcus, Pediastrum boryanum*) (Fig. 9a, b).

Evidence of human activities around the lake is documented throughout the studied pollen record by the presence of pollen grains of cultivated cereals (e.g. *Triticum* and *Secale*) (Fig. 4). The presence of cereal pollen grains in sediment cores infers that crop cultivation occurred in the study area but not necessarily in the direct vicinity of the lake, suggesting that anthropogenic impact around the LKL remained low. The majority of cereal pollen in LKL is comprised of *Secale*. Being the most common cereal pollen in Estonian pollen diagrams (Poska et al. 2004) due to good distribution abilities allows us to claim that its share in the LKL pollen sum is not extraordinary. We may therefore rule out direct human impact from field activities in the lake catchment. Moreover, tree pollen constitutes approximately 85% of the trees/terrestrial herbs relationship in sediments during that time period (Fig. 4), indicating a landscape dominated mainly by forest. The results of PCA also indicate that the natural lake period was associated with different

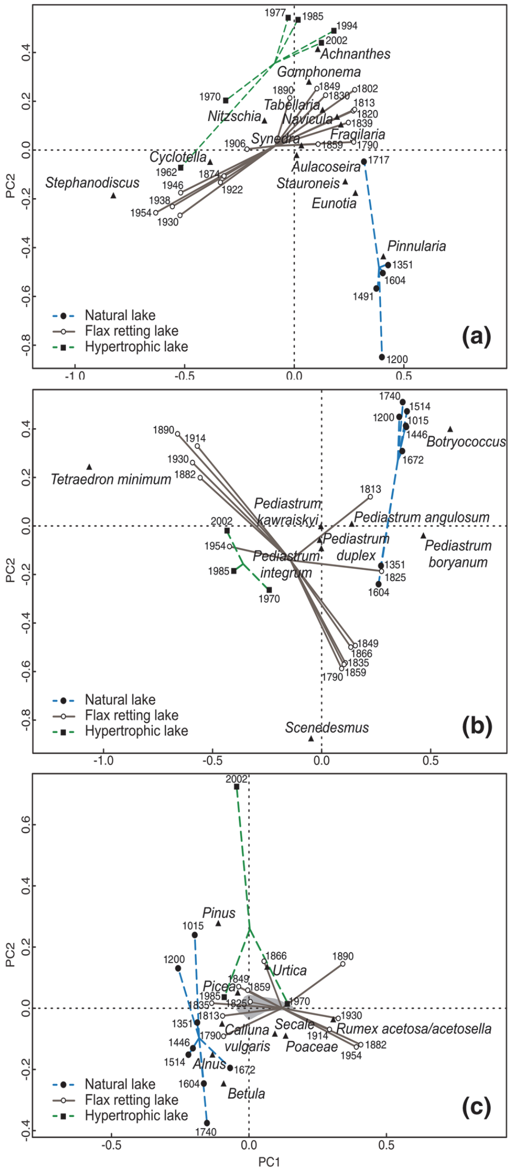


Fig. 9 Principal component (PC) analysis of **a** diatom groups, **b** green algae and **c** pollen of land plants of Lake Kooraste Linajärv sediments. Grey elongated area shows the location of land plant pollen taxa that were indistinguishable on the figure and do not have a strong association with the first two PC axes (PC1 and PC2)

tree taxa (*Pinus, Alnus, Betula*) (Fig. 9c), confirming the above statement. Furthermore, it appears that lake showed no response to the man-made land-use around the study area, as the extremely small catchment area of the lake was not affected by forest clearing or field cultivation.

In Estonia many small lakes, particularly those in rich soil areas, have been altered by permanent human impact over thousands of years in response to the start and development of primitive agriculture and forest clearances (Poska et al. 2004). Due to this, lake ecosystem changes are in many cases not primarily linked to the direct effect of long-term climate change (Poska et al. 2004). For example, sedimentary pollen evidence from Lake Rõuge Tõugjärv, southern Estonia, indicates arable farming activities around the lake from the onset of the Bronze Age, around 1800 BC. Simultaneously, the diatom data suggest that the lake was contemporarily sensitive to early catchment disturbance; in-lake nutrient concentrations increased and the lake switched from a mesotrophic to eutrophic state (Heinsalu and Alliksaar 2009a). The major water quality changes in these lakes occurred contemporarily with rural land-use activities, the maximum extension of both arable and pastoral farming activities in the area being reached during the 18–19th century AD (Veski et al. 2005), wherein diatoms infer that lake water TP values were the highest (Heinsalu and Alliksaar 2009b). Compared to other investigated lakes in southern Estonia (Kangur 2005; Veski et al. 2005; Niinemets and Saarse 2007), LKL, probably due to nutrient-poor soils on the catchment and isolated location, differs in a number of ways: it shows considerably less "traditional human impact" from cereal crops, grazing and pastures, but exhibits a quite specific and strong signal of flax retting not seen in other studied lakes in the area. The effect of lake level changes on the natural development of LKL is limited as the threshold of the lake does not allow water level rise. Moreover, reconstructed water level changes in southern Estonia do not show any notable changes within the last 1,000 years (Punning et al. 2005).

Possible initial flax retting

Flax fibre extraction was achieved through a process known as "retting". In order to obtain high-quality, colourless fibres, small soft and clear-water lakes situated some distance from villages and fields were preferred and chosen for flax retting. The process of water retting includes several steps. Bundles of flax stems were submerged in the littoral of the lake (i.e. littoral sediment disturbance), anchored with blocks and left to ferment (with the help of bacteria) for several weeks, during which time bacteria decomposed the pectin that binds the lignin fibres together and thus loosened the fibres in the stem (Pedaste 1939).

The first, but rare, fragments of *L. usitatissimum* occur in the sediments dated to the beginning of the 16th century AD, suggesting that flax retting might go far back in the lake's history (Fig. 5). However, the early retting seemed not to have any far-reaching consequences or severe impact on the ecological conditions of the lake, indicating that flax retting might have been rather chaotic and modest at that time. Still there is a possibility that these early findings of *L. usitatissimum* macroremains are misleading. Although we cannot entirely exclude contamination possibilities during sampling, flax fragments are relatively large; therefore, it should be considered that the fragments could sink into a deeper layer of soft gyttja sediment over time. Further, one should keep in mind that the continuous macrofossil sub-samples were of a vertical thickness of ca. 10 cm, which in the lower part of the core would cover a timespan of up to 230 years. Unfortunately, this eliminated the possibility of pinpointing the exact depth/age of the sediment layer from where macrofossils were originating. However, the most valuable indicator for helping determine the possible starting-point of flax retting in LKL is the first find of *L. usitatissimum* pollen in its sediments (Fig. 5). Dated to ca. AD 1500, this find strongly suggests that flax retting took place in the lake from at least the 16th century AD. Nevertheless, a low TS content (Fig. 3) and homogeneous gyttja indicate that the lake possessed a well-mixed water column with a good oxygen supply in the profundal zone and that hypolimnetic conditions were aerobic. Furthermore, the C/N ratio varies between 14 and 16 (Fig. 3); thus, this ratio is not within the limits indicative of OM input purely from aquatic sources, nor above the threshold characterizing terrestrial sources (Meyers 1994). Source division, based on C/N ratio values, is possible due to the unique biochemical signal of OM, i.e., nonvascular plants, such as algae, contain little or no carbon-rich cellulose and lignin, while vascular plants, such as grasses, shrubs, and trees, contain large proportions of these fibrous tissues (Meyers and Ishiwatari 1993). Thus, in LKL, a higher C/N ratio can be the indication of flax retting, however, probably due to modest use of flax retting at that time, the C/N ratio values are diluted in the sediment matrix and do not exceed limits of terrestrial provenance. A C/N ratio which fluctuates around 15 (Fig. 4) infers a mixed composition of OM, typical for a lake in its natural state without any external alterations or remarkable erosional events.

Flax retting and its consequences

The end of the 18th century AD marks the period when significant changes in the composition of LKL sediment started to occur. Major disturbances of the littoral area of the lake were recorded within the ca. 20 cm thick sandy/silty gyttja layer (ca. AD 1780–1830) when a distinct increase in the MM content occurred (Fig. 3). Maps from the Estonian Historical Archives from AD 1685 and AD 1903 covering the surrounding areas of the lake (Fig. 5 in Alliksaar and Heinsalu 2012) do not show any changes in the small catchment area of LKL or any alterations in its hydrological network. Due to the closed water system of the lake this high amount of MM can only be explained by reworking of the littoral area of the lake as a result of intensive flax retting and relocation of the minerogenic littoral sediment into deeper part of the basin. It is possible that these sediment relocation works were conducted because of the fairly deep nature of the lake, as usually for flax retting much shallower lakes were chosen. Given the isolated nature of LKL, the flax decomposition process generated impure decay products that probably appreciably increased nutrient concentrations of the lake ecosystem. Similar MM content increase was recorded by Heinsalu and Alliksaar (2009b) from the sediments of Lake Nohipalu Valgjärv, southern Estonia. The resemblance to LKL comes down to the similar forested catchment and the same hydrology—both lakes have a closed water system. In the case of Lake Nohipalu Valgjärv, abrupt change in the composition of the sediments was associated with soil erosion due to large scale forest clearance around the lake as shown by historical maps. Old maps of the LKL area (Alliksaar and Heinsalu 2012) exclude forest clear-cutting around this lake.

The retting process essentially leaves a palaeoecological signature in lake sediments (Grönlund et al. 1986; Bradshaw et al. 2005; Koff and Vandel 2008). Finds of *Linum* fragments and seeds (Fig. 5) reveal flax retting in LKL. Moreover, direct evidence of *L. usitatissimum* presence in the sediments of LKL was detected by finding of its pollen grains there (Fig. 5). Although flax pollen was patchily distributed, its presence is still significant and matches well with macrofossil record (Fig. 5). Much of the *Linum* pollen could have been carried there together with retting bundles. After these flax bundles were placed into the water to ret, the *Linum* pollen separated from the flowers and settled on the lake bottom. In fact, flax pollen grains are usually found in retting-pools (Andresen and Karg 2011) and not in natural lakes, therefore rarely more than a few pollen grains of *L. usitatissimum* indicate where retting occurs (Punning et al. 1994; Veski et al. 2005). This implies that the occurrence of *Linum* pollen in LKL is a strong indicator that it was used for retting. Moreover, the signs of flax retting can be deduced indirectly by common flax weeds, such as *Spergula arvensis*-type and *Galium* (Fig. 4) described by Latałowa (1998).

The occurrence of the intensive flax retting process in LKL is reflected by remarkable changes in C/N ratio starting from approximately AD 1830 (Fig. 3). The sudden increase in C/N ratio (to its maximum values in AD 1850) is associated with the evident input of allochthonous OM (Meyers 1994). The retting of the vascular carbon-rich flax plants has resulted in high C/N ratio values which confirmed that intensive flax retting activities were taking place from at least AD 1830.

The in-lake fermentation and input of dissolved nutrients is also indicated by significant increase in sediment TP

(Fig. 3), which in turn led to changes in the size, abundance and structure of the phytoplankton community. A sharp increase in all of the investigated palaeopigments (Fig. 8) supports the above statements and clearly shows that the trophic status of the lake was starting to change. The diatom composition is dominated by small sized benthic fragilaroid taxa (e.g. *Staurosira construens* var. *venter* and *Pseudostaurosira brevistriata*), which are often epipsammic diatoms, i.e. they live attached to mineral grains. In addition epipsammic diatoms are adapted to alkaline conditions and take advantage of high initial supplies of nutrients (Zimmermann et al. 2015). Small-sized *Fragilaria* spp. *sensu lato* taxa are considered as opportunistic species, because they have a rapid growth rate in the rapidly changing environment (Denys 1990). The results of PCA also confirm that the initial retting period is associated with smaller more fast-growing fragilaroid taxa (Fig. 9a).

Intercontinental effects between America and Europe where events on one continent (American Civil war) influenced conditions on the other (rise of flax cultivation) align well with the flax retting history of LKL. Although the increase in area of flax cultivation in Estonia occurred during AD 1840s and peaked in AD 1860s (Fig. 5), we could infer noticeable changes in the lake already by AD 1820s (i.e., an increase in MM and TP) but also in AD 1850s (i.e., peak in C/N ratio and in evidence of *Linum*). To support this concept of intercontinental influence, we should consider the possibility that varves in our study site are slightly over-counted. That is, it is possible that at high sediment accumulation rates, more than two layers may form annually, which were mistakenly interpreted as additional years in the timescale.

The landscape openness and the proportion of synanthropic plants increased towards the 19th and 20th century AD and showed statistically significant changes throughout the history of the lake (Fig. 9c; ESM 3 Table 2). Examining the maps from the Estonian Historical Archives of parishes in Kooraste region from AD 1685 and a plan of Karste Manor, originating from AD 1903 (Fig. 5 in Alliksaar and Heinsalu 2012), did not show any arable fields on the lake shores and the direct surroundings of the lake have always been covered with forests with the nearest fields more than 300 m away. We can, therefore, assume that the effects of landscape opening have not been very distinct in this small and isolated lake and that most of the changes in the ecosystem of the lake are due to the retting.

Ongoing flax retting in LKL led to an unstable ecosystem, indicated by a distinct succession of phytoplanktonic communities, cyclic appearances, sub-domination and declines of several diatom and green algae taxa one after another (including *Synedra* spp., *Cyclotella pseudostelligera, Stephanodiscus parvus, Scenedesmus, Pediastrum* and *Tetraëdron minimum*) (Figs. 6, 7). Rapid changes in the lake environment due to nutrification, were eventually leading to eutrophication of the lake. Nutrient, namely phosphorus (P) shortage seemed to be no longer a limiting factor for lake productivity. High values of β-car content in sediments indicating increased phytoplankton biomass also confirms this concept (Fig. 8). Increase of sedimentary palaeopigment dynamics usually means acceleration in eutrophication (Lami et al. 2000; Leeben et al. 2008; Tõnno et al. 2013). The dynamics of marker pigments Chl *b* and Lut-Zea are in good agreement with peaks in fossils of green algae (*Scenedesmus* spp., *Pediastrum* spp. and *Tetraëdron minimum*) (Figs. 7, 9b), in which increased concentrations usually indicate hypertrophic conditions (Huber 1996; Eilers et al. 2006).

Elevated autochthonous bioproductivity enhanced OM accumulation and reduced light conditions in the water column of the lake. Intense OM degradation led to increased oxygen consumption in the profundal zone, causing permanent anoxic conditions in the hypolimnion. Increasing quantities of TS (Fig. 3) in the lake sediments clearly indicate enhanced anoxia development in the bottom water layer (Enters et al. 2006). A similar sulphide peak associated with *Cannabis* and *Linum* pollen in sediments, denoting flax retting in the lake, was recorded by Barber et al. (1999), who also referred to the reducing conditions created by OM decomposition as the main cause of high TS. The water column probably became strongly stratified, meromictic conditions developed, and annually laminated sediments i.e., varves started to form from the AD 1860s. Anoxic conditions in bottom waters are crucial for varve formation, hence preventing sediments from being disturbed by bottom-crawling animals (Ojala et al. 2000). The linkage between the biochemical cycles of sulphur, phosphorus and iron under oxic/anoxic conditions can explain their potential mobility in the water/sediment boundary. Under oxidized conditions, P is sorbed onto redox-sensitive Fe^{3+} compounds, while under anoxic conditions Fe^{3+} is reduced to Fe^{2+} (Søndergaard et al. 2003). As a result, both P and Fe return into solution. Also under anoxic conditions, dissolved sulphates are microbially reduced to sulphides that are stored in the sediments as ferrous sulphides (Olsson et al. 1997). This process removes Fe from iron cycle and could be the main cause of P release from the sediments to the water column. Internal P loading and its seasonal transfer to the water column via diffusion can trigger phytoplankton blooms in early spring and during the summer.

Fluctuations in the C/N ratio indicate that the lake ecosystem was seriously disturbed. Previously observed high C/N ratios were based on the terrestrial plants specific biochemical composition (Meyers 1994) interpreted as a signal of flax retting. However, the following abrupt decrease from high C/N ratios to low C/N ratios during the AD 1860s (Fig. 3), suggests a compositional change in sediment OM and a shift in the lake trophy. Despite flax retting continuing throughout this period and material carrying high C/N ratio signal still being added to the lake as before, released nutrients caused accelerated algae taxa growth and domination (Figs. 6, 7), which in turn overpowered the terrestrial signal. Since the values of the C/N ratio were from now on (ca. AD 1860s) less than or just above 10 (Fig. 3), there is no doubt that nitrogen-rich algal material was the main source of OM in LKL since the second half of the 19th century AD (Meyers and Ishiwatari 1993; Meyers 1994). A similar abrupt decrease in C/N values was also recorded by Punning and Tõugu (2000) in the core of Lake Viitna Linajärv in northern Estonia, which was interpreted as a mark of the change in the lake ecosystem due to the flax retting.

Hypertrophic lake—changes in water chemistry and phytoplankton communities

Although flax retting in Estonia sharply declined during the early 20th century AD (Fig. 5) and was abandoned during AD 1950s when retting in natural water bodies was forbidden in Estonia, internal nutrient loading in LKL is still so significant that it prevents improvements in water quality until the present-day. Once the oligotrophic lake had become highly hypertrophic, intensive water blooms occurred throughout the year and changes in water chemistry underwent long-term inter-annual variations. The biodiversity of the lake also decreased significantly. The lake composition shifted towards domination by small-sized phytoplankton because they could outcompete larger algal taxa due to their ability to uptake available P more rapidly. The primary dominants, by biomass, are small-sized green algae from the order Chlorococcales and cryptophytes. Surprisingly, cyanobacteria do not constitute a very large proportion of total biomass and are rarely represented (e.g. *Chroococcus, Cyanodictyon, Dolichospermum*). Sedimentary diatom composition and low concentration suggests unsuitable environmental conditions and inhibition of planktonic diatoms (Fig. 6). Periphytic diatoms were probably transported to deeper parts of the lake from the littoral zone, whereas planktonic diatoms were outcompeted by other groups of algae. In addition, the PCA of diatoms and green algae (Fig. 9a, b) indicates that the algal composition during the last 60 years is somewhat different from the flax retting-period. However, the difference was not statistically significant (ESM 3 Table 2). Even though the algal communities have changed since the retting has stopped, they do not differ significantly, indicating that the lake has not recovered from the anthropogenic disturbances, not to mention that there is no sign of the communities that would be recovering back to the natural pre-flax retting condition of the lake. A concise summary of the most significant changes in LKL as shown by its sediment evidence and monitoring data is given in Fig. 10.

Typically for LKL nowadays, different algal groups dominate in different water layers. Sometimes desmids, which often indicate oligotrophy (Rawson 1956), and dinoflagellates prevail in the upper water layers, while Chlorococcales and cryptomonads dominate in the deeper water layers. Due to their morphological characteristics, most of the currently prevailing algae tend to decompose easily, leaving no visible palaeolimnological evidence in the sediments. Nonetheless, preserved chemical signals in the form of the C/N

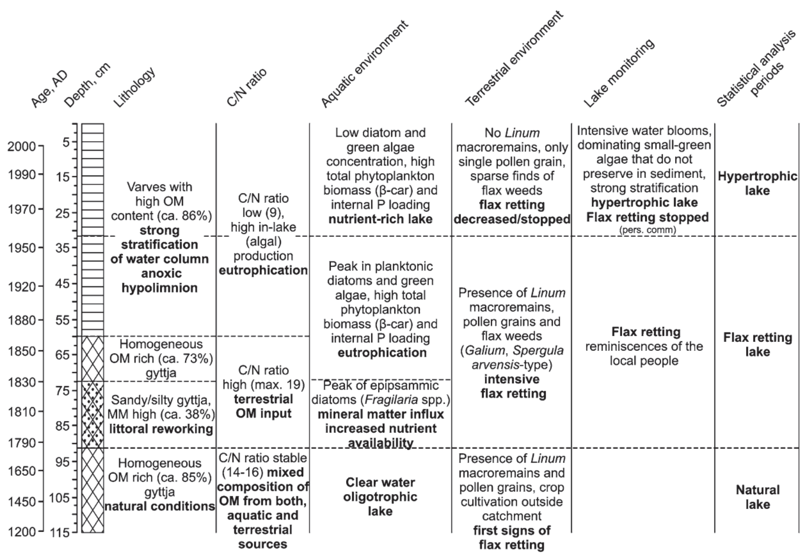


Fig. 10 Concise summary of the most significant changes in Lake Kooraste Linajärv by its sediment evidence and monitoring data

ratio (Fig. 3) and palaeopigments (Fig. 8), indicate the algal domination in the lake.

Palaeobotanical investigations of other lakes in southern Estonia have shown a decrease of arable land and reforestation of the area during the last 100 years induced by the consolidation of farmsteads and more efficient land-use practices (Poska et al. 2008). As a result, the lakes responded rapidly to diminishing catchment activities and external loading reductions as seen from the diatom composition data of Lake Rõuge Tõugjärv (Alliksaar et al. 2005; Heinsalu and Alliksaar 2009a). However, this is not the case for the ecosystem of LKL. Due to the severe human impacts in the past, LKL has now a major internal nutrient loading accumulated in its sediments, which makes it unlikely that the lake will recover to its natural, unaltered state anytime in the near future.

Conclusions

Evaluating responses of the natural biological system to man-induced changes using multiple palaeolimnological proxies revealed significant disturbances in the history of LKL. Using data accumulated in the lake sediments helped us to reconstruct the recent history of flax retting in the lake as well as to shed more light on potential consequences of human impact on a natural lake system (Fig. 10). As flax pollen is not dispersed over great distances, it is palynologically under-represented in pollen diagrams. Therefore using the knowledge obtained by archaeologists about the accompanying herbs of *L. usitatissimum* gives indirectly supplemental evidence of flax cultivation and retting. In the present study combining findings of flax weed pollen (Fig. 4) and macroscopic fragments of flax (Fig. 5) with different geochemical sediment proxies (Figs. 3, 8) and changes in algae composition (Figs. 6, 7) confirmed the scenario of successively intensified flax retting activities in LKL.

Over the years, various studies from different lake sediments have found only one or two flax pollen grains (Punning et al. 1994; Veski et al. 2005; Niinemets and Saarse 2007) or just acknowledged the fact that flax retting has probably taken place in their study site (Punning et al. 2004). Therefore finds in LKL can be considered unique due to the relatively high abundance of *L. usitatissimum* macrofossils and pollen in sediments confirming flax retting in the lake. Moreover, common flax weeds such as *Spergula arvensis*-type and *Galium* were also represented during that time-interval (Fig. 4). The study confirmed that although pollen grains were present in the sediments of the lake with flax retting history, they were recorded in quite low quantities and were at times sporadic. This affirms the opinion that even single findings of flax pollen in lake sediments can be considered as evidence for the occurrence of retting.

Different geochemical sediment proxies and alterations in algal composition (diatoms, green algae, fossil pigments) show the role of flax retting in the changes in the water chemistry of the lake, increases in its bioproductivity and decreases in biodiversity. The retting activities in LKL have been so intense that until now, 60 years later after flax retting was stopped, there are no signs that the lake is recovering from them.

Although today LKL is far from its natural condition it is still a highly valuable research object. Development of a strong stratification, sudden variations in the nutrient concentrations and in phytoplankton taxonomic composition and ongoing eutrophication processes makes this lake a real-time "nature experiment". These unusual circumstances have given us an opportunity to observe and study the severe consequences to the biota of the lake of human impact history, showing clearly that the natural systems are in many cases not capable of recovery even though the source of pollution has stopped.

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Paper IV

Stivrins, N., Liiv, M., Brown, A., Banerjea, R. Y., Heinsalu, A., Veski, S. Investigating the impact of anthropogenic land use on a hemiboreal lake ecosystem using carbon/nitrogen ratios and coupled-optical emission spectroscopy. *Manuscript*.

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Related publications not included in this Thesis

Stivrins, N., Brown, A., Veski, S., Ratniece, V., Heinsalu, A., Austin, J., Liiv, M., Ceriņa, A. (2016). Palaeoenvironmental evidence for the impact of the crusades on the local and regional environment of medieval (13th–16th century) northern Latvia, eastern Baltic. The Holocene, 26: 61–69.

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[1] sh 01.09.2014–31.08.2015 akadeemiline puhkus